9-1949

Some reactions of Tris (hydroxymethyl) aminomethane

Ralph Walton Raiford

SOME REACTIONS OF TRIS(HYDROXYMETHYL)AMINOMETHANE

BY

RALPH WALTON RAIFORD JR

THESIS

SUBMITTED TO THE GRADUATE FACULTY

OF THE UNIVERSITY OF RICHMOND

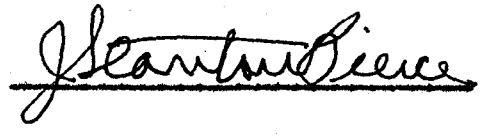
IN CANDIDACY

FOR THE DEGREE OF

MASTER OF SCIENCE IN CHEMISTRY

SEPTEMBER, 1949

APPROVED BY:



ACKNOWLEDGEMENT

The author is indebted to Dr. J. Stanton Pierce, who directed this research and corrected the proof of the manuscript embodied herein. His personal friendship and guidance will always be held in great esteem.

I wish to express my thanks to Mr. Carl D. Lunsford, Mr. J. Lee Rush, and Mr. Douglas W. Wiley, who carried out the necessary analyses and contributed immeasurably with their advice and criticism.

Finally, I am recording acknowledgement to the Office of Naval Research for its financial assistance of this research during 1949.

TABLE OF CONTENTS

INTRODUCTION

Most of the work on alkanolamines has been confined to the preparations and reactions of the ethanolamines. The results reported herein deal with the reactions of $H_2NC(CH_2OH)_3$, tris(hydroxymethyl)aminomethane, which is a beta-hydroxy amine.

The aminoalcohols are prepared, in the majority of cases, by a) the reaction of amines with epoxides, and b) the reaction between nitroparaffins and aldehydes, with subsequent reduction of the nitro group; both of these preparations give beta-aminoalcohols. Therefore, the reactions of the aminoalcohols, especially the ethanolamines and other beta-aminoalcohols, have been studied to uncover any reactions applicable to the compound above, since there is very little information in the literature on the reactions of the compound itself.

HISTORICAL

REACTIONS OF ALKANOLAMINES

The reactions of alkanolamines may be divided into a) addition to form salts, b) decomposition with acids, bases, or oxidizing agents, c) reaction of the H atoms of the amino group, d) reaction of the H atoms of the hydroxyl group, e) replacement of the amino group, f) replacement of the hydroxyl group, and g) various miscellaneous reactions.

Mineral acid salts of amino alcohols form easily according to the following equation, which is perfectly general, X being any mineral acid residue:

$$HOCH_2CH_2NH_2 + HX \longrightarrow HOCH_2CH_2NH_2 \cdot HX$$

The hydriodides are described in a patent (1). It is claimed that the hydrogen chloride salts are formed most readily by passing dry hydrogen chloride gas into a propyl alcohol solution of the amino alcohol (2). Krasuskii and Kosenko (3)

---

(1) Fisk, US Pat. 2,128,741, Aug. 30, 1938
(2) Jones, J. Assoc. Official Agr. Chem. 27, 467 (1944)
(3) Krasuskii and Kosenko, Ukrainskii Khem. Zhur. 4, Sci. Pt., 199 (1929(

Note: Chemical Abstract references are given in the bibliography.

describe hydrochlorides in which the amino alcohol holds more than one equivalent of HCl, a tertiary N forming a tri-hydrochloride, a secondary N forming a di-hydrochloride, and a primary N forming a monohydrochloride. However, these authors state that the tri- and di-hydrochlorides decompose into the normal monohydrochloride when heated in air or in vacuo.

The hydrobromides are made by methods similar to those described for the hydrochlorides. They form also, when the stoichiometric amount of HBr solution is added to a solution of the amino alcohol and the resulting mixture is evaporated to dryness.

Sulfuric acid added to an alcohol solution of the amino alcohol will precipitate the compounds as the hydrogen sulfates. The nitrate is not so easily made. To a solution of the base in water, 36% nitric acid is added slowly with stirring and cooling On removal of the water in vacuo, the hydrogen nitrate is left (4). In much the same way, one obtains the salts of various organic acids, i.e., by mixing solutions of the amino alcohol and the acid, and evaporating the resulting solution to dryness, keeping the temperature below that required to remove the elements of water and form an amide.

Mono- and di-ethanolamine react peculiarly with p-nitrobenzoic acid (5). By mixing diethanolamine and p-nitrobenzoic

---

(4) Barbiere, Bull. soc. chim. 7, 621 (1940)
(5) Meltsner, Greenfield, and Rosenzweig, J. Am. Chem. Soc. 62, 991 (1940)

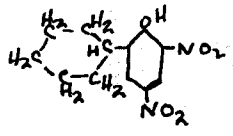
acid in molar ratios and heating the mixture at 100° for four hours, one obtains the salt of the amino alcohol. But heating the same reactants for two hours at 180° results in the formation of the di(diethanolamine) salt of azoxybenzoic acid, the diethanolamine acting as a reducing agent, and partially reducing the nitro group to one of azoxy function.

$$p\text{-}O_2NC_6H_4COOH + (HOCH_2CH_2)_2NH \longrightarrow (HOCH_2CH_2)_2NH \cdot HOOCC_6H_4NO_2$$

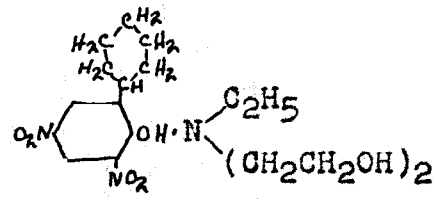
$$p\text{-}O_2NC_6H_4COOH + (HOCH_2CH_2)_2NH \longrightarrow$$

$$(HOCH_2CH_2)_2NH \cdot HOOCC_6H_4N^{\nearrow O}{=}NC_6H_4COOH \cdot HN(CH_2CH_2OH)_2$$

Likewise, the aminoalcohols form salts with negatively substituted phenols. For example, 26.6 gms of 2,4-dinitro-6-cyclohexylphenol and 50 ml of benzene are heated to about 78°, at which temperature solution takes place; then 13.3 gms of ethyldiethanolamine in 10 ml of methyl alcohol are added over a period of 15 minutes. After heating and stirring, followed by cooling, the crude salt precipitates, is filtered, washed with cold benzene, and air dried, giving a crystalline product as shown.(6)



$+ \quad C_2H_5N(CH_2CH_2OH)_2$



Thiocyanic acid undergoes two reactions with alkanolamines, rearrangement and addition to form substituted thioureas, and addition to form salts. The first of these reactions will be

---

(6) Abbey, Brit. Pat. 600,082, Mar. 31, 1948

treated at a later stage in this manuscript. The thiocyanic acid salts (7) are formed by mixing one mole of ammonium thiocyanate and one mole of amino alcohol in water solution, heating at 85-90° until ammonia evolution ceases, and then holding the product at 50° until the water is completely removed, leaving the crystalline product. It is important to keep the temperature low, to prevent the formation of thioureas mentioned above.

In general, the salts of the amino alcohols are easily formed, crystallize well, and have sharp, definite melting points. In many instances, they can be used as therapeutic agents, especially if the compounds contain important functional groups other than the amino and hydroxy groups.

Salts of a quaternary nature are formed when alkanolamines are treated with alkyl halides or alkylating agents (8). For example, 30 parts of triethanolamine mixed slowly with 27 parts of dimethyl sulfate and heated at 160-70° for awhile gives the water soluble quaternary ammonium salt.

A type of "polymer bond" exists in the polysulfides of the aminoalcohols. There are many patents covering the conversion of amino alcohols into their polysulfide derivatives. Generally, this consists of heating an alkanolamine or mixture containing it with sulfur and hydrogen sulfide (9), if desired

---

(7) Mathes, Stewart, and Swedish, J. Am. Chem. Soc. 70, 3455 (1948)
(8) French Pat. 860,910, Jan. 28, 1941
(9) Blank, French Pat. 839,775, Apr. 12, 1939

with the addition of an appropriate diluent. Water may be present, but only in quantities such that no sulfur will separate or otherwise interfere with the reaction. Products obtained in this way have the formula $(\text{aminoalcohol})_x S_y$, (x) usually being 2 or 3.

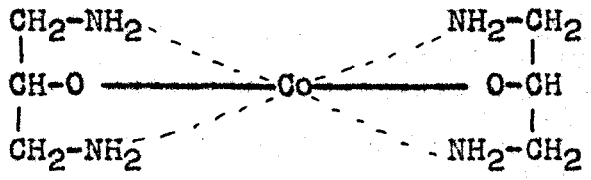
Compounds of somewhat similar nature are the coordination compounds of the amino alcohols. The halide salts of the alkaline earth metals form complex ions similar to those which they form with the alcohols (10). They may be formed by treating the amino alcohol with the halide of the metal in water or alcohol solution, or by reacting a hydrohalide of the aminoalcohol with an alkali or alkaline earth metal hydroxide (11). These compounds probably set up their auxiliary bonds between the metal ion and both the alcohol and amine groups. However, there is no evidence to point to one of these bonds taking preference over the other.

Antimonylcatechol coordination compounds with amino alcohols have been investigated by Wheeler and Banks (12). Although they have proposed structures for these compounds, it is not certain just what their exact formulas might be. Generally, the antimony atom forms one covalent bond with one alcoholic oxygen and donates a pair of electrons to another oxygen to form a coordinate-covalent bond.

---

(10) Kropp, US Pat. 2,017,976, Oct. 22, 1935
(11) I. G. Farbenind A.-G., Ger. Pat. 606,400, Dec. 1, 1934
(12) Wheeler and Banks, J. Am. Chem. Soc. 70, 1266 (1948)

With cobalt, the amino alcohols form complex salts of the general formula $((C_3H_9N_2O)_2Co)X$ (13). Breckenridge and Hodgins assign the following structure to the complex cation:



These men also postulate the formulas below for salts with copper and silver and claim that the zinc salts do not have a simple formula.

$CuX_2 \cdot (C_3H_{10}N_2O)_2$ and $C_3H_{10}N_2O \cdot AgNO_3 \cdot O \cdot 5H_2O$

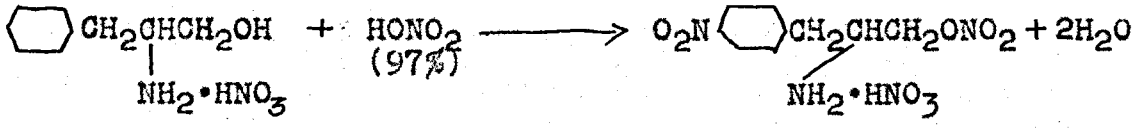
The nitric acid salt of an amino alcohol is easily prepared (see p 3). By a slight modification of this procedure, the ester is obtained.(14) 97% nitric acid in excess is added to the nitrate of the amino alcohol, the solution being kept below 0° throughout. On removal of the excess nitric acid in vacuo, the ester is precipitated with ethyl ether at -10° and may be recrystallized from a suitable solvent. This treatment preserves, rather, forms the salt if it is not present originally, but the free aminoalkyl nitrate may be obtained from the salt by the action of sodium carbonate in the presence of ethyl ether.

The presence of an aromatic group in the amino alcohol causes yet another reaction to take place, the aromatic group

---

(13) Breckenridge and Hodgins, Can. J. Research 17, B, 331 (1939)
(14) Barbiere, Bull. soc. chim. 11, 470 (1944)

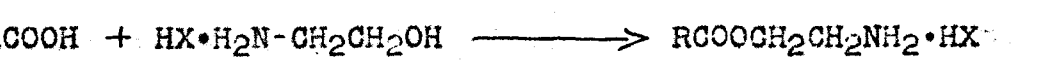
being nitrated in addition to the ester and salt formation. For example,



The sulfuric ester is formed similarly. To assure a good yield, a great excess of sulfuric acid must be used (15). Too, a better yield is obtained by reacting the components in an inert solvent such as benzene and distilling the water-benzene azeotrope as it is formed. Possibly a better method for getting the sulfate is to esterify the alcohol with sulfonyl chloride, alone or in an indifferent solvent, but the neutral ester is obtained at the same time.

Other esters are formed in much the same way, including the phosphates (16), phosphotungstates (17), silicotungstates (18), and borates (19), which are reported in the literature.

Many procedures are available for the esterification of amino alcohols with organic acids. Direct esterification of the amino alcohol with the acid proceeds with ease, as the following equation shows:



A good illustration lends itself from the procedure for the determination of the number of hydroxyl groups in a given

---

(15) Saunders, J. Chem. Soc. 121, 2667 (1922)
(16) Ralston and Harwood, US Pat. 2,229,307, Jan. 21, 1941
(17 & 18) Kahane and Kahane, Bull. soc. chem. (5), 3, 621 (1936)
(19) Gilmann, US Pat. 2,441,063, Apr. 4, 1948

compound.(20) The amino alcohol is reacted with a large excess of acetic acid, insuring completeness of reaction, and the water formed in the reaction is titrated with Karl Fischer reagent, the possible calculations giving the number of alcoholic hydroxyl groups in the starting compound. Conversely, the method may be used to determine the number of carboxyl groups in the molecule. Usually an esterification catalyst, an acidic substance, is present.

A patented process for the esterification of the alcohol group involves the mixing and heating of the reactants at a temperature which will eliminate the water formed in the reaction (21). Many processes entail using a solvent, though this is not absolutely necessary.

A good method for the esterification, though indirect, involves elimination of a molecule of hydrogen halide by reaction of an acid halide and an amino alcohol. For example,

$$RCOCl + HOCH_2CH_2NH_2 \cdot HX \longrightarrow RCOOCH_2CH_2NH_2 \cdot HX + HCl$$

2,2-diphenylbutanoyl chloride and dimethylaminoethanol in the ratio 1:2 are refluxed in benzene for 10 hours (22). After heating, the mixture is made alkaline with 10% sodium hydroxide and extracted with benzene. The benzene extracts are washed with water, concentrated at the water pump, the residue taken up in dry ethyl ether, and the hydrochloride of the

---

(20) Smith, Mitchell, and Hawkins, J. Am. Chem. Soc. 66, 715 (1944)
(21) Young and Rubenstein, US Pat. 2,429,445, Oct. 21, 1947
(22) Larsen, et al., J. Am. Chem. Soc. 71, 532, (1949)

basic ester is precipitated with alcoholic HCl. The precipitate is washed with ether and recrystallized twice from ethyl-acetate to give 57% of the product, MP 164-165°.

Should the hydrohalide of the amino alcohol be used as a starting material, it is only necessary to use slightly more than one mole of the alcohol to one mole of the acid chloride, for a given amount of product, since one-half of the amino alcohol used above reacted with the hydrogen chloride produced in the reaction, forming the salt.

The ester may be formed by the interaction of haloalkyl-amino compounds with the salts of substituted fatty acids.(23)

$$RCOONa + ClCH_2CH_2NH_2 \longrightarrow RCOOCH_2CH_2NH_2 + NaCl$$

(R is any substituted fatty acid residue)

Examples of other than aliphatic acids being used in this reaction have escaped this writers attention.

If desired, the acid may be used with the halo compound directly.(24) For example (25), 9.65 gms of 1-naphthyl-butyric acid and 6.1 gms of diethylaminoethyl chloride in 50 ml of anhydrous isopropyl alcohol are refluxed 14 hours, the solution evaporated, and the residue recrystallized from anhydrous ethyl acetate to give 13.1 gms of 2-diethylaminoethyl-1-naphthalene butyrate hydrochloride. The volatility permitting, the compound may be purified by distillation in vacuo.

---

(23) Blankart, US Pat. 1,987,546, Jan. 8, 1935
(24) Hoffman and Schellenberg, Helv. Chim. Acta 30, 292 (1947)
(25) Blicke, US Pat. 2,415,079, Feb. 4, 1947

The ester may also be formed by transesterification, using an alkali catalyst, an example being: 1 gm of sodium in 3 gm-mols of diethylaminoethanol and 2 gm-mols of ethyl p-aminobenzoate is refluxed with a water cooled condenser with a vacuum of 5 mm, the displaced ethyl alcohol condensing in a trap cooled to -20°. The reaction is complete in 15 minutes, after which the pressure is lowered to 1 mm, the excess amino alcohol removed, and the diethylaminoethyl p-aminobenzoate purified by known processes (26). Similar procedures employ sodium ethylate or sodium methylate instead of the sodium metal (27), and the results are equally as good.

Another preparation involves addition of the amino alcohol to a substituted ketene. Diethylaminoethyl phenylacetate

$$(C_6H_5)_2C{=}C{=}O + (C_2H_5)_2NCH_2CH_2OH \longrightarrow (C_6H_5)_2CHCOOCH_2CH_2N(C_2H_5)_2$$

is formed when diphenylketene is treated with a solution of diethylaminoethanol in benzene.(28)

Legerlotz, in 1933, claimed that, through acylation and saponification, optically active amino alcohols show an inversion of their effect of plane polarized light. (29) However, very little has been done as regards further investigation of this property.

In certain instances, salts may rearrange to give esters.

---

(26) Meade, Brit. Pat. 588,032, May 13, 1947
(27) Meade, Brit. Pat. 587,534, Apr. 29, 1947
(28) Soc. pour l'ind. chim. a Bale, Ger. Pat. 653,778, Dec. 2, 1937
(29) Legerlotz, Fr. Pat. 763,428, Apr. 30, 1934
Ger. Pat. 585,164, Sept. 29, 1933

Trimethylbromoethylammonium bromide is dissolved in water and treated with silver lactate (30). After a short time there is no ionized bromine present. Silver bromide is filtered off and the solution concentrated until a sirupy residue is left. The residue is allowed to stand and is then crystallized from butyl alcohol. The product is the bromide of the choline ester of lactic acid. The equations follow.

$$CH_3CHCOOAg + BrCH_2CH_2N(CH_3)_3Br \longrightarrow AgBr + CH_3CHCOON(CH_3)_3CH_2CH_2Br$$
(OH)

$$CH_3CHCOON(CH_3)_3CH_2CH_2Br \longrightarrow CH_3CHCOOCH_2CH_2N(CH_3)_3Br$$
(OH)

The esters of the amino alcohols are very important therapeutically both as their free bases and as their salts. The free bases are usually, though not always, oils which are rather insoluble in water or other polar liquids, and as such find limited application in medicines. However, the hydrohalide salts are soluble in the type liquids described and are commonly used in this form for injection purposes.

There are few other reactions of the hydroxyl group. By treating the amino alcohol with thionyl chloride (31), preferably at a low temperature, and in an inert solvent such as

$$HOCH_2CH_2NH_2 \cdot HX + SOCl_2 \longrightarrow ClCH_2CH_2NH_2 \cdot HX + H_2O + SO_2$$

benzene or chloroform, the hydroxyl may be replaced with

---

(30) Horenstein and Pahlicke, Ger. Pat. 673,841, Mar. 30, 1939
(31) Pyman and Levene, Brit. Pat. 402,159, Nov. 30, 1933

chlorine. This compound may be used as an intermediate in the preparation of other compounds, for example, ethers. The ether may be produced from the amino chloride by condensing it with a metal alcoholate in the usual Williamson synthesis.

Conversely, the ether may be formed by making the alcoholate of the amino alcohol and treating this molecule with an halogen compound. This is best accomplished by treating the amino alcohol with less than the calculated amount of alkali metal, adding the halogen compound, adding more sodium, then more halogen compound, etc., until all the amino alcohol has been converted into the desired ether (32). For example, sodium in small portions is added to triethanolamine at 105° under reflux, the product is cooled to 75° and butyl chloride added with heating to 105°, more sodium is added, followed by more butyl chloride, the process repeated as often as necessary or until the desired amount of ether has been formed.

A patent claims that the alcoholate of the amino alcohol may be formed by reacting the amino alcohol with a strong alkali hydroxide solution (33). After forming the alcoholates, they are freed from the mother liquor and caused to react, at an elevated temperature, with the requisite amount of an high molecular weight alkyl halide to give the ether.

The Friedel-Crafts reaction is applicable to amino

---

(32) Schwarz, et al., Brit. Pat. 508,525, Jul. 3, 1939
(33) Bertsch and Kogl, Ger. Pat. 742,148, Oct. 14, 1943

alcohols (34). 2,2-Dimethyl-2-phenylethylamine is prepared by adding 17.8 gms of 2,2-dimethyl-2-hydroxyethylamine to a cooled, stirred mixture of 80 gms of anhydrous aluminum chloride and 78 gms of benzene. The resulting mixture is refluxed 3 hours and then allowed to stand overnight. The mixture is poured on ice and, after a short time, the two layers are separated. The benzene layer is washed with dilute hydrochloric acid, the acid washings are combined with the aqueous layer, and the resulting solution is made alkaline to liberate the amine, which is taken up in ethyl ether and distilled after removing the ether.

The amino group can be alkylated easily. If the dialkyl sulfate is available, it can be used to introduce one or two alkyl groups into the molecule, according to the following equation:

$$HOCH_2CH_2NH_2 + R_2SO_4 \longrightarrow HO\text{-}CH_2CH_2NHR + RHSO_4$$

$$HOCH_2CH_2NHR + R'_2SO_4 \longrightarrow HOCH_2CH_2NRR' + R'HSO_4$$

One mole of the monoalkylolamine is treated with one mole of the dialkyl sulfate (35), the resulting mixture is neutralized with alkali and a second mole of dialkyl sulfate is introduced into the mixture. The dialkylaminoalcohol is liberated by treatment with alkali, the temperature being below 100°, the product is taken up in ether and purified by distillation in

---

(34) Suter, US Pat. 2,443,206, June 15, 1948
(35) Perkins and Purse, Can. Pat. 370,083, Nov. 23, 1937

vacuo or recrystallization from a suitable solvent.

The reaction takes place equally well with alkyl halides, or any other reactive halides. Some compounds which react readily are alkylidene halides (36), ethyl carbonate(37), halohydrins (38), arylmethyl halides (39), and dichlorides (40) of diverse nature. One example should suffice for these compounds. A mixture of 242 gms of tris(hydroxymethyl)aminomethane, 92.5 gms of epichlorohydrin, and 200 cc of 95% ethyl alcohol is heated on a water bath for 5 hours and acidified with 100 cc of concentrated HCl.(41) In this manner, one obtains a white precipitate of 190 gms (51%) of $[(HOCH_2)_3CNHCH_2]_2CHOH \cdot 2HCl$.

The halogen atoms in aromatic nuclei may be replaced if they are sufficiently active. The halonitrobenzenes have been studied rather thoroughly to determine their action on alkanolamines. If molar quantities of amino alcohol and an o- or p-chloronitrobenzene are refluxed in the presence of 2 molar quantities of anhydrous sodium carbonate for 6-8 hours (42), and the mixture steam distilled to remove unreacted chloronitrobenzene and reduction products of the reaction, the condensation products settle out as oils and solidify on cooling.

---

(36) I. G. Farbenind A.-G., Fr. Pat. 801,121, Jul. 28, 1943
(37) Hodgins and Hovey, US Pat. 2,215,038, Sept. 17, 1940
(38) Kartaschoff, US Pat. 2,149,527, Mar. 7, 1939
(39) Eisleb, US Pat. 1,949,247, Feb. 27, 1934
(40) Kremer and Bendich, J. Am. Chem. Soc. 61, 2658 (1939)
(41) Pierce and Wotiz, US Pat. 2,408,096, Sept. 24, 1946
(42) Kremer, J. Am. Chem. Soc. 61, 1321 (1939)

They may be crystallized from a suitable solvent, for example, benzene. Longer heating than 8 hours tends to produce tars. The use of sodium carbonate is optional, though if the operation is carried out in its absence, there are obtained fewer reduction products and products of other side reactions. However, in the absence of sodium carbonate, one must use two moles of the amino alcohol to one mole of the aromatic compound. Evidence proves that the condensation depends on the activation of the halogen atom, those compounds in which the halogen is meta to the nitro group not condensing readily.

This last statement is further proved by the condensation of ethanolamine with 1,3,4,6-trinitrotoluene(gamma TNT). The reaction with the symmetrical TNT will not take place, but with the gamma-TNT the nitro group in the 3- position is replaced by the ethanolamine residue, the resulting compound (43) being a substituted toluidine. Only monoethanolamine will react in this way, the di- and tri-ethanolamines giving addition products with the gamma-TNT. The equations and formulas follow.

$$CH_3C_6H_2(NO_2)_3 + HN(CH_2CH_2OH)_2 \longrightarrow 2CH_3C_6H_2(NO_2)_3 \cdot HN(CH_2CH_2OH)_2$$

$$CH_3C_6H_2(NO_2)_3 + N(CH_2CH_2OH)_3 \longrightarrow CH_3C_6H_2(NO_2)_32N(CH_2CH_2OH)_3$$

An early reference on amide formation with alkanolamines claims that the only method insuring amides with no esters

---

(43) Racciu, Atti accad. sci. Torino, Classe sci. fis., mat. nat. 69, 364 (1934)

being formed entails the use of aroyl polysulfides (44), such as benzoyl disulfide.

$$C_6H_5COSSCOC_6H_5 + 2\ HOCH_2CH_2NH_2 \longrightarrow 2\ C_6H_5CONHCH_2CH_2OH + H_2S + S$$

The Schotten-Baumann reaction applies as well to amino alcohols as it does to amines alone. Fourneau (45) claims that the hydroxyl groups are not effected in this reaction, even with a large excess of acyl chloride. The amino alcohol is dissolved in a strongly basic solution of sodium hydroxide, and the acyl chloride is added in small portions with shaking. In the case of aromatic acid chlorides, the reaction is more easily controlled, so the acyl chloride may be added in one batch.

A patent (46) describes the preparation of amides from secondary amino alcohols. Acylation of

$$(HOC_2H_4)_2N(C_2H_4NH)_2C_2H_4N(C_2H_4OH)_2$$

or a dimer or trimer thereof may be effected by ricinoleic acid in 4-10 hours at 150-175° or until the product gives a clear solution in acetic acid. As stated before, the acyl radical enters the molecule at the secondary amino group.

Various aromatic sulfonamides have been prepared, the preparation being essentially that of the Schotten-Baumann reaction.(47) Two moles of amino alcohol in a solution of 10-20% potassium hydroxide and pyridine added to one mole of

---

(44) Bergmann, Ulpts, and Camacho, Ber 55B, 2796 (1922)
(45) Fourneau, J. pharm. chim., (7), 2, 397
(46) De Groote, US Pat. 2,395,400, Feb. 26, 1946
(47) Adams, Long and Johanson, J. Am. Chem. Soc. 61, 2342 (1939)

p-acetaminobenzenesulfonylchloride gives the expected amide. If the p-amino group is not substituted, it is the usual practice to use a large excess of aqueous ammonia also in the reaction flask. The equation follows.

$$CH_3CONHC_6H_4SO_2Cl + (HOCH_2)_3CNH_2 \longrightarrow CH_3CONHC_6H_4SO_2NHC(CH_2OH)_3 + HCl$$

Garelli and Racciu (48) produce beta-hydroxyphthalimide by the action of ethanolamine on o-phthalic anhydride. The components are refluxed in absolute ethyl alcohol at 100-10° for a short time and the imide crystallizes on cooling.

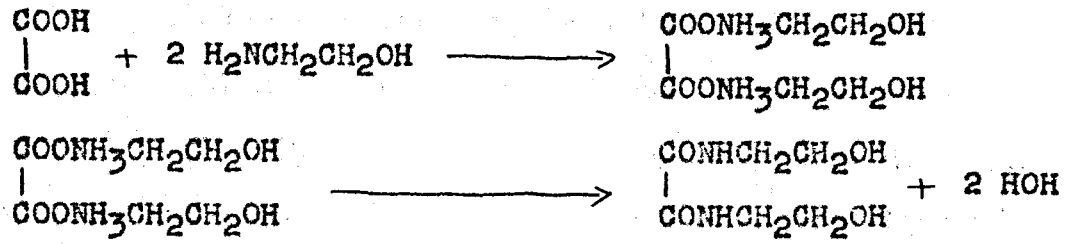
The same compound may be prepared in quantitative yield by heating the components without a solvent for about 30 minutes at 210°, the product solidifying on cooling. The product may be recrystallized from water or from an anhydrous solvent if inorganic impurities happen to be present (49).

A similar preparation involves the use of oxalic acid and ethanolamine (50). Equimalar quantities of the reactants are mixed and evaporated to dryness. After heating at 110° for five minutes, the solid is recrystallized from 79% alcohol. The product so obtained is the disubstituted ammonium salt of the oxalic acid and is soluble in water, but insoluble in absolute alcohol or concentrated acetic acid. If this salt is heated rapidly past its melting point to approximately 222°, a brisk

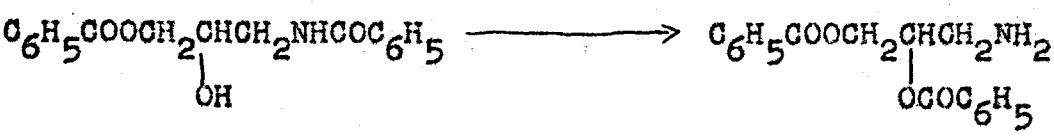
---

(48) Garelli and Racciu, Atti. accad. sci. Torino. Classe sci. fis., mat. nat. 69, 358 (1934)
(49) Wenker, J. Am. Chem. Soc. 59, 422 (1937)
(50) Keiser, Ind. Eng. Chem., Anal. Ed., 12, 284 (1940)

boiling takes place with the formation of N,N'-bis-(2-hydroxyethyl)-oxamide (51).

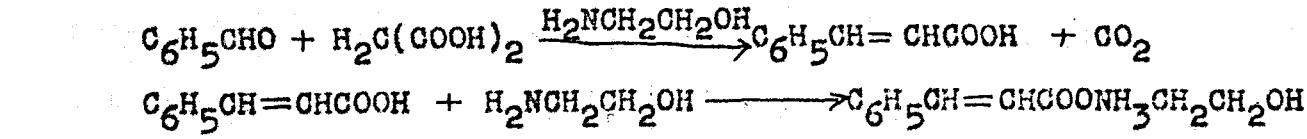


The amides undergo the following reaction (52).



This may be effected by boiling the amide with concentrated hydrochloric or sulfuric acid (53).

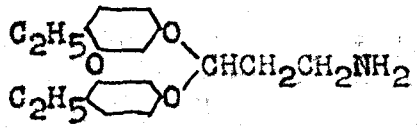
Kiprianov and Kusner (54), investigating the possibility of amino acid formation from amino alcohols, refluxed benzaldehyde, malonic acid, and ethanolamine in alcohol and thus obtained 61% of cinnamic acid and none of the expected amino acids. On standing overnight, the only change in the product was the formation of the cinnamic acid salt of the amino alcohol used. Apparently, the amino alcohol acts as a basic catalyst for the condensation of the benzaldehyde and the malonic acid. Equations follow.



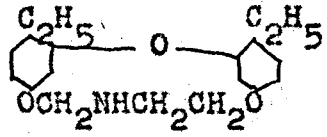
---

(51) See Ref. #50.
(52) Bergmann and Brand, Ber 56B, 1280 (1923)
(53) Bettzieche, Z. physiol Chem. 146, 227 (1925)
(54) Kiprianov and Kusner, J. Gen. Chem. (USSR) 6, 641 (1936)

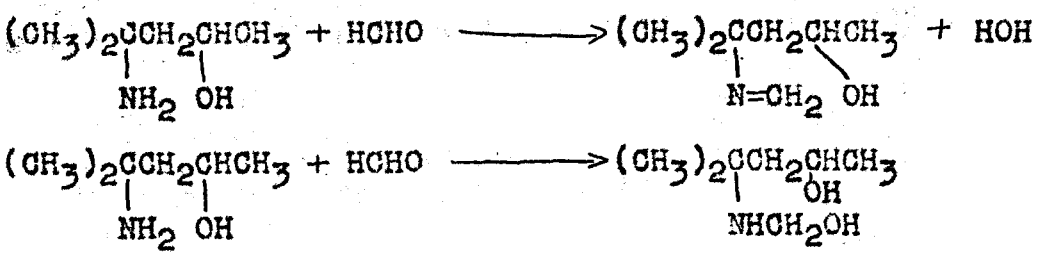
Gomez and Fermin in 1941 (55) investigated the condensation products of ethanolamine and formaldehyde in the presence of a third compound. To 0.1 mole of ethylresorcinol dissolved in 17 cc of methyl alcohol cooled to -5 to -9°, 0.1 mole of formaldehyde is added slowly and then 0.1 mole of ethanolamine is added. On standing for 16-249 hours, various condensation products are obtained;as the time of standing is increased it is found that the products are harder and more insoluble. Following are two possible formulas for the 93 hour product, neither of which may be correct.



AND



Earlier, Hess and Uibrig (56), experimenting with mixtures of aldehydes and amino alcohols only, concluded that the two reactants formed a Schiff base or that the aldehyde used formed an alkylol group attached to the nitrogen atom.



It is also known that low temperatures favor the first reaction and higher temperatures favor the second.

Other investigators claim that the Schiff bases are formed when the aldehydes concerned are hindered or exist in chelate

---

(55) Gomez and Fermin, Univ. Phil. Nat. and Applied Sci. Bull. 8, 287, (1941)
(56) Hess and Uibrig, Ber. 48, 1974 (1915)

form, and that simpler aldehydes form other types of products.

The amino alcohols form amides and esters of carbamic acid in addition to the organic acids mentioned in the preceding pages. These compounds, called, respectively, ureas and urethanes, often have unusual medicinal properties. Saunders and Slocombe (57), claim that in the absence of protection for either the alcohol or the amino group, that the amino group reacts faster than the alcohol group towards the isocyanates, though both reactions take place simultaneously.

$$C_6H_5NCO + H_2NCH_2CH_2OH \longrightarrow C_6H_5NHCONHCH_2CH_2OH$$

$$C_6H_5NCO + HOCH_2CH_2NH_3Cl \longrightarrow C_6H_5NHCOOCH_2CH_2NH_3Cl$$

If the urethan is desired, it may be prepared by saturating a solution of the amino alcohol in chloroform with dry HCl (58), treating this solution with the isocyanate in chloroform, cooling the solution to 0° for 45 minutes, and then heating the solution at 50° for 40 hours. The product is purified by removing the solvent in vacuo, making the residue alkaline, extracting the product with ether, and precipitating the salt of the urethan by passing dry HCl gas into the ethereal solution. Further purification may be effected by recrystallization from acetone.

The urea is formed by similar methods using unprotected amino alcohols.

---

(57) Saunders and Slocombe, Chem. Revs. 43, 203
(58) Cope and Hancock, J. Am. Chem. Soc. 66, 1448 (1944)

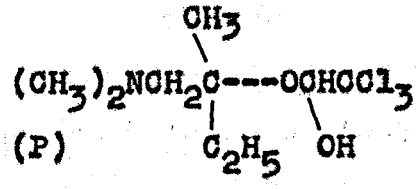
The substituted ureas may also be prepared though the use of nitrourea, by adding a slight excess of nitrourea to a concentrated aqueous or alcoholic solution of the proper amino alcohol and allowing the reaction mixture to stand until reaction is complete. The solution is concentrated on the steam bath and the crude ureas are recrystallized from water, alcohol, or dioxane. The equations are;

$$H_2NCONO_2 \longrightarrow HNCO + HNO_2$$

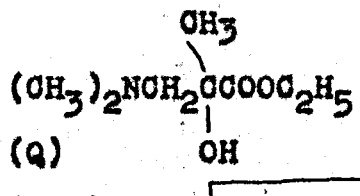
$$HNCO + H_2NCH_2CH_2CH_2OH \xrightarrow{HNO_2} H_2NCONHCH_2CH_2CH_2OH$$

The preparation of the thioureas and thiourethans is similar to the preparation of the oxygen analogs given above, though the thio compounds form more easily since the isothiocyanates are insensitive to water and alcohols, where the isocyanates are not.

Chloral mixed with $(CH_3)_2NCH_2C(CH_3)(C_2H_5)OH$ evolves a large quantity of heat (59). The product decomposes on vacuum distillation and recombines in the receiver for form (P). However, when chloral is treated with (Q), the product obtained

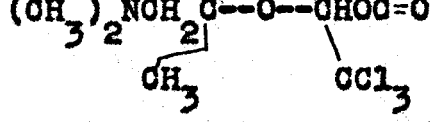


(P)



(Q)

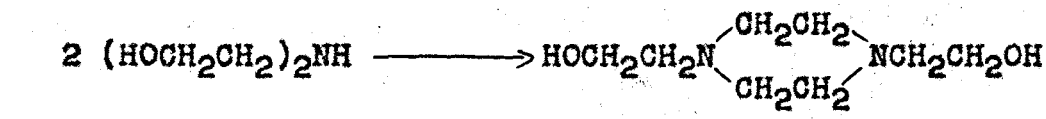
is a ring compound of the formula



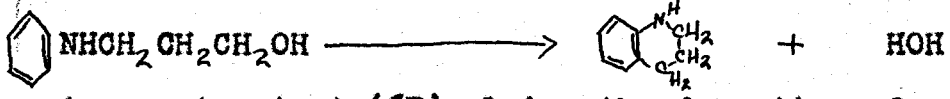
---

(59) Fourneau and Brydowna, Bull. Soc. Chim. 43, 1023 (1928)

Certain alkanolamines condense with themselves in the presence of catalysts to form piperazine derivatives (60). By mixing two moles of N-cyclohexylethanolamine with 25 gms ofa Cr-Cu oxide catalyst in 600 ml of dioxane, heating the batch at 250-270° and shaking the mixture for 3-4 hours in a hydrogen atmosphere at 34 atmospheres pressure, one obtains 20% of 1,4-dicyclohexyl piperazine. Similarly, diethanolamine gives piperazyl-1,4-bis-beta-ethanol (61).



Rindfusz and Harnack (62) in 1920 prepared tetrahydroquinoline by refluxing 90 gms of 3-phenylaminopropanol for one hour in 125 cc of xylene with 40 gms of phosphorus pentoxide, obtaining 17-8 gms of the expected product, the equation being;

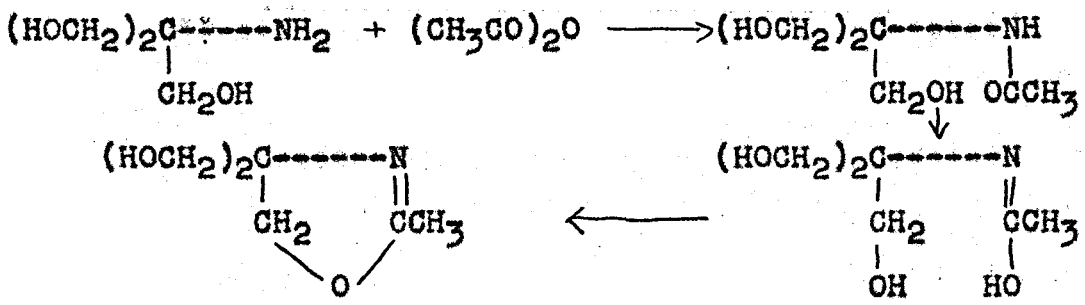


A recent patent (63) claims the formation of oxazolines from beta-aminoalcohols through cyclization of the amides of the amino alcohols. For example, the gradual heating of 120 parts of tris(hydroxymethyl)aminomethane with 50 parts of acetic anhydride in the absence of condensing agents to 230°, until approximately 27 parts of water distil and are collected in a water separator, gives 2-methyl-4,4-bis(hydroxymethyl)

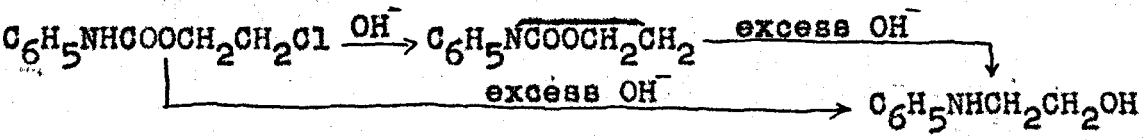
---

(60) Bain and Pollard, J. Am. Chem. Soc. 61, 2704 (1939)
(61) Bain and Pollard, J. Am. Chem. Soc. 61, 532 (1939)
(62) Rindfusz and Harnack, J. Am. Chem. Soc. 42, 1720 (1920)
(63) Valco, US Pat. 2,416,552, Feb. 25, 1947

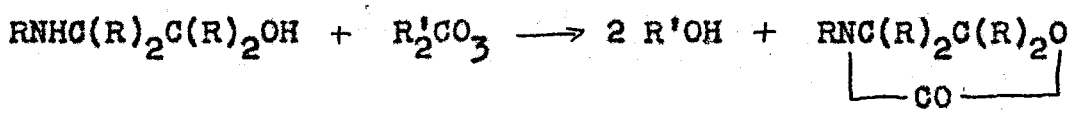
oxazoline.



Another oxazole derivative may be prepared by cyclizing urethans to form oxazolidones. For example, the urethan obtained by the action of phosgene on ethylene chlorohydrin (64), and this product condensed with aniline, giving $C_6H_5NHCOOCH_2CH_2Cl$, is cyclized by treatment with alkali. Treatment of the oxazolidone with excess concentrated alkali results in the formation of N-arylamino alcohols, which may also be obtained directly from the urethan by treating it with a large excess of concentrated alkali.



The oxazolidones may also be prepared as follows; the amino alcohol is condensed with a dialkyl carbonate according to the equation below,



giving the cyclic compound (65). 61 gms of ethanolamine, 150 ml

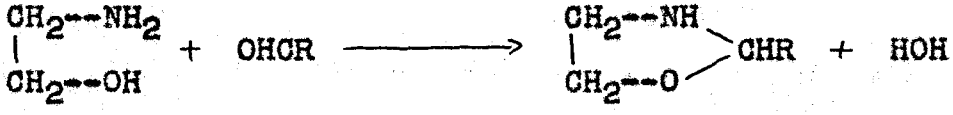
---

(64) Adams and Segur, Science 52, 185 (1920)
(65) Homeyer, US Pat. 2,399,118, Apr. 23, 1946

of diethylcarbonate, and 0.5 gms of sodium methylate are heated in an oil bath with stirring. After 112 ml of ethyl alcohol are fractionated off, the residue crystallizes on cooling and is recrystallized from 100 ml of chloroform to give 57% of 2-oxazolidone.

Other oxazole derivatives are the oxazolidines. These may be prepared a number of ways. The work of Hess and Uibrig, page 20, is discussed by Kohn, who claims that their compounds should be assigned cyclic structures (66) instead of the Schiff base formulas given them in the earlier reference. According to Kohn, these compounds would assume an oxazolidine configuration.

Knorr and Mathes (67) in 1901 prepared oxazolidines by heating equivalent amounts of amino alcohol and aldehyde in ether solution over potassium carbonate for one hour, removing the ether, and distilling the products in vacuo.



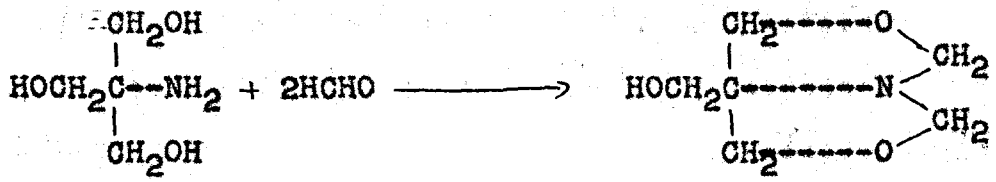
The same type of preparation is used by Meltsner, Waldman, and Kremer (68), who form aryl substituted oxazolidines by refluxing aromatic aldehydes and amino alcohols in butyl alcohol or butyl alcohol-butyl ether mixtures for approximately four hours.

---

(66) Kohn, Ber. 49, 250 (1916)
(67) Knorr and Mathes, Ber. 34, 1484 (1901)
(68) Meltsner, Waldman, and Kremer, J. Am. Chem. Soc. 62, 3494 (1940)

On cooling, the expected products separate from the solvent in the reaction flask, and can be recrystallized from solvents similar to those used during refluxing.

Senkus (69) extended the work on oxazolidines to include the oxazolidines of polyhydric alcohol amines unsubstituted at at the nitrogen. As expected, the monocyclic oxazolidine is obtained when the reactants are mixed in molar amounts. However, when two moles of aldehyde are used to one mole of the amino alcohol, a bicyclic oxazolidine, an 1-aza-3,7-dioxabicyclo-(3.3.0)octane, is obtained.



The following procedure exemplifies Senkus' methods.

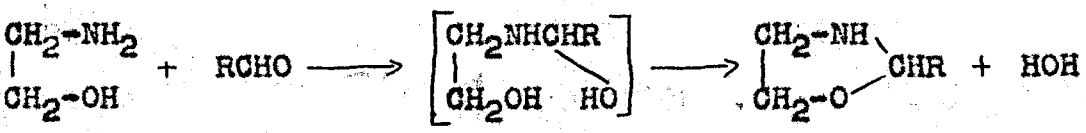
The amino alcohol is put into benzene and the aldehyde, one or two moles, depending on the product desired, is added. The mixture is refluxed, using a Dean and Stark (70) moisture trap, until the requisite amount of water has been collected in the trap, when the reaction is assumed to be complete. The benzene is removed with a vacuum and the products are distilled in vacuo or crystallized from a suitable solvent.

Senkus gives this mechanism for the condensation between the aldehyde and the amino alcohol, although none of the

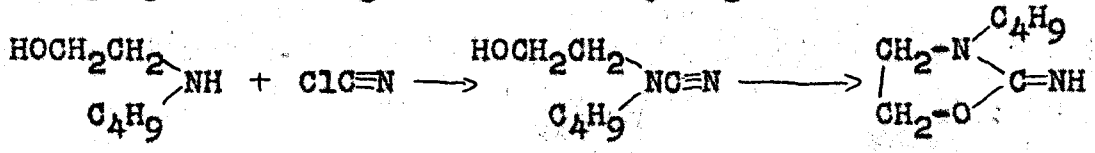
---

(69) Senkus, J. Am. Chem. Soc. 67, 1515 (1945)
(70) Dean and Stark, Ind. Eng. Chem. 12, 486 (1920)

intermediates have yet been isolated.



Recently, 1948 (71), imino derivatives of oxazolidines have been prepared through the use of cyanogen chloride.



One mole of butylethanolamine is mixed with 3.8 moles of hexane and to this mixture is added one mole of cyanogen chloride in 2.25 moles of benzene. The resulting mixture is stirred 45 minutes at room temperature and 20 minutes at 40-50°, when an oil separates which is extracted with water. The pH is adjusted to 9-10 with 10% sodium hydroxide and the solution extracted with ethyl ether. Removal of the ether and distillation gives 11% of 2-imino-3-butyloxazolidine. The hydrochloride is formed by passing dry HCl gas through a benzene solution of the oxazolidine.

Care must be exercised that the amino alcohols are not decomposed during the course of a reaction. This decomposition occurs readily under acidic, neutral, or basic conditions.

Krasuskii (72) found that by heating an amino alcohol with dilute acids it can be decomposed into a quaternary ammonium salt and an aldehyde or ketone.

---

(71) Abramovitch, US Pat. 2,443,062, Jun. 8, 1948
(72) Krasuskii, Ukrainskii Khem. Zhur. 4, Sci. Pt., 61 (1929)

$$(CH_3)_2C(OH)-CH(NH_3Cl)CH_3 \longrightarrow (CH_3)_2CHC(=O)CH_3 + NH_4Cl$$

Forty-eight per cent hydrobromic acid dehydrates the amino alcohols(73), leaving an unsaturated amine which is immediately hydrolyzed to give a secondary amine and an aldehyde or ketone. For example, $R_2NCH_2C(OH)Ar_2$ is dehydrated by warming with HBr to give an amine, $R_2NCH=CAr_2$, which is immediately hydrolyzed to give R_2NH and $HC(=O)CHAr_2$. The formulas may be assumed to be perfectly general. If Ar is replaced by R, dehydration may be effected by the action of phosphorus pentachloride in ethyl ether and the reaction has two possible courses: 1) the reaction gives the products above, and 2) the reaction gives an alpha-beta unsaturated amine which is not hydrolyzable.

$$(C_2H_5)_2C(OH)CH_2N(C_2H_5)_2 \xrightarrow{PCl_5} CH_3CH=C(C_2H_5)N(C_2H_5)_2 \xrightarrow{H^+} \text{no reaction}$$

$$(C_2H_5)_2C(OH)CH_2N(C_2H_5)_2 \xrightarrow{PCl_5} (C_2H_5)_2C=CHN(C_2H_5)_2 \xrightarrow{H^+} (C_2H_5)_2CHCHO$$

Bettzieche (74) claims that the alkali cleavage of amino alcohols follows both of two possible courses. Hydrolysis occurs when the amino tertiary alcohols are heated to 160-220° in a sealed tube with 2N NaOH, the main products being a ketone and an amine, though some ammonia is formed in the side reaction. The main reaction for the decomposition is,

$$CH_3CH(NH_2)C(OH)(C_2H_5)_2 \longrightarrow CH_3CH_2NH_2 + (C_2H_5)_2C=O$$

---

(73) Sou, Bull. faculte sci. univ. franco-chinoise Peiping 1935, No 5, 1
(74) Bettzieche, Z. physiol. Chem. 172, 69 (1927)

while the secondary reaction taking place is

$$CH_3CH(NH_2)C(OH)(C_2H_5)_2 \longrightarrow CH_3C(=O)CH(C_2H_5)_2 + NH_3$$

The main reaction gives about 98% of the amine and 70-90% of the ketone while the secondary reaction gives only 0.5-0.92% ketone and 0.3-1.8% of ammonia.

More recently it has been found that the alkali cleavage of the amino alcohols in many cases gives amino acids among other products of the reaction. A patent held by the Carbide and Carbon Chemicals Corporation (75) claims that 61 gms of ethanolamine and 112 gms of 85% aqueous potassium hydroxide solution heated at 210° for 60 hours gives 34.9% of glycine, 23.5% of recovered amino alcohol, and 10.3% of potassium oxalate, the other products of the reaction not being identified to date.

It is not necessary to have acid or alkali present to decompose the amino alcohol, since tertiary amino alcohols undergo cleavage into ketone and amine when heated (76) in a sealed tube with water at comparatively high temperatures(120-200°). Dry heating at 150-180° gives a smaller yield of like nature.

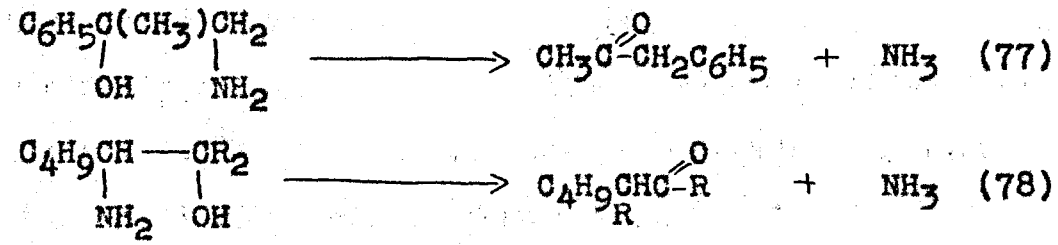
$$C_6H_5CH(NH_2)C(OH)(C_6H_5)_2 \longrightarrow C_6H_5CH_2NH_2 + C_6H_5COC_6H_5$$

Deamination is easily effected by treating a solution of the amino alcohol in acid at 0° with an aqueous solution of sodium nitrite in the usual diazotization reaction. There are two

---

(75) Carbide and Carbon Chem. Corp., Brit. Pat. 601,816, May 13, 1948
(76) Bettzieche and Ehrlich, Z. physiol. Chem. 150, 191 (1925)

ways the reaction may procede, both splitting out ammonia with the hydrogen atom of the alcohol group.

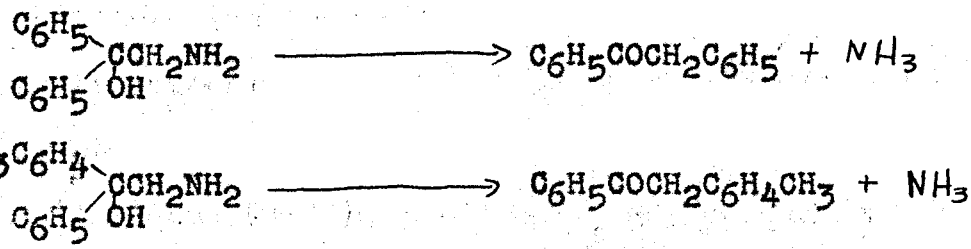


(77)

(78)

The exact mechanism of the reaction is unknown. After removal of ammonia, the compound may assume an epoxide configuration and then rearrange to form the aldehyde or ketone. Or the rearrangement may take place before the oxygen valences have been even temporarily filled.

There may be rearrangement of the various groups within the molecule. In the equations above, there is migration of the phenyl group, but no migration of the butyl group. Practically, migration is limited to aromatic radicals, heavier radicals tending to migrate first.(79).



The amino alcohols will also decompose under the action of ozone and oxidizing agents. Ozone decomposes some alkanolamines

---

(77) Tiffeneau and Cahmann, Bull. soc. chim (5) 2, 1876 (1935)
(78) Kanao and Yaguchi, J. Pharm. Soc. Japan 48, 252 (1928)
(79) Orekhoff and Roger, Compte rend. 180, 70 (1925)

into formaldehyde and other products of indefinite nature.

$$(CH_3)_2C(NH_2)CH_2OH \longrightarrow HCHO + \text{indefinite products}$$

The oxidation of amino alcohols with lead tetraacetate (80) proceeds rapidly with the formation of an amine. The investigators, Leonard and Rebenstorf, oxidized ethanolamine, 2-diethylamino-2-propanol, 1-diethylamino-2-methyl-2-propanol, and 2-(1-piperidyl)ethanol. With the first three compounds, they isolated diethylamine, and from the last compound, piperidine. In all cases, the other product isolated proved to be glyoxal. On the basis of these facts and the structure of the reagent, the following mechanism is postulated.

$$Pb(OOCCH_3)_4 \longrightarrow Pb^{++++} + 4\ CH_3COO^-$$

$$(C_2H_5)_2NCH_2CH_2OH + CH_3COO^- \longrightarrow (C_2H_5)_2N\dot{C}HCH_2OH + CH_3COOH$$

$$(C_2H_5)_2N\dot{C}HCH_2OH + CH_3COO^- \longrightarrow (C_2H_5)_2N\underset{\displaystyle OCOCH_3}{\underset{|}{C}}HCH_2OH$$

$$(C_2H_5)_2N\underset{\displaystyle OCOCH_3}{\underset{|}{C}}HCH_2OH \longrightarrow (C_2H_5)_2NH + CH_3COOH + OHCCH_2OH$$

Oxidation with periodic acid yields formaldehyde and other products, according to Jones (81), but Nicolet and Shinn (82), working with diethanolamine, isolated formic acid from the reaction mixture. Equations for both reactions follow.

$$HN(CH_2CH_2OH)_2 + 2\ HIO_4 \longrightarrow 4\ HCHO + NH_3 + 2\ HIO_3$$

---

(80) Leonard and Rebenstorf, J. Am. Chem. Soc. 67, 49 (1945)
(81) Jones, J. Assoc. Official Agr. Chem. 27, 462 (1944)
(82) Nicolet and Shinn, J. Am. Chem. Soc. 61 1615 (1939)

$$HN(CH_2CH_2OH)_2 + HIO_4 \longrightarrow 4\ HCOOH + \text{mixture}$$

In addition to being oxidized by the usual oxidizing agents, the alkanolamines themselves exhibit an oxidizing ability.(83). By refluxing dry diethanolamine with benzonitrile for 48 hours, one obtains 52% of benzoic acid. In the same way, phenylacetonitrile gives 77% of phenylacetic acid. The water required for hydrolysis apparently is supplied by a cyclic dehydration of diethanolamine to form 1,4-piperazinediethanol.

$$2\ (HOCH_2CH_2)_2NH \longrightarrow HOCH_2CH_2N\begin{matrix}\diagup CH_2CH_2 \diagdown \\ \diagdown CH_2CH_2 \diagup\end{matrix}NCH_2CH_2OH + 2\ HOH$$

$$C_6H_5CN + 2\ HOH \longrightarrow C_6H_5COOH + NH_3$$

The amino alcohols also exhibit a reducing property. The best examples of this are the reductions of the nitrobenzenes and substituted nitrobenzenes to give the azo compounds and the aniline compounds. For example (84), three moles of the amino

$$C_6H_5NO_2 + H_2NCH_2CH_2OH \longrightarrow C_6H_5N{=}NC_6H_5 + C_6H_5NH_2$$

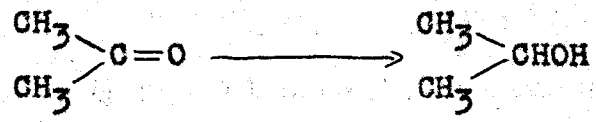
alcohol are mixed with one mole of nitrobenzene and the mixture is refluxed in an oil bath at 180° for five hours. The reaction mixture is then steam distilled, giving both a solid and an oil in the distillate. The solid is filtered and , after recrystallization from alcohol, proved to be azobenzene. The oil is extracted with ether and dried. On removal of the ether and distilling the residue, one obtains aniline. The use of

---

(83) Rauscher, et al, J. Am. Chem. Soc. 71, 358 (1949)
(84) Kremer and Kress, J. Am. Chem. Soc. 60, 1031 (1938)

sodium hydroxide during the reaction markedly increases the yield of the azo compound and decreases the yield of the aniline derivative. It has been found that the amino alcohol decomposes into ammonia and an aldehyde during the reaction, which decomposition is necessary for the reduction to take place.

Other compounds similarly reduced by Meltsner (85) and his co-workers include anthraquinone to anthranol, acetone to isopropyl alcohol, azobenzene to aniline, and chrysoidine to 1,2,4-triaminobenzene.



$$C_6H_5N{=}NC_6H_5 \longrightarrow 2\ C_6H_5NH_2$$

In the main, the reactions of the alkanolamines have been covered. However, there are a large number of references in the literature dealing with reactions of the amino alcohols which cannot be easily put down in ~~the form of~~ an equation. These references are mainly patents obtained on commercial processes and as such are somewhat vague as to the exact nature of the products. They have been included in the bibliography and nothing more will be said of them here, except that all of them, if studied carefully, will fall under one or more of the classifications given herein.

---

(85) Meltsner, Wohlberg, and Kleiner, J. Am. Chem. Soc. 57, 2554 (1935)

APPLICATIONS OF ALKANOLAMINE REACTION PRODUCTS

Esters of amino alcohols find extended use as medicinals and therapeutic preparations. To date, the esters of dimethylamino- and diethylaminoethanol have been found best as local anesthetics, though esters of other aminoalcohols, as yet undeveloped, may be just as good. Salts of coumarin-3-carboxylic acid are useful for increasing respiration or blood pressure (86), and ethanolamine mandelate can be used orally in the treatment of infections of the urinary tract (87).

Products such as that obtained by esterifying triethanolamine trihydroxyethyl ether with stearic acid are good disinfectants and may be used also as fungicides (88). Aminoalcohols containing halogen atoms are also effective disinfectants (89). The tertiary amino alcohol salts of dinitro- (90) and

---

(86) Merck, Ger. Pat. 612,592, Mayll, 1935
(87) Schonle, US Pat. 2,413,247, Dec. 24, 1946
(88) I. G. Farbenind A.-G., Ger. Pat. 642,744, Mar. 23, 1937
(89) Maier-Bode, Ger. Pat. 696,346, Aug. 15, 1940
(90) Smith and Hansen, US Pat. 2,328,505, Aug. 31, 1943

polyhalophenols (91) are very good in fungicidal dispersions and insecticidal sprays. But, the mono-, di-, and tri-ethanolamine salts of alpha-naphthylacetic acid are suitable for stimulating root growth on plant cuttings (92).

By coating finely divided particles of insoluble organic coloring matter with the esters of higher aliphatic acids, e. g. lauric acid, and polyalkanolamines, one obtains pigment powders which may be used in paints and lacquers (93). Untreated fossil resins, when heated directly with amino alcohols to form amides or amido esters are subsequently useful as varnish resins (94). Ester amides of simpler structure can be used as solvents or plasticizers for film forming materials, since these compounds exhibit a marked activity as surface-active materials (94a). Esters of unsaturated acids may be polymerized to form films and plastics. Addition salts of alpha-alkyl-alpha-methylene carboxylic acids and tertiary amino alcohols may be polymerized by heating with water and benzoyl peroxide to produce hard, almost colorless films (95). Beta-hydroxyalkylammonium salts may be used as softeners for polymers of polyvinyl alcohol (96), and find applications in wrapping films. Resins from ureas and polyhydroxyalkylamines are hard, glossy films, and are useful

---

(91) Coleman, US Pat. 2,386,037, Oct. 2, 1945
(92) Smith and Hansen, US Pat. 2,278,499, Apr. 7, 1942
(93) Detrick and Lang, US Pat. 2,305,379, Dec 15, 1941
(94) Weber, US Pat. 2,382,838, Aug 14, 1945
(94a) Tryon, US Pat. 2,410,318, Oct. 29, 1946
(95) Harmon, US Pat. 2,138,762, Nov. 29, 1938
(96) Watkins, US Pat. 2,271,468, Jan. 27, 1942

as stabilizers for rubbers, dyestuffs, and plastic compounds (97).

The salts of the aminoalcohols are widely used in the textile industry as preparative treatments in cleansing, dyeing, bleaching (98), and softening processes. They can be used in soft or hard water and may be used alone or in combination with dressing and sizing materials (99). A patent of Seymour and Brooks (100) describes a conditioning agent for fibers and filaments of cellulose derivatives which improves their susceptibility to textile operations. The compound is formed by reacting a mineral oil, a fatty acid, a vegetable oil, and fuming sulfuric acid, and adding to the reaction product an alkali, an alkanolamine, and water. The whole resulting compound is stabilized, preserved against oxidation, and given an enhanced covering power by the addition of alkylated phenol or other spreading or penetrating agents.

Wood pulp, treated with a small amount of a cation active agent, such as an alkylhydroxyalkylamine, breaks down readily in subsequent shredding or comminution, and is thereby more reactive to the xanthate or any similar treatment (101). Dyeing is facilitated by mixing the dye with a product resulting from the saponification of a higher fatty acid and a glyceride with

---

(97) Burke, US Pat. 2,374,077, Apr. 17, 1945
(98) Ulrich and Nusslein, US Pat. 2,206,928, Jul. 9, 1940
(99) Ulrich, Nusslein, and Scholler, Ger. Pat. 699,110, Oct. 24, 1940
(100) Seymour and Brooks, US Pat. 2,406,408, Aug. 27, 1946
(101) Schlosser and Gray, US Pat. 2,432,126, Dec. 9, 1947

an alkylolamine (102). Dispersants for the dyes in organic solvents are made by condensing alkylol amines and amides (103).

Alkylolamine-copper complexes, when added to solutions of cellulosic materials, modify the properties of the materials (104). The treatment, if carried out after scouring or bleaching, diminishes the luster, but increases the firmness of the treated goods. Chromium complexes of polynuclear compounds and ethanolamines harden sheet glass and aid in the conversion of raw hides into leather (105). The leather, however, undergoes considerable shrinkage by heat and also has the blue coloration of the ethanolamine complex.

Hydroxyalkylammonium polysulfides find use in dyeing, for protecting plants against disease, and for vulcanizing rubber (106). Soft vulcanized rubber may be reclaimed by heating it with alkanolamine at a temperature above 200°F, when it will become plastic (107). A patent describes a lubricant for rubber which is an aqueous emulsion containing a fatty acid, an aminohydroxy compound in great excess, bentonite, and colloidal graphite. The aminoalcohol is isobutanolamine, triethanolamine, tris(hydroxymethyl)aminomethane, 2-amino-2-methyl-1-propanol, or 2-amino-2-methyl-1,3-propanediol (108).

---

(102) Kern and Sala, US Pat. 1,799,821, Apr. 7, 1931
(103) Goodman, US Pat. 2,323,391, Jul. 6, 1943
(104) Whitner, US Pat. 2,446682, Aug. 10, 1948
(105) Brintzinger and Hesse, Z. anorg. chem. 252, 293 (1944)
(106) Blank, Fr. Pat. 839,775, Apr. 12, 1939
(107) Dasher, US Pat. 2,304,548, Dec. 8, 1942
(108) Johnson, US Pat. 2,389,855, Nov. 27, 1945

Antioxidants for rubber, hydrocarbon mixtures containing sulfur, gasoline in contact with metals (109), or organic unsaturated compounds (110), are compounds formed by the reaction of aldehydes with aminoalcohols, the resulting compound being in the form of a Schiff base.

Esters of amino alcohols derived from unsaturated fatty acids having 18 carbon atoms, for example, ricinoleic acid, added to the conventional doctor solution of elementary sulfur and an alkaline solution of sodium plumbite, affects its properties as a sweetener of hydrocarbon distillates (111). They speeds the organic breakdown and reduces the amount of sulfur necessary in the treatment. The soaps of the fatty acids added to detergent lubricating oils act as agglomerates for impurities and thus aid in their removal by filtration (112). These salts are very desirable for this purpose since they have a limited solubility in mineral oils. The salts also aid by the dispersion of the oil in water, permitting better washing (113). Triethanolamine sulfonate is used as an oil emulsifying agent, or, in small portions, for improving the emulsifying capacity of various oil soluble sodium sulfonates (114).

Other uses of the salts of the higher fatty acids are

---

(109) White and Walters, US Pat. 2,300,998, Nov. 3, 1942
(110) Gublemann, US Pat. 2,381,952, Aug. 14, 1945
(111) Morris, US Pat. 2,366,545, Jan. 2, 1945
(112) Bray and Russell, US Pat. 2,435,734, Feb. 10, 1948
(113) Wampur, US Pat. 2,359,066, Sept. 26, 1944
(114) Steik, US Pat. 2,204,326, Jun. 11, 1940

found in insecticides, disinfectants, creams, inks, orchard sprays, lotions, and polishes. When soaps are mixed with alkylolamine salts of acids (115), other than soap forming acids and their sulfonation products, the soaps are stabilized and the lathering properties are much improved.

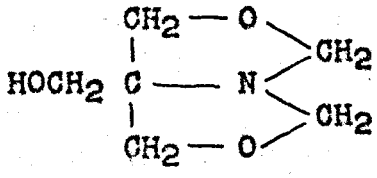
Oxazolidines and 1-aza-3,7-dioxabicyclo(3.3.0)octanes have excellent drying properties (116). However, by reaction of these compounds with fatty acids of the linseed or soybean oil type, much better drying agents are obtained (117).

---

(115) Leben and Ormul Products Ltd., Brit. Pat. 414,077, Jul. 23, 1934
(116) Amer. Cyan. Co., Brit. Pat. 564,506, Oct. 2, 1944
(117) Johnston, US Pat. 2,448,890, Sept. 7, 1948

EXPERIMENTAL

1-aza-5-hydroxymethyl-3,7-dioxabicyclo(3.3.0)octane (118)



Reactants: HCHO and $H_2NC(CH_2OH)_3$

Procedure: (a) To a mixture of 40 gms (0.3 mol) of tris(hydroxymethyl)aminomethane (A) was added 100 gms of 35% formalin solution containing 35 gms (1.16 mol) of formaldehyde. The resulting mixture was refluxed ten hours under a Dean and Stark moisture trap (119), while 87 cc of water collected. The benzene was removed on the water bath and the product distilled in vacuo. Yield-- 33.4 gms, 70%, BP $173\text{-}6^{\circ}_{57}$ mm. On cooling, the distillate solidified and was recrystallized from ethyl ether, MP 59-60°.

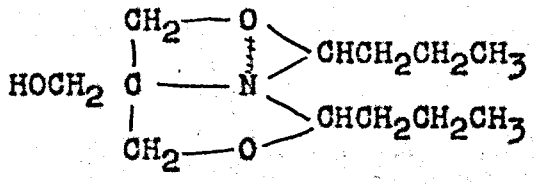
(b) Sixty grams (2 mol) of paraformaldehyde

---

(118) Also prepared by Senkus; see J. Am. Chem. Soc. 67, 1515 (1945)
(119) Dean and Stark, Ind. Eng. Chem. 12, 486 (1920)

was decomposed on an oil bath, and the vapors passed through a mixture of 40 gms (0.3 mol) of (A) and 100 cc of benzene over a period of ten hours. Water formed during the reaction collected in a water trap and amounted to 14 cc (3 cc too many). The benzene was removed with a water bath and vacuum and the residue distilled in vacuo. Yield-- 37 gms, 75.5%, BP 150-3°$_{20\ mm}$. On cooling, the distillate solidified, MP 56-9°.

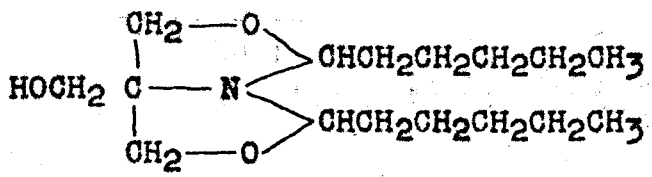
1-aza-2,8-di-n-propyl-5-hydroxymethyl-3,7-dioxabicyclo-(3.3.0)octane



Reactants: $n\text{-}C_3H_7CHO$ and $H_2NC(CH_2OH)_3$ (A)

Procedure: To a mixture of 12.1 gms (0.1 mol) of (A) and 80 cc of benzene was added 14.4 gms (0.2 mol) of butyraldehyde. The resulting mixture was refluxed for six hours under a water separator while 3.6 cc of water collected. The benzene was removed with a water bath and vacuum and the residue distilled in vacuo. Yield-- 17.2 gms, 75.4%, BP 179.5-182°$_{32\ mm}$.

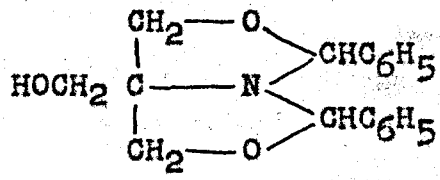
1-aza-2,8-di-n-amyl-5-hydroxymethyl-3,7-dioxabicyclo(3.3.0)-octane



Reactants: $CH_3CH_2CH_2CH_2CH_2CHO$ and $H_2NC(CH_2OH)_3$ (A)

Procedure: To a mixture of 12.1 gms (0.1 mol) of (A) and 80 cc of benzene was added 20 gms (0.2 mol) of caproaldehyde. The resulting mixture was refluxed for four hours under a water separator while 3.6 cc of water collected. The solution was treated with 50 cc of acetone and filtered. Volatile material was removed with a water bath and vacuum and the residue distilled in vacuo. Yield-- 23.9 gms, 84.1%, BP $216\text{-}7^{\circ}_{32}$ mm.

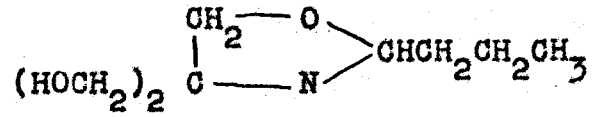
1-aza-2,8-diphenyl-5-hydroxymethyl-3,7-dioxabicyclo(3.3.0)-octane



Reactants: C_6H_5CHO and $H_2NC(CH_2OH)_3$ (A)

Procedure: To a mixture of 36.3 gms (0.3 mol) of (A) and 130 ml of benzene was added 56.6 gms (0.54 mol) of benzaldehyde. The resulting mixture was refluxed under a water trap for 20 hours while 11 cc of water collected. The benzene was removed with a water bath and vacuum and the residue dissolved in ethyl alcohol. The addition of water to the alcoholic solution threw out the product as an oil which crystallized on stirring. This was purified by recrystallization from cyclohexane and hexane. Yield-- 74.3 gms, 85.3%. Recrystallized from (a) cyclohexane, MP $77\text{-}8^{\circ}$, (b) hexane, MP 77-77.5

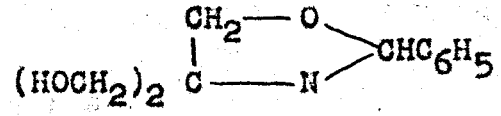
2-propyl-4,4-dihydroxymethyloxazolidine



Reactants: $CH_3CH_2CH_2CHO$ and $H_2NC(CH_2OH)_3$(A)

Procedure: To a mixture of 12.1 gms (0.1 mol) of (A) and 80 ml of benzene was added 7.2 gms (0.1 mol) of butyraldehyde. The resulting mixture was refluxed eight hours (overnight) under a water separator while approximately 2 cc of water collected. To the reaction mixture was added 50 cc of acetone and the unreacted (A) filtered out. The acetone and benzene were removed with a water bath and vacuum and the residue distilled in vacuo. Yield-- 4.7 gms, 45.2%, BP $195\text{-}206^{\circ}_{34\ mm}$. On standing in a desiccator, the liquid became very pasty.

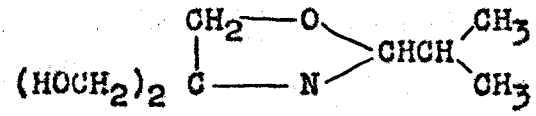
2-phenyl-4,4-dihydroxymethyloxazolidine



Reactants: C_6H_5CHO and $H_2NC(CH_2OH)_3$ (A)

Procedure: Benzaldehyde and (A) were reacted as in the preceding example to give 2-phenyl-4,4-dihydroxymethyloxazolidine.

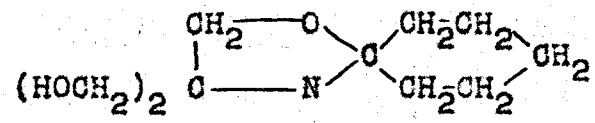
2-isopropyl-4,4-dihydroxymethyloxazolidine

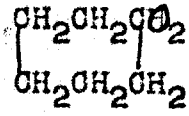


Reactants: $(CH_3)_2CHCHO$ and $H_2NC(CH_2OH)_3$ (A)

Procedure: To a mixture of 12.1 gms (0.1 mol) of (A) and 80 cc of xylene was added 14.4 gms (0.2 mol) of isobutyraldehyde. The resulting mixture was refluxed six hours under a water separator while 3.6 cc of water collected. On cooling, the reaction mixture partially solidified. The xylene was removed with a water bath and vacuum. Acetone was added to the residue and solution took place on heating the mixture. The solution was filtered while hot and the acetone was removed with the water bath and vacuum. The residue solidified on cooling and was crystallized twice from cyclohexane. Yield-- 8.3 gms, 47.4%, MP 103.5-105.

2-spiro(cyclohexyl)-4,4-dihydroxymethyloxazolidine



Reactants:  and $H_2NC(CH_2OH)_3$

Procedure: To a mixture of 12.1 gms (0.1 mol) of (A) and 75 cc of xylene was added 20 gms (0.2 mol) of cyclohexanone. The resulting mixture was refluxed 22 hours with a water separator while 2 cc of water collected. To the hot

solution was added 150 cc of acetone, the whole heated to boiling and filtered while hot. On cooling the filtrate, crystals separated from the solution. These were filtered and recrystallized from anhydrous acetone. Yield-- 12.6 gms, 62.7%, MP 118.1-120°.

Ethyl acetoacetate and tris(hydroxymethyl)aminomethane were reacted by methods similar to those above. A definite compound was isolated, yield-- 17.1 gms, BP 136-7°.7 mm, anal. for N-- 8.86%, which corresponded to neither the expected 2-methyl-2-carbethoxymethyl-4,4-dihydroxymethyloxazolidine nor to 1-aza-2,8-dimethyl-2,8-dicarbethoxymethyl-5-hydroxymethyl-3,7-dioxabicyclo(3.3.0)octane. Further study of the compound is being made.

N-phenyl-N'-tris(hydroxymethyl)methyl-thiourea

$$C_6H_5NHCSNHC(CH_2OH)_3$$

Reactants: C_6H_5NCS and $H_2NC(CH_2OH)_3$ (A)

Procedure: A mixture of 6 gms (0.05 mol) of (A) and 20 cc (17.5 gms, 0.13 mol) of phenylisothiocyanate was heated gently until a homogeneous solution resulted. On cooling, the reaction mixture set to a hard, yellowish gum. This was broken up in 75 cc of 50% ethyl alcohol and boiled in that solvent for 20 minutes. After cooling the solution, crystalline material was filtered and recrystallized twice

from 95% ethyl alcohol. Yield-- 7.3 gms, 57%, MP 153-4°.

N-phenyl-N'-tris(hydroxymethyl)methyl-urea

$C_6H_5NHCONHC(CH_2OH)_3$

Reactants: C_6H_5NCO and $H_2NC(CH_2OH)_3$ (A)

Procedure: A mixture of 3 gms (0.025 mol) of (A) and 3 gms (0.025 mol) of phenylisocyanate was refluxed 20 minutes in chloroform (50 cc). After cooling, the mixture was filtered and the filtrate discarded. The residue was recrystallized three times from absolute alcohol. Yield-- 4.2 gms, 70%, MP 191.4-191.6°.

N-o-tolyl-N'-tris(hydroxymethyl)methyl-urea

$O\text{-}CH_3C_6H_4NHCONHC(CH_2OH)_3$

Reactants: $o\text{-}CH_3C_6H_4NCO$ and $H_2NC(CH_2OH)_3$ (A)

Procedure: A mixture of 3 gms (0.025 mol) of (A) and 4.4 gms (0.025 mol) of o-tolylisocyanate was heated in an open flame until reaction took place. After cooling, the reaction was broken up in chloroform and filtered. The product was recrystallized four times from alcohol-water mixtures. Yield--4.1 gms, 64.5%, MP 190.5-191.4°.

Tris(hydroxymethyl)aminomethane reacted with p-tolylisocyanate, alpha-naphthylisocyanate, and beta-naphthylisocyanate by methods similar to that directly preceding to

yield, respectively, N-p-tolyl-N'-tris(hydroxymethyl)methylurea, N-alpha-naphthyl-N'-tris(hydroxymethyl)methylurea, and N-beta-naphthyl-N'-tris(hydroxymethyl)methylurea.

p-Hydroxybenzaldehyde and furfural were reacted with tris(hydroxymethyl)aminomethane but the products could not be purified.

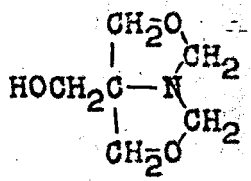
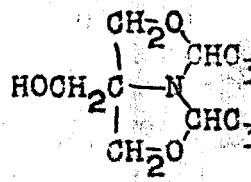
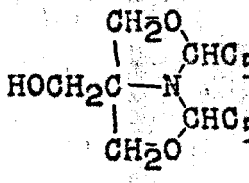
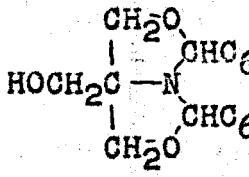
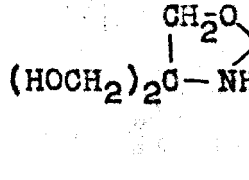
There was no evidence of reaction when tris(hydroxymethyl)aminomethane and acetone were refluxed in ethyl ether over potassium carbonate for seven hours.

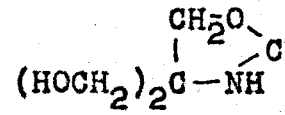
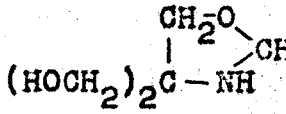
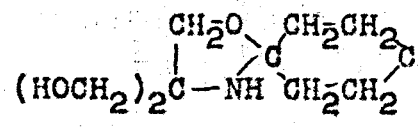
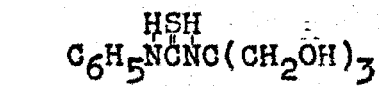
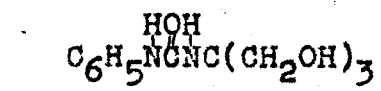
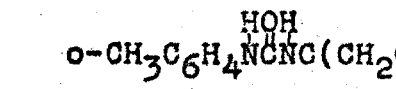
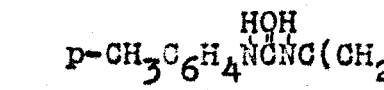
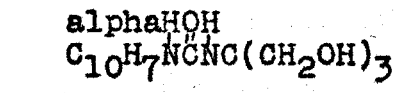
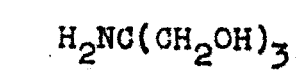
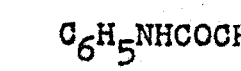
There was no evidence of reaction when tris(hydroxymethyl)aminomethane and ethylmethyl ketone were refluxed in butyl alcohol for four hours.

Ethylmethyl ketone, methylisobutyl ketone, diisobutyl ketone, and glyoxal gave no evidence of reaction with tris(hydroxymethyl)aminomethane when the components were refluxed in benzene.

Methylisobutyl ketone and diisobutyl ketone gave no evidence of reaction with tris(hydroxymethyl)aminomethane when the components were refluxed in xylene.

TABULATED RESULTS

Formula	M.P. (B.P.)	Refr. Ind. $(Daylight)_{25°}$	Sp. Gr. $\frac{20°}{4°}$	Nitrogen Analysis Exp.	Cal.	Yield Gms.	%
1-AZA-3,7-DIOXABICYCLO(3.3.0)OCTANES							
	59-60°	----	---	---	---	37.0	76.6
	(179.5-182) at 32 mm (112.5-3.5) at .2 mm	1.4641	1.040	6.10	6.11	17.2	75.4
	$(216-7)_{32}$ $(151-3)_{.3}$	1.4641	.9933	5.00	4.91	23.9	84.1
	77-8	----	---	4.92	4.71	74.3	85.3
OXAZOLIDINES							
	$(195-206)_{34}$ Sol. on stdg	----	---	8.35	8.00	4.7	45.2

Formula	M.P. (B.P.)	Refr. Ind. (Daylight)$_{25°}$	Sp. Gr.$\frac{20°}{4°}$	Nitrogen Analysis Exp.	Nitrogen Analysis Cal.	Yield Gms.	Yield %
OXAZOLIDINES (CONT'D)							
	103.5-105	---	---	8.21	8.00	8.3	47.4
	(185-9)$_{.5}$	1.5640	---	6.90	6.70	12.1	57.9
	118.1-120			7.22	6.97	12.6	62.7
THIOUREA							
	152.5-2.7	---	---	11.22	10.94	7.3	57.0
UREAS							
	191.4-1.6	---	---	11.86	11.67	4.2	70.0
	190.5-1.4	---	---	11.31	11.02	4.1	64.5
	184.6-185	---	---	11.15	11.02	5.6	88.2
alpha 	202.2-202.5	---	---	9.68	9.65	4.7	64.0
beta 	213-4 decomp.	--	---	10.03	9.65	7.0	96.7
MISCELLANEOUS							
	165-166	---	---	11.89	11.57		
		---	---	10.60	10.36		Blank

DISCUSSION OF RESULTS

The tris(hydroxymethyl)aminomethane (A) used as the starting material for the work described herein was the commercial product of the Commercial Solvents Corporation. Their publications list the melting point as 171-2°, but this melting point is obtained only after several recrystallizations of the technical product, which melts at 165-6°.

Practically, (A) is soluble in water, alcohol, pyridine, and hot N,N-diethylacetamide. (A) is soluble to the extent of 80 parts in 100 parts of water and this high water solubility is useful in purification procedures. (A) will dissolve in absolute alcohol readily when warmed, but only 0.025 mole can be put into solution in 100 cc of cold ethanol. (A) will not dissolve appreciably in cold pyridine, but may be put into solution warm and will not precipitate on careful cooling. N,N-Diethylacetamide dissolves (A) readily on heating, but much of the product comes out of solution on cooling.

Although (A) is insoluble in the majority of organic solvents, it will react with some reagents to give products soluble in these solvents. For example, (A) is insoluble in benzene but it reacts with aldehydes in the presence of benzene to give benzene soluble products.

Generally, the 1-aza-3,7-dioxabicyclo(3.3.0)octanes formed readily when a mixture of (A) and an aldehyde were mixed in a 1:2 ratio and refluxed in benzene. The water formed in the reaction was removed by using a modified Dean and Stark moisture trap. Various sources claim that the time necessary for completeness of reaction does not exceed one hour, but in this laboratory the components were refluxed at least three hours; in one case the reaction was not complete until 70 hours of refluxing.

At the completion of the reaction, the reaction flask contained no undissolved material and the necessary amount of water had collected in the water trap. After the addition of acetone, any unreacted (A) was removed by filtration, volatile material was removed with a water bath and vacuum, and the products purified by distillation or recrystallization. They can be readily recrystallized from solvents such as hexane, cyclohexane, and petroleum ether.

The oxazolidines were prepared by similar methods from (A) and an aldehyde or ketone. These compounds showed a greater tendency to crystallize than the 1-aza-3,7-dioxabicyclo(3.3.0)octanes. However, (A) would not react with

cyclohexanone and isobutyraldehyde in benzene to give the oxazolidines, no evidence of reaction being obtained when that solvent was used. A higher operating temperature was obtained by using xylene and the reaction readily took place in that solvent. Purification of these products was similar to that given above.

When (A) and cyclohexanone were reacted, it was expected that the 1-aza-3,7-dioxabicyclo(3.3.0)octane would be formed. However, only one equivalent of water was obtained, pointing to the formation of the oxazolidine. Analysis of the product proved that this assumption was correct, since the product analysed as the oxazolidine.

Analogously, only the oxazolidine was formed by the reaction of (A) and isobutyraldehyde. In this reaction two equivalents of water were collected, though, pointing to the formation of the 1-aza-3,7-dioxabicyclo(3.3.0)octane. Only the analysis indicates the formation of the oxazolidine.

Tris(hydroxymethyl)aminomethane reacts with ethyl acetoacetate to give a product boiling at 136-7°$_{.7mm}$. The nitrogen analysis of this product corresponds to neither the oxazolidine nor the 1-aza-3,7-dioxabicyclo(3.3.0)octane and its exact structure is yet to be determined.

All efforts to date to form the oxazolidine from (A) and caproaldehyde have been unsuccessful, the 1-aza-3,7-dioxabicyclo(3.3.0)octane being formed in each attempt.

One-half of the tris(hydroxymethyl)aminomethane used in these reactions was recovered in each attempt, although the requisite amount of water was obtained in each case.

The specific syntheses referred to above are being studied further in an attempt to determine the factors causing the deviations from the expected reactions.

The thiourea from (A) and phenylisothiocyanate was prepared by the procedure recommended in many textbooks on qualitative analysis. The reactants were mixed in a small beaker and heated on an open flame until a homogeneous liquid resulted. On cooling, a solid was obtained which was broken up and boiled in 50% alcohol. On recrystallization from 95% alcohol, the pure product was obtained.

An excess of phenylisothiocyanate was used to insure completeness of reaction, since it is known that the isothiocyanates will not react with alcoholic groups under mild conditions. The excess is easily removed during the purification, being soluble in alcohol.

When (A) and phenyl-, o-tolyl-, p-tolyl-, alpha-naphthyl-, or beta-naphthylisocyanate were mixed and warmed gently, a reaction took place. The products were crystallized to constant melting points from alcohol-water mixtures. As stated previously, Hist. p 21, the amino group reacts with an isocyanate before an alcohol group. Since the products formed in this reaction are insoluble in acid, this is further proof that the urea and not the urethan

was formed.

The analyses of the products described in the preceding section were made using the Dumas method for nitrogen. All of the analyses are high, including that of a known sample of acetanilide, indicating that the analyses are very reliable.

SUMMARY

Some derivatives of tris(hydroxymethyl)aminomethane are described. These include four 1-aza-3,7-dioxabicyclo(3.3.0)-octanes, four oxazolidines, one thiourea, and five ureas. Background material for the experimental work is included, as is a section indicating uses of aminoalcohol reaction products.

BIBLIOGRAPHY

Abbey, Salts of 2,4-dinitro-6-cyclohexylphenol, Brit. Pat. 600,082, March 31, 1948; C.A. 42, 7329

Abramovitch, 2-Imino-3-alkyloxazolidines, US Pat. 2,443,062, June 8, 1948; C.A. 43, 252

Adams, Long, and Johanson, Sulfanilamide Derivatives, J. Am. Chem. Soc., 61, 2342-6 (1939).

Adams and Segur, Preparation and Physiological Action of Oxazolidones and Their Decomposition into beta-Aminoethyl Alcohols, Science, 52, 185 (1920). C.A. 16, 4211

Alframine Corporation, Detergents, Brit. Pat. 515,882, December 18, 1939. C.A. 35, 6026

Alquist and Slagh, Secondary Xenoxyalkylamines, US Pat. 2,252,828, August 19, 1941. C.A. 35, 7416

American Cyanamid Co., Condensation of Aldehydes with Polyhydroxyalkylamines, Brit. Pat. 564,506, October 2, 1944. C.A. 40, 4084

Antropoff and Friedrichsen, Polysulfides of Organic Bases, Ger. Pat. 711,007, August 21, 1941. C.A. 37, 4077

Antropoff and Friedrichsen, Polysulfide Solutions of Organic Bases, Ger. Pat. 731,504, January 7, 1943. C.A. 38, 551

Antropoff and Friedrichsen, Hydroxyalkylammonium Polysulfides, US Pat. 2,167,319, July 25, 1939. C.A. 33, 8924

Bain and Pollard, Piperazine Derivatives from Amino Alcohols, J. Am. Chem. Soc., 61, 532 (1939).

Bain and Pollard, Derivatives of Piperazine. XVIII. Synthesis of Substituted Piperazines and the Hydrolysis of Amines, J. Am. Chem. Soc., 61, 2704-5 (1939).

Barbiere, Nitration of Aromatic Alkylamino Alcohols, Bull. Soc. Chim., 7, 621-6 (1940). C.A. 36, 1913

Barbiere, Nitric Acid Esterification and Nitration of Amino Alcohols, Bull. Soc. Chim., 11, 470-80 (1944). C.A. 40, 2110

Bergel, Morrison, Moss, Konigstein, Rinderknecht, Bile Acid Derivatives--Esters, Brit. Pat. 584,722, January 21, 1947. C.A. 41, 4177

Bergmann and Brand, Shifting of Acyl from Nitrogen to Oxygen in Amino Alcohols, Ber 56B, 1280-3 (1923).

Bergmann, Ulpts, and Camacho, Miscellaneous Notes on the Aldehyde Compounds of Hydroxyamines and on the Partial Acylation of These Amines, Ber. 55B, 2796-812 (1922).

Bertsch and Kogl, Etherlike Condensation Products, Ger. Pat. 742,148, October 14, 1943. C.A. 40, 899

Bettzieche, Action of the Grignard Reagent on Amino Alcohols. V. Acyl Migration in Aminoalcohols and Glycols, Z. physiol. Chem. 146, 227-40 (1925). C.A. 19, 3254

Bettzieche, Alkali Cleavage of Amino Alcohols, Z. physiol. Chem. 172, 69-71 (1927). C.A. 22, 584

Bettzieche and Ehrlich, Action of the Grignard Reagent on Amino Acids. VI. Fusion Cleavage of Amino Alcohols, Z. physiol. Chem. 150, 191-6 (1925). C.A. 20, 388

Bettzieche and Menger, Synthesis of Peptide Alcohols, Cleavage by Acid and Alkali, Z. physiol. Chem. 161, 37-65 (1926) C.A. 21, 568

Blair, Breaking Petroleum Emulsions, US Pat. 2,422,177, June 17, 1947. C.A. 41, 6397

Blank, Organic Polysulfides, Fr. Pat. 839,775, April 12, 1939. C.A. 33, 7932

Blank and Blank, Polysulfides of Organic Bases and Their Solutions, Brit. Pat. 514,288, November 3, 1939. C.A. 35, 4551

Blankart, Phenyl Substituted Fatty Acid Esters of Amino Alcohols, US Pat. 1,987,546, January 8, 1935. C.A. 29, 1432

Blicke, Dialkylaminoalkyl Alkyl-1-naphthylacetates, US Pat. 2,415,079, February 4, 1947. C.A. 41, 2753

Blicke and Olsuki, 1-Alkyl-2-dialkylaminoalkyl-3-aminophthalates as Local Anesthetics, J. Am. Chem. Soc. 63, 1945-7 (1941).

Blicke and Olsuki, 1-Dialkylaminoalkyl-2-alkyl-3-aminophthalates as Local Anesthetics, J. Am. Chem. Soc. 63, 2435-6 (1941).

Blicke and Parke, Alkylaminoalkyl Esters of Aminonaphthoic Acids as Local Anesthetics, J. Am. Chem. Soc. 61, 1200-3, (1939)

Boggs and Sullivan, Greaseproof Paper, US Pat. 2,416,734, March 4, 1947. C.A. 41, 2900

Bray and Russell, Agglomerating Agent in Filtration of Used Lubricating Oils, US Pat. 2,435,707, February 10, 1948. C.A. 42, 3560

Bray and Russell, Oil Filter and Treatment of Same, US Pat. 2,435,734, February 10, 1948. C.A. 42, 2762

Breckenridge and Hodgins, Coordination Compounds of 1,3-diaminoisopropanol, Can. J. Research 17, B, 331-5 (1939). C.A. 34, 1269

Brill, Alkamine Esters of Aromatic Acids; Novocaine Analogs, J. Am. Chem. Soc. 54, 2484-7 (1932).

Brill and Bulow, Procaine Analogs. IV. Alkamine Esters of Aliphatic Acids, J. Am. Chem. Soc. 55, 2059-61 (1933).

Brill and Cook, Procaine Analogs. V. Some Alkamine Esters of Cinnamic Acid and Derivatives, J. Am. Chem. Soc. 55, 2062-5 (1933).

Brintzinger and Hess, Coordination Compounds of Ethanolamines and Ethylethanolamines, and the Tanning Action of Ethanolaminechromium Complexes, Z. anorg. Chem., 252, 293-304 (1944) C.A. 40, 4311

Brodersen and Quaedvlieg, High Molecular Fatty Acid Esters of Hydroxyalkylamines, Ger. Pat. 741, 689, September 30, 1943. C.A. 39, 2514

Brown, Resinous Reaction Product of Polymerized Fatty Acid Ester, Rosin, and Trialkanolamine, US Pat. 2,416,433, February 25, 1947. C.A. 41, 4003

Brubaker and Maxwell, beta-Ethylaminoethanols, US Pat. 2,212,149, August 20, 1940. C.A. 35, 1070

Bruning, Alkamine Esters of Salicylic Acid, Ger. Pat. 188,571, May 29, 1906. C.A. 2, 604

Bruson, Aralkylamino Alcohols, US Pat. 2,114,122, April 19, 1938 C. A. 32, 4251

Burke, Resins Obtained from Ureas and Hydroxyalkylamines, US Pat. 2,374,077, April 17, 1945. C.A. 39, 3694

Burnett, Jenkins, Peet, Dreger, and Adams, Dialkylaminoalkanol Esters of p-Aminobenzoic Acid, J. Am. Chem. Soc. 59, 2248-52 (1937).

Burtner, Antispasmodic Salts of Amino Alcohol Esters of 9-Fluorenecarboxylic Acid, US Pat. 2,262,754, November 18, 1941. C.A. 36, 1738

Cahn, Esters of Alcoholic Nontertiary Amines, US Pat. 2,449,926, September 21, 1948. C.A. 43, 674

Cahn and Harriss, Compounds Containing Ester and Amide Linkages, US Pat. 2,371,097, March 6, 1945. C.A. 39, 4089

Campbell and Campbell, Amino Alcohols. I. Preparation and Dehydration of Certain Aliphatic Tertiary Amino Alcohols, J. Am. Chem. Soc. 60, 1372-6 (1938).

Campbell and Campbell, The Rearrangement of beta-amino alcohols with Heat and Alkali, J. Org. Chem. 9, 178-83 (1944).

Carbide and Carbon Chemicals Corp., Alkali Metal Salt of an Amino Carboxylic Acid, Brit. Pat. 601,816, May 13, 1948. C.A. 42, 7324

Carbide and Carbon Chemicals Corp., Dialkylamino Alcohols, Fr. Pat. 792,046, December 21, 1935. C.A. 30, 4176

Carr, Reaction of 2-Mercaptothiazoles with Alkanolamines, US Pat.. 2,393,507, January 22, 1946. C.A. 40, 2684

Cass and K'burg, N-Substituted Alkylolamines, US Pat. 2,194,294, March 19, 1940. C.A. 34, 4742

Cazier, Quaternary Derivatives of (methylamino)tris(hydroxymethyl)methane, Bull. soc. chem. belges 57, 232-5 (1948). C.A. 43, 134

Cazier and Govaert, Quaternary Salts of tris(aminomethyl)(hydroxymethyl)methane, 3-(aminomethyl)-3-bromomethyl)oxacyclobutane, and 3,3-bis(aminomethyl)oxacyclobutane, Bull. soc. chem. Belges 56, 251-60 (1947). C.A. 42, 1876

Charlton and Day, Urea Derivatives in the Alkanolamine Series, J. Org. Chem. 1, 552-8 (1937).

Christ, Fiber-forming Polymers. US Pat. 2,312,879, March 2, 1943 C.A. 37, 5169

Christ, Fiber-forming Polymers, US Pat. 2,396,248, March 12, 1946. C.A. 40, 3000

Christiansen and Harris, Amino Alcohol Esters, Can. Pat. 401,190, December 2, 1941. C.A. 36, 1738

Christiansen and Harris, Hydroxybenzoic Acid Esters, US Pat. 2,243,694, May 27, 1941. C.A. 35, 5646

Christiansen and Harris, Amino Alcohol Esters of Hydroxybenzoic Acids, US Pat. 2,404,691, July 23, 1946. C.A. 41, 155

Christiansen and Harris, Dialkylaminoalkyl p-alkoxybenzoates, US Pat. 2,412,966, December 24, 1946. C.A. 41, 2442

Christiansen and Harris, Dialkylaminoalkyl Aralkyloxybenzoates, US Pat. 2,415,235, C.A. 41, 2753

Christiansen and Harris, Alkoxy benzoates of N-(2-hydroxyethyl)-N-(2-hydroxy-2-phenylethyl)-substituted Amino Alcohols, US Pat. 2,418,501, April 8, 1947. C.A. 41, 4514

Coleman, N-Alkyl Alkanolamine Salts of Halophenols, US Pat. 2,386,037, October 2, 1945. C.A. 40, 1543

Coleman and Smith, Substituted Alkanolamine Salts of Dinitrophenols, US Pat. 2,385,795, October 2, 1945. C. A. 40, 163

Compagnie nationale de matieres colorantes and manufactures de produits chimiques du Nord reunies etablissements Kuhlmann, Quaternary Ammonium Salts, Fr. Pat. 860,910, January 28, 1941. C.A. 42, 7328

Cook and Rider, Phenylurethan Anesthetics II. , J. Am. Chem. Soc. 58, 1079-81 (1936).

Cope, Secondary Alkylamino Alkyl Esters of Arylsubstituted Aliphatic Acids, US Pat. 2,456,555, December 14, 1948. C.A. 43, 2639

Cope, Secondary Alkylaminoalkyl Esters of p-Dialkylamino-benzoic Acids, US Pat. 2,456,556, December 14, 1948. C. A. 43, 2640

Cope and Hancock, Synthesis of 2-Alkylaminoethanols from Ethanolamine, J. Am. Chem. Soc. 64, 1503-6 (1942).

Cope and Hancock, Benzoates, p-Aminobenzoates and Phenyl-urethans of 2-Alkylaminoethanols, J. Am. Chem. Soc. 66, 1448-53 (1944).

Curme, Chitwood, and Clark, Amino Carboxylic Acids and their Salts, US Pat. 2,384,816, September 18, 1945. C.A. 40, 353

Dasher, Reclaiming Soft-vulcanized Rubber, US Pat. 2,304,548, December 8, 1942. C. A. 37, 2960
See also--US Pats. 2,304,549 and 2,304,550

De Groote, Breaking Petroleum Emulsions of the Water-in-oil type, US Pat. 2,342,648, February 29, 1944. C.A. 38, 5070
See also--US Pats. 2,342,649 and 2,342,650

De Groote, Condensation Products of Higher Molecular Weight Monocarboxylic Acids and Polymerized Hydroxylated Poly-Amines, US Pat. 2,395,400, February 26, 1946. C. A. 40, 4079

De Groote and Keiser, Ricinoleic Acid Esters Suitable for Use as Demulsifiers with Crude-oil Emulsions or in the Doctor Treatment of Gasoline, US Pat. 2,282,646, May 12, 1942 C.A. 36, 6789

De Groote and Keiser, Breaking Petroleum Emulsions of the Water-in-oil Type such as Oil in Wells, US Pat. 2,324,488, July 20, 1943. C.A. 38, 475
See also--US Pats. 2,324,489 through 2,324,495.

De Groote and Keiser, Acylated Polyamino Ethers and the Like, US Pat. 2,354,578, July 25, 1944. C.A. 38, 6437
See also-- US Pats. 2,354,579 and 2,354,580.

De Groote and Keiser, Condensation Products as Demulsifying Agents, US Pat. 2,373,174, April 10, 1945. C.A. 39, 3420

De Groote and Keiser, Interaction of a Monocarboxylic Acid Ester with the Alkyl Ester of a Polycarboxylic Acid, US Pat. 2,382,612, August 14, 1945. C.A. 39, 5106

De Groote and Keiser, Acylated Amino Alcohol Esters of Carbonic Acid, US Pat. 2,384,608, September 11, 1945. C.A. 40, 356

De Groote and Keiser, Certain Dicarboxylic Acid Esters of Hydroxyalkylated Polymerized Hydroxy Amines, US Pat. 2,430,004, November 4, 1947. C.A. 42, 1970

De Groote, Kieser, and Blair, Wetting, Dispersing, and Emulsifying Agents, US Pat. 2,228986, January 14, 1941 C. A. 35, 3008

De Groote and Wirtel, Process for Breaking Petroleum Emulsions, US Pat. 2,442,075, May 25, 1948. C.A. 42, 5654
See also-- US Pat. 2,442,076.

Detrick and Lang, Pigment Powders Suitable for Use in Paints and Lacquers, US Pat. 2,305,379, December 15, 1941. C.A. 37, 3284

Donleavy, Alkyl Thio-substituted Benzoic Acid Alkamine Ester Salts and Intermediates, US Pat. 2,173,827, September 26, 1939. C.A. 34, 1132

Donleavy and English, Some Alkamine Esters of Disubstituted Methylcarbamic Acids, J. Am. Chem. Soc. 62, 218-19 (1940).

Donleavy and English, Synthesis of Some Alkamine Esters of Alkylthiobenzoic Acids, J. Am. Chem. Soc. 62, 220-1 (1940)

Dreyfus, Amino Alcohol Derivatives (Sizing, Wetting, Cleansing, Dispersing and Emulsifying Agents), US Pat. 2,067,176, January 12, 1937. C.A. 31, 1524.

E. I. du Pont de Nemours and Co., Detergent Compounds, Brit. Pat. 428,142, May 7, 1935. C.A. 29, 6670

E. I. du Pont de Nemours andCo., Esters of Acrylic Acids, Brit. Pat. 475,131, November 15, 1937. C.A. 32, 3418

Eidebenz and Mengele, Salts of Diarylaminoalkylcarbinols, Ger. Pat. 675,817, May 17, 1939. C.A. 34, 1996

Eisleb, Alkylolamine Derivatives, US Pat. 1,949,247, February 27, 1934. C.A. 28, 2850

Epstein and Katzmann, Sulfonated Carboxylic Acid Esters of Amino Alcohol Derivatives (Wetting, Cleansing, Penetrating, Emulsifying, Lathering, Frothing, Flotation, and Anti-spattering Agents), US Pat. 2,178,139, October 31, 1939. C.A. 34, 1418

Epstein and Katzmann, Derivatives of Amino Alcohols, US Pat. 2,236,528, April 1, 1941. C. A. 35, 4521
See also-- US Pat. 2,236,529.

I. G. Farbenind A.-G., Halogenated Alkylamines, Belg. Pat. 451,090, July, 1943. C.A. 42, 202

I. G. Farbenind A.-G., Alkylolamine Derivatives, Fr. Pat. 718,398, June 8, 1931. C.A. 26, 3119

I. G. Farbenind A.-G., Hydroxyalkylamine Compounds, Fr. Pat. 740,410, July 23, 1932. C.A. 27, 2318

I. G. Farbenind A.-G., Hydroxyalkylalkylenediamines, Fr. Pat. 801,121, July 28, 1943. C.A. 31, 111

I. G. Farbenind A.-G., Condensation Products of Formaldehyde with Hydroxyalkylamines, Ger. Pat. 545,269, August 24, 1929. C.A. 26, 3080

I. G. Farbenind A.-G., Amino Alcohols, Ger. Pat. 538,456, June 1, 1930. C.A. 26, 1714

I. G. Farbenind A.-G., Compounds of Hydroxyamines with Metal Halides, Ger. Pat. 606,400, December 1, 1934. C.A. 29, 1587

I. G. Farbenind A.-G., Wetting, Cleansing and Emulsifying Agents, Ger. Pat. 612,686, May 2, 1935. C.A. 29, 6331

I. G. Farbenind A.-G., Condensation Products of Hydroxyamines, Ger. Pat. 642,744, March 23, 1937. C.A. 31, 6418

I. G. Farbenind A.-G., Nitrogenous Condensation Products, Ger. Pat. 648,793, August 9, 1937. C.A. 31, 8758

Farbenindustrie, Amino Double Compounds, Brit. Pat. 436,008, October 3, 1935. C.A. 30, 1520

Fisk, Amine Hydriodides, US Pat. 2,128,741, August 30, 1938. C.A. 30, 1520

Fosdick and Calandra, Synthesis of bis(Dialkylaminoalkyl) esters of 4-Fluoroisophthalic Acid, J. Am. Chem. Soc. 65, 2308-9, 1943.

Fosdick and Campaigne, Some Alkamine Esters of p-Fluorobenzoic Acid and Their Salts, J. Am. Chem. Soc. 63, 974-5, 1941.

Fosdick and Fancher, Some Normal and Alkamine Esters of 4-Methoxyisophthalic Acid, J. Am. Chem. Soc. 63, 1277-9 (1941).

Fourneau, Derivatives of Amino Alcohols; Esters or Derivatives Acylated at the Oxygen, J. pharm. chim. (7), 2, 337-44. C.A. 5, 3798

Fourneau, Derivatives of Amino Alcohols. II. Derivatives Acylated at the Nitrogen, J. pharm. chim. (7), 2, 397-401 C.A. 5, 3799

Fourneau and Brydowna, Action of Anhydrous Chloral on the Amino Alcohols and the Hydroxyamino Esters with a Tertiary Amine Grouping, Bull. soc. chim. 43, 1023-7 (1928). C.A. 23, 374

Garelli and Racciu, Condensation of Phthalic Anhydride with Amino Alcohols, Atti accad. sci. Torino, Classe sci. fis., mat. nat. 69, 358-63 (1934). C.A. 29, 6223

J. R. Geigy A.-G., Basic Esters and Amides of 1-phenyl-1-cycloalkanecarboxylic Acids, Brit. Pat. 582,535, November 20, 1946. C.A. 41, 2438

J. R. Geigy A.-G., Esters of 1-Substituted 4-Hydroxypiperidines, Brit. Pat. 585,729, February 21, 1947. C.A. 42, 621

J. R. Geigy A.-G., Basic Esters of Aliphatic Carboxylic Acids, Brit. Pat. 594,294, November 7, 1947. C.A. 42, 2615

Gilmann, Salts of Alkylolamine Boric Acid Esters, US Pat. 2,441,063, April 4, 1948. C.A. 42, 8815

Goldberg, Ringk, and Spoerri, Preparation of Aminobenzoic Acid Esters of Substituted Monoalkylamino Alcohols, J. Am. Chem. Soc. 61, 3562-4 (1939).

Goldberg and Whitmore, Preparation of p-Aminobenzoic Acid Esters of Monoalkylamino Alcohols, J. Am. Chem. Soc. 59, 2280-2, (1937).

Gomez and Fermin, Condensation of Phenolic Compounds with Ethanolamines and Formaldehyde, Univ. Philippines Nat. and Applied Sci. Bull. 8, 287-312 (1941). C.A. 36, 4104

Goodman, Condensation of Alkylolamines with Acetoacetamides, US Pat. 2,323,391, July 6, 1943. C.A. 38, 263

Goodson and Christopher, Reaction of o-Hydroxy- and o-Chlorobenzaldehyde with Ethanolamine, J. Am. Chem. Soc. 71, 1117-19 (1949).

Graves, Amino Alcohol Acrylates, US Pat. 2,138,031, November 29, 1942. C.A. 33, 1759

Gublemann, Stabilization of Organic Substances, US Pat. 2,381,952, August 14, 1945. C.A. 40, 362

Guest, Detergent Compounds, Emulsifying and Wetting Agents, US Pat. 2,277,015, March 17, 1942. C.A. 36, 4632
See also-- US Pat. 2,277,016.

Guggenheim, Basic Esters of Fatty-aromatic Acids, US Pat. 1,932,341, October 24, 1934. C.A. 28, 578

Hancock and Cope, Monoalkylaminopropanols and Butanols and Their Esters, J. Am. Chem. Soc. 66, 1738-47, (1944).

Hancock, Hardy, Heyl, Wright, and Cope, Amino Alcohols and Their Esters, J. Am. Chem. Soc 66, 1747-52 (1944).

Harmon, Polymerizing Methacrylic Esters of Amino Alcohols, US Pat. 2,138,762, November 29, 1938, C.A. 33, 2250

Harris, Wetting Agents, etc., Brit. Pat. 488,490, July 5, 1948 C.A. 33, 279

Hartung, Murch, and Kester, Amino Alcohols. XIII. Benzoic Esters of Arylalkanolamines, J. Am. Chem. Soc. 54, 1526-30, (1932).

Hess and Uibrig, The Action of Aldehydes on Primary Hydramines, Ber. 48, 1974-85 (1915).

Hill and Holmes, Alcoholysis of Alkamine Esters of Diarylhydroxyacetic Acids, US Pat. 2,394,770, February 12, 1946. C.A. 40, 3141

Hodgins and Hovey, Aminohydroxy Compounds and Derivatives, US Pat. 2,215,038, September 17, 1940. C.A. 35, 830

Hoffman, Esters of Amino Alcohols, Ger. Pat. 586,247, October 19, 1933. C.A. 29, 577

See also-- Brit. Pat. 396,318, August 3, 1933
Ger. Pat. 591,677, January 25, 1934
Ger. Pat. 594,085, March 10, 1934

Hoffman, Alkylamine Esters, Ger. Pat. 603,624, October 4, 1934. C.A. 29, 813

Hoffman and Schellenberg, Preparation of Basic Esters, Helv. Chim. Acta 30, 292-5 (1947). C.A. 41, 3074

Holmes and Hill, Esters of Alkoxybenzilic Acids, US Pat. 2,430,116, November 4, 1947. C.A. 42, 1609

Homeyer, 2-Oxazolidones, US Pat. 2,399,118, April 23, 1946 C.A. 40, 4084

See also-- US Pats. 2,437,388, March 9, 1948 C.A. 42, 4613
2,437,389, March 9, 1948

Horenstein and Pahlicke, A New Rearrangement Reaction and Its Use for the Preparation of Esters of Amino Alcohols, Ber. 71B, 1644-57 (1938).

Horenstein and Pahlicke, Alkamine Esters, Ger. Pat. 673,841, March 30, 1939. C.A. 33, 6529

Huang, Chang, and Lu, The Synthesis, Toxicity, and Anesthetic Potency of Two New Local Anesthetics, Brit. J. Pharmacol., 1, 273-7 (1946). C.A. 41, 2011

Huter, Preparation of Substituted Thioureas, Chem. Ber. 80, 273-7 (1947). C.A. 42, 4947

Jacobs and Heidelberger, Monohalogenacetyl Derivatives of Amino Alcohols, J. Biol, Chem. 21, 403-37 (1915). C.A. 9, 2074

Jayne, Amino Alcohol Esters, US Pat. 2,355,442, August 8, 1944. C.A. 39, 86

Jayne and Day, Amino Alcohol Esters, US Pat. 2,305,083, December 15, 1942. C.A. 37, 2848

Jayne and Day, Reaction Products of Hydroxypolyamines, High Molecular Weight Carboxylic Acids, and Organic Sulfonic Acids, US Pat. 2,391,830, December, 25, 1945. C.A. 40, 2329

Johnson, Products Having Emulsifying and Other Interface Modifying Properties, US Pat. 2,354,320, July 25, 1944. C.A. 38, 6438

Johnson, Rubber Lubricant, US Pat. 2,389,855, November 27, 1945 C.A. 40, 5951

Johnston, Poly(hydroxyalkyl)amine-aldehyde Condensation Products, US Pat. 2,448,890, September 7, 1948. C.A. 43, 2633

Jones, Oxidation of Alkanolamines by Periodate, J. Assoc. Official Agr. Chem. 27, 462-7 (1944). C.A. 38, 6276

Jones, Preparation of Alkanolamine Hydrochlorides, J. Assoc. Official Agr. Chem. 27, 467-72 (1944). C.A. 38, 6275

Jones, Amino Aliphatic Hydrogen Sulfates, US Pat. 2,264,759, December 2, 1941. C.A. 36, 1619

Kahane and Kahane, New Research on Phosphotungstates and Silicotungstates, Bull. soc. chem. (5), 3, 621-5 (1936). C.A. 20, 5521

Kanao, and Yaguchi, Deaminization of Tertiary Amino Alcohols, J. Pharm. Soc, Japan 48, 252-8 (1928). C.A. 22, 2937

Kartaschoff, Basic Derivatives of Fatty Acids (Lake-forming and Wetting, Emulsifying and Detergent Substances), US Pat. 2,149,527, March 7, 1939. C.A. 33, 4350

Katz, Surface-active Anionic Compounds of Amino Alcohols, US Pat. 2,216,617, October 1, 1940. C.A. 35, 830

Katz, Surface-active Boric Acid Ester Compounds of Amino Alcohols, US Pat. 2,216,618, October 1, 1940. C.A. 35, 830

Katzman, Chemical Compounds, US Pat. 2,411,434, November 19, 1946. C.A. 41, 876

Katzman and Epstein, Alkylolamine Derivatives (Detergent, Emulsifying, and Flotation Agents), US Pat. 2,173,448, September 19, 1939. C.A. 34, 552

Katzman and Epstein, Polymerized Alklolamine Derivatives (Detergent, Emulsifying, and Flotation Agents, etc.), US Pat. 2,178,173, October 31, 1939. C.A. 34, 1417

Katzman and Epstein, Derivatives of Polymerized Alkylolamines (Detergent, Emulsifying, and Flotation Agents, etc.), US Pat. 2,248,089, July 8, 1941. C.A. 35, 6699

Katzman and Epstein, Esters of Alcohol Amines, US Pat. 2,390,942, December 11, 1945. C.A. 40, 1334

Keiser, Phthalic Anhydride and Oxalic Acid with Ethanolamines, Ind. Eng. Chem., Anal. Ed., 12, 284 (1940).

Kern and Sala, Alkylolamine Salts of Aliphatic Acids and Sulfonated Fatty Acids (Dye Assistants), US Pat. 1,799,821, April 7, 1931. C.A. 25, 3176

Kern and Sala, Alkylolamine Derivatives of Aliphatic Acids, US Pat. 1,946,079, February 6, 1934. C.A. 28, 2365
See also-- US Pat. 1,946,080.

Kiprianov and Kusner, Reaction of Ethanolamine with Aldehydes and Malonic Acid, J. Gen. Chem. (USSR) 6,641 (1936). C.A. 30, 6350

Kohn, Action of Aldehydes on Primary Hydroxyamines, Remarks on the Communication of Hess and Uibrig, Ber. 49, 250-1 (1916).

Krabbe, Eisenlohr and Schone, Formation of Oxazolines and Isoquinolines from N-Acylaminocarbinols, Ber. 73, 656-60. (1940).

Krabbe, Polzin, and Culemeyer, Synthesis of Isoquinoline Derivatives. III. Preparation of some N-Acylvinylamines from N-Acylaminoalcohols, Ber. 73B, 652-5 (1940).

Krasuskii, The Decomposition of alpha-Amino Alcohols and their Salts on Heating, Ukrainskii Khem. Zhurnal 4, Sci. Pt. 61-74 (1929). C.A. 24, 1083

Krasuskii and Kosenko, Hydrochlorides of alpha-Aminoalcohols, Ukrainskii Khem. Zhur. 4, Sci. Pt. 199-209 (1929). C.A. 24, 2106

Kremer, Synthesis of N-phenylpiperazino-N'-beta-ethanol, J. Am. Chem. Soc. 58, 379 (1936).

Kremer, Alkanolamines. II. Reaction of the Chloronitrobenzenes with Monoethanolamine, J. Am. Chem. Soc. 59, 1681-2 (1937).

Kremer, Preparation of Substituted Anilino Alcohols, J. Am. Chem. Soc. 61, 1321-4 (1939).

Kremer and Bendich, Alkanolamines. VII. Condensation Products of Monoethanolamine and the Isomeric Dichloronitrobenzenes, J. Am. Chem. Soc. 61, 2658-61 (1939).

Kremer and Bendich, Alkanolamines.IX. Reducing and Hydrolyzing Action of the Ethanolamines on the Dichloronitrobenzenes, J. Am. Chem. Soc. 62, 1279-81 (1940).

Kremer and Kress, Alkanolamines. IV. Reducing Properties of the Amino Alcohols, J. Am. Chem. Soc. 60, 1031-2 (1938).

Kremer and Meltsner, Chloronitroanilino Alkanols, J. Am. Chem. Soc. 64, 1285-6 (1942).

Kremer, Meltsner and Hindin, Action of Monoethanolamine on Ethyl Bromomalonate, J. Am. Chem. Soc. 64, 1010 (1942).

Kremer and Waldman, Alkanolamines. XI. Monoalkylamino Alcohols and their Esters, J. Am. Chem. Soc. 64, 1089-90 (1942).

Kritchevsky, Hydrotropic Materials Suitable for Use as Dispersing and Emulsifying Agents, US Pat. 2,089,212, August 10, 1937. C.A. 31, 6773

Kritchevsky, Hydrotropic Condensation Products Suitable for Use as Dispersing Agents with Pigments, etc., US Pat. 2,094,608, October 5, 1937. C.A. 31, 6773
See also-- US Pat. 2,094,609.

Kritchevsky, Acid Substituted Hydroxy Alkylamines, US Pat. 2,173,058, September 12, 1939. C.A. 34, 552

Kritchevsky, Alcohol Amine Condensation Products (Emulsifying Agents, etc.), US Pat. 2,192,664, March 5, 1940. C. A. 34, 4491

Kritchevsky, Condensation Products Suitable for Use as Emulsifying, Dispersing, and Wetting Agents with Oils, Dyes, etc., US Pat. 2,260,384, October 28, 1941. C.A. 36, 857

Kropa, Polyester-polyamide Condensation Products, US Pat. 2,240,516, April 27, 1948. C.A. 42. 5274

Kropp, Complex Compounds of Alkali Metal and Alkaline Earth Metal Halides with Hydroxy Alkylamines, US Pat. 2,017,976, October 22, 1935. C.A. 30, 249

Lafage and Lebermann, Hydroxyalkylamine Derivatives, Fr. Pat. 850,761, December 26, 1939. C.A. 36, 1949

Larsen, Ruddy, Elpern, MacMullin, Dialkylaminoalkyl Esters of Trisubstituted Acetic Acids, J. Am. Chem. Soc. 71, 532-3 (1949).

Leben and Ormul Products Ltd., Soap; Alkylolamine Salts, Brit. Pat. 414,077, July 23, 1934. C.A. 29, 370

Legerlotz, Phenylalkanolamines, Fr. Pat. 763,428, April 30, 1934 C.A. 28, 5470

Legerlotz, Optically Active Amino Alcohols, Ger. Pat. 585,164, September 29, 1933. C.A. 28, 1355

Leonard and Rebenstorf, Lead Tetraacetate Oxidation of Amino Alcohols, J. Am. Chem. Soc. 67, 49-51 (1945).

Link and Jaccard, Textile Assistants, Ger. Pat. 737,738, June 17, 1943; Fr. Pat. 866,855, September 15, 1941. C.A. 38, 4814

Lott, Acrylates, US Pat. 2,158,239, May 16, 1939. C.A. 33, 6530

Lott, Esters and Amides of Unsaturated Acids, US Pat. 2,251,946, August 12, 1941. C.A. 35, 7415

Lott and Braker, Carbanilic Acid Derivatives, US Pat. 2,109,492, March 1, 1938. C.A. 32, 3094

Lott and Christiansen, Relation between Chemical Constitution and Local Anesthetic Activity. III. Substituted Cinnamic Acid Esters of Dialkylamino Alcohols, J. Am. Pharm. Assoc., 28, 499-502 (1939). C.A. 34, 88

Lycan and Eyre, Artificial Drying Oil, US Pat. 2,373,250, April 10, 1945. C.A. 39, 3168

Maier-Bode, Disinfectant, Ger. Pat. 696,346, August 15, 1940. C.A. 35, 6070

Mannich, Alkamine Esters, Brit. Pat. 361,493, September 25, 1930. C.A. 27, 997

Mannich, Aromatic Esters of Amino Alcohols, US Pat. 1,889,678, November 29, 1932. C.A. 27, 1638

Martin, Wetting Agents for Use in Mercerizing, Dyeing, or Other Textile Treatments, US Pat. 2,181,534, November 28, 1939. C.A. 34, 2186

Martin and Hafliger, Basic Esters of 1-Arylcycloalkanecarboxylic Acids, US Pat. 2,404,588, July 23, 1946. C. A. 40, 6500

Martin and Hafliger, Derivatives of alpha-Substituted Aryloxyacetic Acids, US Pat. 2,428,978, October 14, 1947. C. A. 42, 1607

Martin and Margot, Basic Esters of Monoalkylisobutylacetic Acids, US Pat. 2,417,208, March 11, 1947. C.A. 41, 3811

Mathes, Stewart, and Swedish, Amine Salts of Thiocyanic Acid, J. Am. Chem. Soc. 70, 3455 (1948).

Mattox, Synthetic Varnish Resins, US Pat. 2,011,064, August 13, 1935. C. A. 29, 6669

Maxwell, Alkylolamines, US Pat. 2,194,314, March 19, 1940. C. A. 34, 4865

Meade, Esters of Tertiary Amino Polyhydric Alcohols, Brit. Pat. 587,534, April 29, 1947. C.A. 42, 590

Meade, Esters of Tertiary Amino Alcohols, Brit. Pat. 588,032, May 13, 1947. C.A. 42, 590

Meltsner, Greenfield and Rosenzweig, Alkanolamines. VIII. Reaction of Ethanolamines on p-Nitrobenzoic Acid, J. Am. Chem. Soc. 62, 991-2 (1940).

Meltsner, Greenstein, Gross, andCohen, Alkanolamines: Reactions of Chloronitrobenzene with Ethanolamines, J. Am. Chem. Soc. 59, 2660-1 (1937).

Meltsner, Kirschenbaum, and Stempel, Reaction of m-Dinitrobenzene with Ethanolamines, J. Am. Chem. Soc. 60, 1236 (1938).

Meltsner, Waldman, and Kremer, Aryl Substituted Oxazolidines, J. Am. Chem. Soc. 62, 3494 (1940).

Meltsner, Wohlberg, and Kleiner, Reduction of Organic Compounds by Ethanolamines, J. Am. Chem. Soc. 57, 2554 (1935).

Merck, Salts of Aromatic Aminoalcohols, Ger. Pat. 612,592, May 11, 1935. C.A. 29, 6365

Miescher, Hoffmann and Panizzon, Preparation of Some Basic Esters of Substituted Acetic Acids, Helv. Chim. Acta. 24, 458-65 (1941). C.A. 36, 2543

Mitscherling, Detergent Compositions, US Pat. 2,244,721, June 10, 1941. C.A. 35, 6026

Mndzhoyan, Synthesis of New Anesthetics.I. Esters of 2-Furancarboxylic Acid and Amino Alcohols, J. Gen. Chem. (USSR) 16, 751-66 (1946). C.A. 41, 2033

Mndzhoyan, Synthesis of New Anesthetics. II. Esters of 5-Bromo-2-furancarboxylic Acid and Amino Alcohols, J. Gen. Chem. (USSP) 16, 767-70 (1946). C.A. 40, 2033

Mndzhoyan, Esters of 3-pyridinecarboxylic Acid, J. Gen. Chem. (USSR) 16, 1029-32 (1946). C.A. 41, 2737

Mndzhoyan, Esters of p-Amino- and of p-Butylaminobenzoic Acids and Some Diamino Alcohols, J. Gen. Chem. (USSR) 16, 1033-40 (1946). C.A. 41, 2737

Monson, Basic Acylated Polyamino Alcohols as Antifoaming Agents, US Pat. 2,408,527, October 1, 1946. C.A. 41, 1054

Monson, Anderson, and Jenkins, Amino Alcohols as Demulsifying Agents for Petroleum Emulsions, US Pat. 2,407,895, September 17, 1946. C.A. 41, 1083

Morris, Sweetening of Light Hydrocarbon Distillates, US Pat. 2,366,545, January 2, 1945. C.A. 39, 2398

Naoum and Sommerfield, Monoethanolamine Dinitrate, Ger. Pat. 514,955, December 6, 1929. C.A. 25, 3362
See also-- Ger. Pats. 516,284 and 517,832.

Nicolet and Shinn, Action of Periodic Acid on alpha-Amino Alcohols, J. Am. Chem. Soc. 61, 1615 (1939).

Nobel and Co., Ethanolamine Nitrates, Brit. Pat. 350,293, November 22, 1929. C.A. 26, 5423

Nobel and Co. Monoethanolamine Dinitrate, etc., Brit. Pat. 357,581, June 23, 1930. C.A. 26, 6141

Nobel and Co., Nitrated Aliphatic Amines, Brit. Pat. 358,157, July 5, 1930. C.A. 26, 6141

Northey and Hultquist, (Alkyl-beta-4-morpholinylalkylamino)-alkanol Esters, US Pat. 2,351,833, June 20, 1944. C.A. 38, 5368

Novocol Chemical Manufacturing Co., Lower Monoalkylamino-ethyl Aminobenzoates, Brit. Pat. 533,012, February 5, 1941. C.A. 36, 782

Oberlin, Phenylaminoalkylcarbinols Substituted in the Phenyl Nucleus, US Pat. 1,898,258, February 21, 1933. C.A. 27, 2762

Orekhoff and Roger, Deamination of Some Amino Alcohols, Compte. rend. 180, 70-3 (1925).

Orelup, Amino Alcohol-Fat Acid Ester Surface-active Agents with Amphoteric Properties, US Pat. 2,388,281, November 6, 1945. C.A. 40, 2659

Parke, Davis and Co., Synthetic Drugs, Brit. Pat. 105,744, February 27, 1917. C.A. 11, 2389
See also--Brit. Pat. 105,745.

Parker and Hill, Alkamine Derivatives of o-Alkoxymethylbenzoic Acids, US Pat. 2,383,074, August 21, 1945. C.A. 40, 96

Parker and Hill, Alkamine Derivatives of p-Aminomethylbenzoic Acid, US Pat. 2,406,627, August 27, 1946. C.A. 41, 486

Parker and Hill, Alkamine Derivatives of m-(Aminomethyl)-benzoic Acid, US Pat. 2,428,239, September 30, 1947. C.A. 42, 603

Parker and Hill, Alkamine Derivatives of o-Aminomethylbenzoic Acid, US Pat. 2,429,275, October 21, 1947. C.A. 41, 486

Perkins and Purse, Dialkylamino Alcohols, Can. Pat. 370,083, November 23, 1937. C.A. 32, 2143

Perlmuteer, Wetting and Other Agents, Fr. Pat. 826,299, March 28, 1938. C.A. 32, 7612

Phrix-Arbeitsgemeinschaft, Mixed Condensation Superpolymer Products, Belg. Pat. 449,356, March,1943. C.A. 41, 6771

Pierce, Amino Alcohols of Arylacetic Acids, US Pat. 2,399,506, April 30, 1946. C.A. 40, 4396

Pierce, Salzbury, and Frederichsen, Esters of Alkoxybenzoic Acids, J. Am. Chem. Soc. 64, 1691, (1942).

Pierce and Wotiz, Tris(hydroxymethyl)aminomethane Derivatives. I. Polyhydroxyamines, J. Am. Chem. Soc. 66, 879-81, (1944).

Pierce and Wotiz, Polyhydroxyamino Compounds, US Pat. 2,408,096, September 24, 1946. C.A. 41, 774

Pinkernelle, Condensation Products from Polycarboxylic Acids, US Pat. 2,246,264, June 17, 1941. C.A. 35, 6021

Plazek, Rodewald, and Krzyzaniak, Synthesis of Alceines; Derivatives of o-Phenyllactic and o-Phenylglycolic Acids, Roczniki Chem. 15, 360-4 (1935). C.A. 30, 1371

Pleger and Hill, Amino Esters of Diaryl Succinic Acids, US Pat. 2,410,791, November 5, 1946. C.A. 41, 2084

Pozzi-Escot, Microchemical Test for Molybdenum by the Phosphomolybdate of tri-beta-ethanolamine, Rev. cienc. (Peru) No. 420, 13-4 (1937). C. A. 31, 8428

Pozzi-Escot, Ethanolamine Iodides, Rev. cienc. (Peru) 39, No. 442, 71-4 (1937). C.A. 32, 4946

Pozzi-Escot, Action of Ethanolamines on Solutions of Various Metallic Salts, Rev. cienc. (Peru) 40, No 424, 303-7 (1938). C.A. 33, 1620

Pyman and Levene, Aminoalkyl Chlorides and Alcohols, Brit. Pat. 402,159, November 30, 1933. C. A. 28, 3081

Racciu, Action of the Ethanolamines on gamma-Trinitrotoluene, Atti. accad, sci. Torino, Classe sci. fis., mat. nat. 69, 364-8 (1934). C. A. 29, 6217

Ralston and Harwood, Inorganic Acid Esters of Dihydroxypropylamines, US Pat. 2,2290307, January 21, 1941. C.A. 35, 3008

Rauscher, Goldstein and Breslau, Reaction of Diethanolamine with Nitriles and Potassium Cyanide, J. Am. Chem. Soc. 71, 358-9 (1949).

Rider, Arylcarbamic Acid Esters of N-substituted Amino Alcohols, Can. Pat. 353,743, October 29, 1935. C.A. 30, 2325

Rindfusz and Harnack, Heterocyclic Compounds of N-arylamino Alcohols, J. Am. Chem. Soc. 42, 1720-5 (1920).

Ringk and Epstein, Preparation of Aminobenzoic Acid Esters of Substituted Monoalkyl Amino Alcohols, J. Am. Chem. Soc. 65, 1222-6 (1943).

Riweschl and Ray, Derivatives of Fluorenecarboxylic Acids, US Pat. 2,377,040, May 29, 1945. C.A. 39, 3305

Rohm and Haas Co., Phenolic Aralkylamino Alcohols, Brit. Pat. 470,636, August 9, 1937. C.A. 32, 684

Rohmann, Aminoalkyl Esters of Substituted Benzoic Acids, Ger. Pat. 658,389, April 2, 1938. C.A. 32, 4726

Salvin and Hill, Alkamine Esters of (Aryloxymethyl)benzoic Acid, US Pat. 2,376,138, May 1, 1945. C.A. 39, 3303

Samdahl and Weider, Some Esters of Amino Alcohols with 9-Acridinecarboxylic Acid, Bull. soc. chim. (5), 2, 2008-16 (1935). C.A. 30, 1790

Sandoz, Iodoethanolamine Derivatives, Fr. Pat. 790,674, November 25, 1935. C.A. 30, 2988

Sandoz, Nitrogenous Condensation Products, Fr. Pat. 828,015, May 9, 1938. C. A. 32, 7168

Sandoz, Basic Condensation Products, Fr. Pat. 828,619, May 24, 1938. C.A. 33, 281

Sargent, Alkamine Esters of 1-Cyclohexyl-3,4-pyrroledicarboxylic Acid, Brit. Pat. 582,903. December 2, 1946. C.A. 42, 610

Sargent, Alkamine Esters of 2,4-Pyrroledicarboxylic Acids, Brit. Pat. 585,833, February 26, 1947. C.A. 42, 610

Sargent, Alkamine Esters of 1-Dialkylaminoalkyl-3,4-pyrroledicarboxylic Acids, Brit. Pat. 592,752, September 29, 1947.

Sargent, Esters of 2,5-Dialkyl-3,4-pyrroledicarboxylic Acids, Brit. Pat. 600,807, April 20, 1948. C.A. 42, 7341

Sargent, Alkamine Esters of 3,4-Pyrroledicarboxylic Acids, Can. Pat. 439,628, February 11, 1947. C.A. 41, 4171
See also-- Can. Pats. 439,630 and 439,851.

Sargent, Alkamine Esters of 2,4-Pyrroledicarboxylic Acids, Can. Pat. 439,850, February 25, 1947. C.A. 41, 4171

Sargent, Esters, US Pat. 2,453,671, November 9, 1948.
See also--US Pats. 2,453,672 and 2,453,673.

Saunders, Esters of the Hydroxyalkylarylamines; Acid Sulfuric Esters of Simple Monohydroxyethylarylamines, J. Chem. Soc. 121, 2667-75 (1922).

Saunders and Slocombe, Chemistry of the Organic Isocyanates, Chem. Revs. 43, 203-18

Schaeffer, Alkanolamine Salts of Fatty Acids, US Pat. 2,448,626, September 7, 1948. C.A. 43, 1052

Schlosser and Gray, Wood Pulp Containing Cation-active Material, US Pat. 2,432,126, December 9, 1947. C.A. 42, 7529 See also--US Pat. 2,432,127.

Scholz, Alkamine Esters of Pyrrole-substituted Acrylic Acids, Brit. Pat. 585,834, February 26, 1947. C.A. 42,611

Scholz, Monoalkanolamine Esters of 1,3,5-Trimethyl-2-pyrrolecarboxylic Acid, Brit. Pat. 587,038, April 11, 1947. C.A. 42, 611

Scholz, Esters of 3-Pyrrolecarboxylic Acids, Can. Pat. 439,629, February 11, 1947. C.A. 41, 4171

Scholz, Monoalkamine Esters of 5-Pyrrolecarboxylic Acids, Can. Pat. 439,849, February 25, 1947. C.A. 41, 4172

Scholz, Esters, US Pat. 2,453,674, November 9, 1948.

Schroeder, Preparation of Alkamine Esters of o-Alkoxybenzoates, Univ. Microfilms (Ann Arbor, Mich.), Pub. No. 612,129 pp; Microfilm Abstracts 5, No. 2, 42-3 (1944). C.A. 38, 5812

Schulz, Monoalkamine Esters of Substituted 3-Pyrrolecarboxylic Acid, Brit. Pat. 581,152, October 2, 1946. C.A. 41, 1712

Schwarz, Zschimmer, et. al., Hydroxyalkylamine Ethers, Brit. Pat. 508,525, July 3, 1939. C.A. 34, 776

Senkus, New Derivatives of Amino Hydroxy Compounds, J. Am. Chem. Soc. 67, 1515-19 (1945).

Senkus, Amino Alcohols, US Pat. 2,363,465, November 21, 1944. See also--US Pat. 2,363,466. C.A. 40, 80

Senkus, N-Substituted Aminomonohydric Secondary Alcohols, US Pat. 2,413,247, December 24, 1946. C.A. 41, 2431

Sergievskaya and Kropacheva, Alkamine Esters of Tetrahydroaryl-4-amino-1-naphthoic Acid, J. Gen. Chem. (USSR) 15, 996-1000 (1945). C.A. 40, 6454

Seymour and Brooks, Treatment of Textile Materials, US Pat. 2,406,408, August 27, 1946. C.A. 41, 293

Sickels, Alkamine Esters of 1-Aralkyl-2,5-dimethyl-3,4-pyrroledicarboxylic Acids, Brit. Pat. 577,628, May 24, 1946 C.A. 41, 1712

Sickles, Bis(dialkylaminoalkyl)diesters of 1-Alkyl-3,4-pyrroledicarboxylic Acids, Brit. Pat. 594,697, November 18, 1947. C. A. 42, 2284

Sickles, Esters, US Pat. 2,453,676, November 9, 1948.

Sickles and Sargent, Diesters of1-Alkyl-3,3-pyrroledicarboxylic Acids, Brit. Pat. 594,698, November 18, 1947. C.A. 42, 2285

Sickles and Sargent, Esters, US Pat. 2,453,675, November 9, 1948

Sickles and Scholz, Monoalkamine Esters of 3-Pyrrolecarboxylic Acids, Can. Pat. 439,631, February 11, 1947. C.A. 41, 4171

Siebenburger, Sulfuric Acid Esters of Aliphatic Alcohols, US Pat. 2,060,254, November 10, 1936. C.A. 31, 416

Shmuk, Phenylcarbimide Derivative of Aminoglucose, J. Russ. Phys. Chem. Soc. 61, 1759-63 (1929). C.A. 24, 5285

Shonle, Alkanolamine Salts of Mandelic Acid, US Pat. 2,144,552, January 17, 1939; Brit. Pat. 496,004, November 23, 1938. C.A. 33, 3077

Slotta and Behnisch, Reaction of Primary and Secondary Amino Alcohols and Amino Phenols with Arylsulfonyl Chlorides, J. prakt. Chem. 135, 225-36 (1932). C.A. 27, 967

Smith and Hansen, Amine Salts Suitable for Use in Stimulating Root Growth on Plant Cuttings, US Pat. 2,278,499, April 7, 1942. C.A. 36, 4861

Smith and Hansen, Alkanolamine Salts of Dinitrophenols, US Pat. 2,328,505, August 31, 1943. C.A. 38, 1318

Smith, Mitchell, and Hawkins, Analytical Procedures Employing the Karl Fischer Reagent. X. The Determination of Aliphatic Hydroxyamines (Amino Alcohols), J. Am. Chem. Soc. 66, 715-16 (1944).

Soc. anon. pour l'ind. Chim. a Bale, Basic Ether of the pyridine Series, Sw. Pat. 148,956, August 10, 1929. C. A. 26, 4915

Societe des usines Chimiques Rhone-Poulenc, Esters of Amino Alcohols with alpha-Phenyl Aliphatic Acids, Brit. Pat. 483,704, April 19, 1938. C.A. 32, 7215

Societe des usines Chimiques Rhone-Poulenc, Organoantimony Compounds, Brit. Pat. 501,232, February 13, 1939. C.A. 33, 6000

Soc. pour l'ind. chim. a Bale, Transposition of Higher Hydroxyalkylamides into Esters of Amino Alcohols, Belg. Pat. 447,696, November 30, 1942. C.A. 39, 1063

Soc. pour l'ind. chim. a Bale, Basic Esters, Fr. Pat. 795,597, March 17, 1936. C.A. 30, 5591

Soc. pour l'ind. chim. a Bale, Therapeutic Compounds, Fr. Pat. 48,503, March 8, 1938. C.A. 33, 319

Soc. pour l'ind. chim. a Bale, Basic Esters of Biphenyleneacetic Acid (9-Fluorenecarboxylic Acid), Fr. Pat. 840,824, May 3, 1939. C.A. 34, 1685

Soc. pour l'ind. chim. a Bale, Esters, Ger. Pat. 653,778, December 2, 1937. C.A. 32, 2956

Sou, A New Method for the Preparation of Aldehydes and Ketones Starting from Amino Alcohols, Bull. faculte, sci. univ. franco-chinoise Peiping 1935, No. 5, 1-7. C.A. 30, 4463

Squibb and Sons, Amino Alcohol Esters, Brit. Pat. 520,179, April 17, 1940. C.A. 36, 870

Steik, Sulfonate Soap, US Pat. 2,204,326, June 11, 1940. C.A. 34, 7132

Suter, Phenylalkylamines, US Pat. 2,443,206, June 15, 1948. C.A. 42, 7331

Suter and Ruddy, Condensation of Amino Alcohols with Benzene, J. Am. Chem. Soc. 65, 762-3, (1943).

Tiffeneau and Cahmann, Deamination of 2-Phenyl-1-amino-2-propanol and 2-phenyl-1-amino-2-butanol. Preferential and exclusive Migration of the Phenyl Group, Bull. soc. chim. (5) 2, 1876-82 (1935). C.A. 30, 1782

Tiffler and Brill, Alkamine Esters. Procaine Analogs, J. Am. Chem. Soc. 55, 364-70 (1933).

Tilford, Campen, Shelton, Amino Esters of Substituted Alicyclic Carboxylic Acids, J. Am. Chem. Soc. 69, 2902-6 (1947).

Tryon, Salts of Sulfamic Acids, US Pat. 2,337,693, December 28, 1943. C.A. 38, 3295

Tryon, Acylated Amino Hydroxy Compounds by Action of Acid Anhydrides on 2-Oxazolines, US Pat. 2,410318, October 29, 1946. C.A. 41, 2076

Ulrich and Kording, Sulfuric Esters of Acylated Hydroxyalkyl Amines, Ger. Pat. 633,334, July 24, 1936. C.A. 30, 7584

Ulrich and Nusslein, Condensation Products Useful as Dispersing Agents, US Pat. 2,206,928, July 19, 1940. C.A. 34, 8115

Ulrich, Nusslein and Kording, Mineral Acid Derivatives of Aliphatic Amines, Ger. Pat. 703,953, February 20, 1941 C.A. 36, 1117

Ulrich, Nusslein, and Scholler, Textile Softener, Ger. Pat. 699,110, October 24, 1940. C.A. 35, 6813

Ushenko, The Synthesis of Heterocyclic Compounds from beta-Aminoalcohols. I. The Condensation of beta-Aminoalcohols with Aldehydes and Ketones into Oxazolidine Derivatives, Trudy Voenno-Khoz. Akad, RKKA im. Molotova 1940, No. 3, 109-20; Khim. Referat. Zhur. 4, No. 3, 32-3 (1941). C.A. 37, 4395

Valco, Conversion of Alkylolamides into Oxazolines, US Pat. 2,416,552, February 25, 1947. C.A. 41, 3823

Vanderbilt, Higher Fatty Acid Salts of Aminopolyhydroxy Compounds Useful as Emulsifying Agents, US Pat. 2,247,106, June 24, 1941. C.A. 35, 6358

Vanderbilt, Fatty Acids Salts of Amino Alcohols Useful as Emulsifying Agents, US Pat. 2,281,177, April 28, 1942. C.A. 36, 5587

Waldkotter, Interaction of beta-Hydroxyethylamine and Halonitrobenzenes, Rec. trav. chim. 57, 1294-1310 (1938). C.A. 33, 1286

Waldkotter, Action of Diethanolamine on the Halonitrobenzenes, Rec. trav. chim. 58, 132-8 (1939). C.A. 33, 3341

Wampner, Stabilization of Oil-in-water Emulsions, US Pat. 2,359,066, September 26, 1944. C.A. 39, 1783

Watkins, Water-soluble Polyvinyl Alcohol Compositions Softened with a beta-Hydroxyalkylammonium Salt, US Pat. 2,271,468, January 27, 1942. C.A. 36, 3594

Weber, Polyethyleneamine Derivatives of Fossil Resins, US Pat. 2,382,838, August 14, 1945. C.A. 39, 5099

Wegler, Hydroxy Lower-alkyl Amines, US Pat. 2,251,245, July 29, 1941. C.A. 35, 6975

Wenker, Synthesis of beta-Chloroethyl Phthalimide, J. Am. Chem. Soc. 59, 422, (1937).

Wheeler and Banks, Antimonylcatechol: Coordinates with Amino Alcohols, J. Am. Chem. Soc. 70, 1266-7 (1948).

White and Walters, Aromatic Nitrogen Containing Hydroxy Compounds, US Pat. 2,300,998, November 3, 1942. C.A. 37, 2016

Whitner, Alkylolamine-copper Complexes, US Pat. 2,446,682, August 10, 1948. C.A. 42, 9198

Wiese and Jones, Preparation of tris(Hydroxymethyl)sulfanilamidomethane, J. Am. Pharm. Soc., Sci. Ed. 37, 380-1 (1948)

Wingfoot Corp., Polymeric Condensation Products from Amino Alcohols and Dicarboxylic Acids, Brit. Pat. 571,017, August 2, 1945. C.A. 40, 6887

Wood and Gardner, Synthesis of Some Dialkylaminoalkyl Arylthiourethans and Thioureas, J. Am. Chem. Soc. 63, 2741-2 (1941).

Young and Rubenstein, Acylated Alkylolamines, US Pat. 2,429,445, October 21, 1947. C.A. 42, 1962

AUTOBIOGRAPHY

I, Ralph Walton Raiford Jr., was born on June 2, 1924, in Richmond, Virginia. I received my primary education in various grade schools throughout West Virginia and Virginia. I graduated from John Marshall High School of Richmond in June, 1940. After working in the First and Merchants National Bank of Richmond for two years, I entered the University of Richmond in the fall of 1942 and attended classes there until the following February, 1943, when I left college to serve with the armed forces of the United States.

I re-entered the University of Richmond soon after my discharge from the service in March, 1946, and completed my undergraduate course ther, graduating in June, 1948, with a B. S. in Chemistry. I was the laboratory assistant in organic chemistry during my senior year at the University.

Returning to the same University for graduate work, I received the Puryear Fellowship in Chemistry for the year 1948-9.

The thesis here submitted is a partial requirement for the M. S. degree for which I am an applicant.