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John Dana Myers

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JOHN DANA MYERS

A THESIS
SUBMITTED TO THE GRADUATE FACULTY
OF THE UNIVERSITY OF RICHMOND
IN CANDIDACY
FOR THE DEGREE OF
MASTER OF SCIENCE
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MAY 1978

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Finally, I want to thank Dr. Jerry Whidby, who willingly assisted this work with the 100.1 MHz and 80 MHz proton magnetic resonance spectra and the 20 MHz and 25 MHz C^{13} nuclear magnetic resonance spectra and to Philip Morris Co., his employer, who permitted the use of the instrumentation.

STATEMENT OF THE PROBLEM

The purpose of this research is to investigate the use of 3,4-diphenyl-3-cyclobutene-1,2-dione as a synthetic precursor to bis-ketenes and to ultimately examine the chemical behavior of this relatively unknown system.

We intend to investigate some of the chemical behavior of bis-phenylketene produced by the well-documented photochemical ring-opening of 3,4-diphenyl-3-cyclobutene-1,2-dione. Specifically, the use of alkenes as chemical traps for the bis-ketene will be investigated. These reactions will be compared and contrasted to the behavior of the ketenes and vinyl ketenes.

It is also our intention to provide further kinetic evidence relevant to the mechanism of the ground state ring opening of diphenylcyclobutenedione in alcoholic solvents where bis-ketenes have been suggested.[1,2,3]

ABSTRACT

The 3,4-diphenyl-3-cyclobutene-1,2-dione (1) was prepared by a known method. The photochemical behavior of 1 in the presence of cyclopentadiene and tetracyanoethylene is described. A 1:1 adduct with cyclopentadiene was isolated and characterized. The mechanistic ramifications of this adduct are discussed.

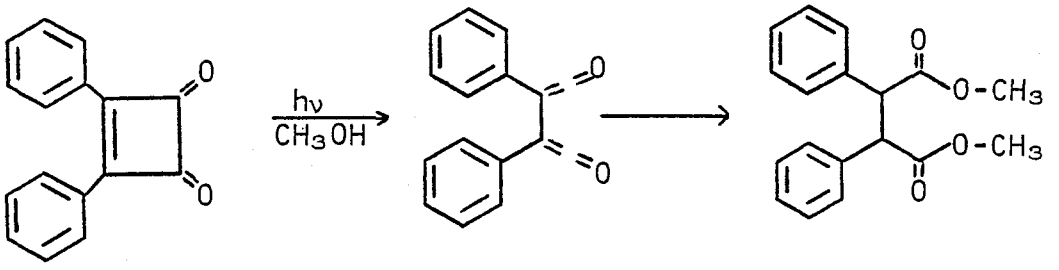
The kinetics of the thermally-induced ring opening of 1 in ethanol and t-butanol is described.

HISTORICAL

The Formation and Characterization of Bis-ketenes

Several investigators have reported that bis-ketenes are intermediates in the ring opening of 3,4-disubstituted-3-cyclobutene-1,2-diones.[1-8] For example, Obata and Takizawa have studied the photolysis of 3,4-diphenyl-3-cyclobutene-1,2-dione and its imine derivative in the presence of an isonitrile which gave ring-expanded products[1] suggestive of the intermediacy of bis-phenyl ketene. Chapman, McIntosh, and Barber observed bis-ketene formation from cyclobutenediones at low temperatures.[2] By irradiating a neat film of 1 at -196° a product was formed whose infrared spectra showed new bands at 2100 and 2112 cm^{-1} which can be assigned to the diphenylbisketene.[1] Irradiation of 1 in methanol at room temperature resulted in the formation of meso and dl-dimethyl-2,3-diphenyl succinate,[2] presumably via the bis-ketene (scheme 1).

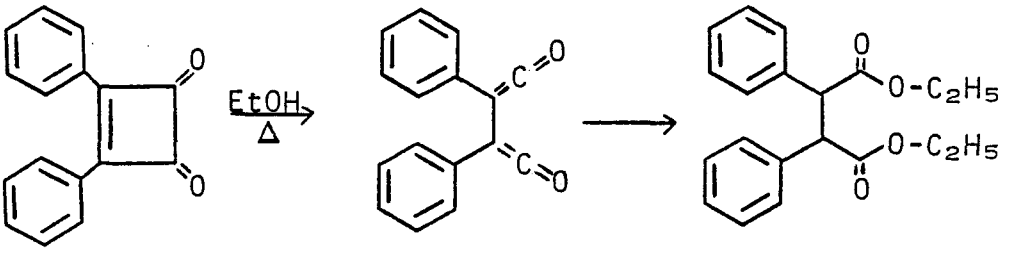
Scheme 1



Bloomquist and LaLancette suggested a bis-ketene intermediate in the formation of meso and racemic diethyl-2,3-diphenyl succinate in ethanol solution.[3] They also reported that 1 is unstable in ethanol. Dilute solutions of 1 were found to convert to d, l and meso diethyl-2,3-diphenyl succinate in 12 hours at room temperature.[9] However, this was found not to be the case by Clough, Coates and Day, whose work showed that when protected from light the solution was stable even in refluxing ethanol. At higher temperatures (T>110°C) reaction of 1 with ethanol resulted in a quantitative conversion to a mixture of d, l and meso diethyl-2,3-diphenyl succinate.[10]

Rational mechanistic paths to the thermal product

Scheme 2

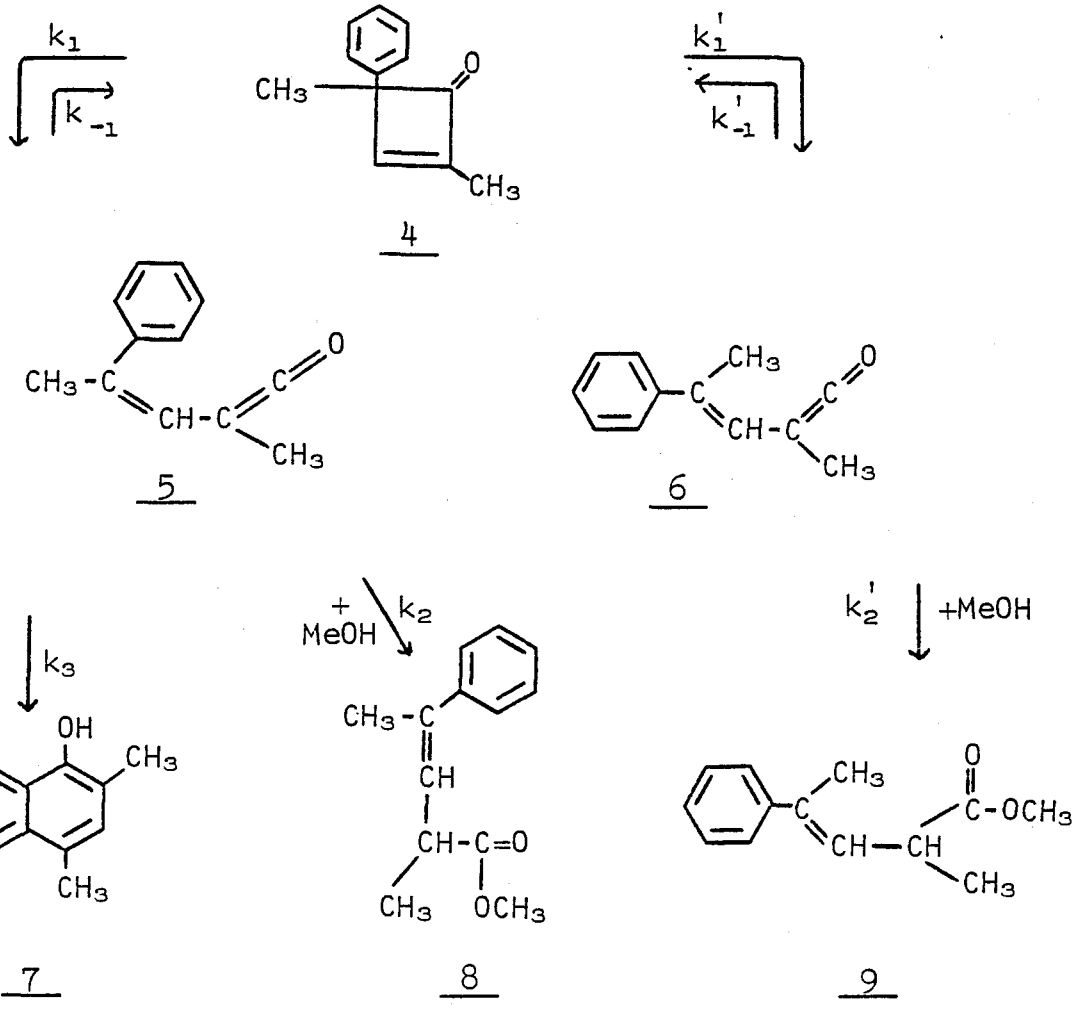


1 2 3

Several literature reports suggest the mechanism indicated in scheme 2 in which the conversion to the bis-ketene would be the rate determining step.[3,9] The assumption that bis-ketene formation is rate limiting is supported by the work done on ring-opening of cyclobuteneones to form vinyl ketenes which obey first order

kinetics.[11,12] In the reaction below of 2,4-dimethyl-4-phenyl-2-cyclobuten-1-one 4 with methanol at 80°C, naphthol 7 was obtained in 6% and ester 9 in 70% yield. When the thermolysis of 4 was carried out in a solution of methanol in benzene (0.6-4.6M) at 80°C, the (Z) ester 8 was no longer detected. The product ratio, 28% 7 and 72% 9 turned out to be independent of the methanol concentration, i.e., k_2 [MeOH] (rate law for alcoholysis of ketenes) becomes small compared with k_3. The independence of (7):(9) on methanol concentration leaves no doubt that $k_{-1} \ll k'_2$ [MeOH]; hence the ring opening (4) → (6) is irreversible under these reaction conditions.[11]

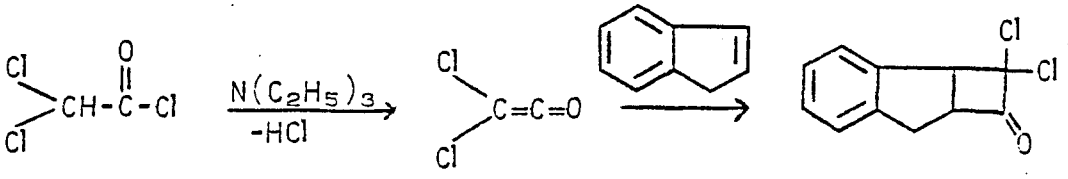
Scheme 3



Reaction of substituted ketenes with alkenes

The 2 + 2 cycloaddition reactions of ketenes with alkenes are well known. Among the ketenes that have been studied is dichloroketene. Turner and Seden obtained an adduct by generating dichloroketene in situ by the dehydrohalogenation of dichloroacetyl chloride with triethylamine in indene at 90°C (scheme 4). The product 12 $C_{11}H_8OCl_2$, b.p. 110-115°/0.5 mm, m.p. 78-79° (hexane), (glc purity 99 + %) was retrieved in a 12% yield. The mass spectral data showed a molecular ion m/e 226 and fragment ions m/e 191 $(M-Cl)^+$, 163 $(191-CO)^+$, 149; 128 $(163-Cl)^+$ and 116 $(indene)^+$.[13]

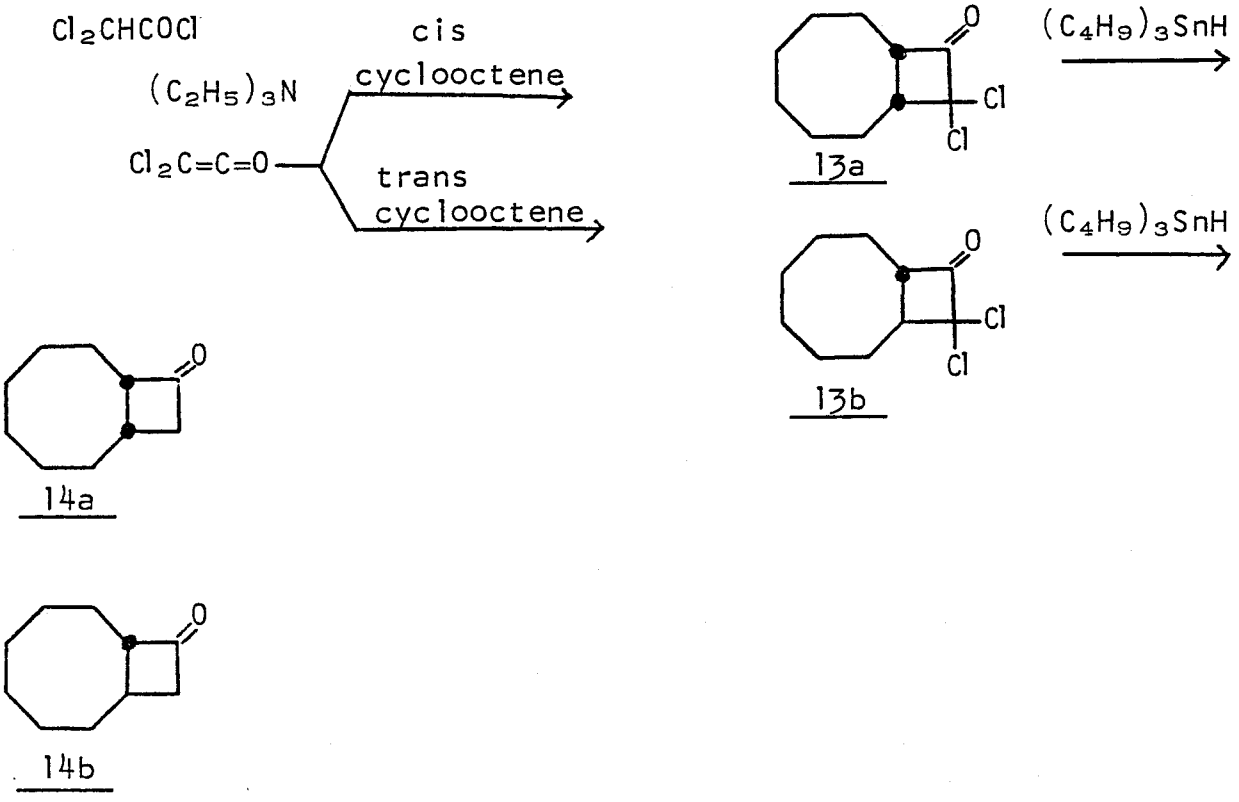
Scheme 4



10 11 12

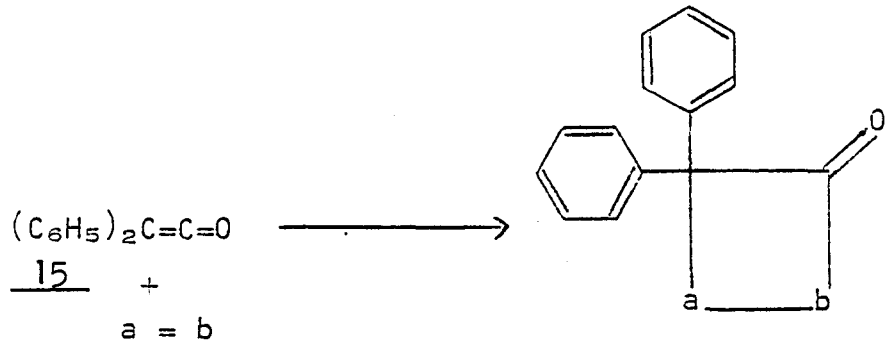
Montaigne and Ghosez studied the stereospecific cis addition of dichloroketene to cis- and trans-cyclooctenes.[14] Dichloroketene (liberated in situ from dichloroacetyl chloride and triethylamine at room temperature) reacts smoothly with cis-cyclooctene to yield the compound cis-10,10-dichlorobicyclo[6.2.0]-decan-9-one (13a) (yield 50%), and with trans-cyclooctene to form the trans-isomer (13b) (yield ca 100%). Interconversion is estimated, gas chromatographically to be lower than 4%. Both adducts show a strong absorption band at 1805 cm^{-1} indicative of 2,3-dichlorobutanone. The structural assignments are supported by the H-NMR spectra. Reduction of (13a) and (13b) with tributyltin hydride in refluxing cyclohexane containing catalytic amounts of azobisisobutyronitrile yields respectively the parent ketones. Thus, the addition of dichloroketene onto olefins is a cis stereospecific cycloaddition.

Scheme 5



The kinetics of the cycloaddition of diphenylketenes was studied by Huisgen, Feiler and Otto.[15] This work described the influence of the structural variation in the alkenes in the cycloaddition of diphenylketene to give cyclobutanones. The solvent dependence of the rate constant for cycloaddition was also studied.

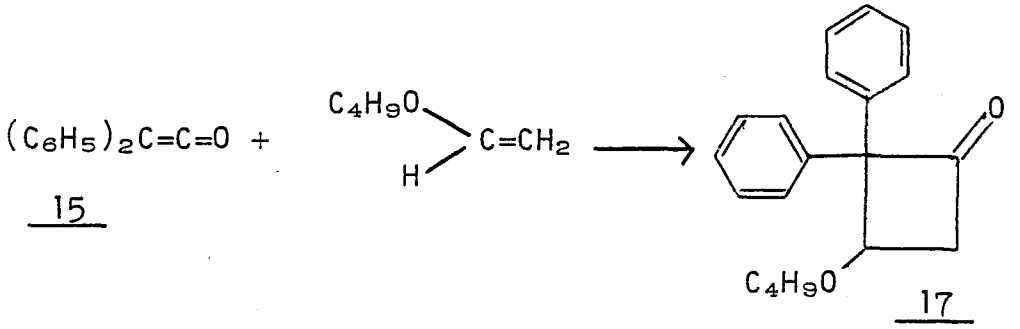
Scheme 6



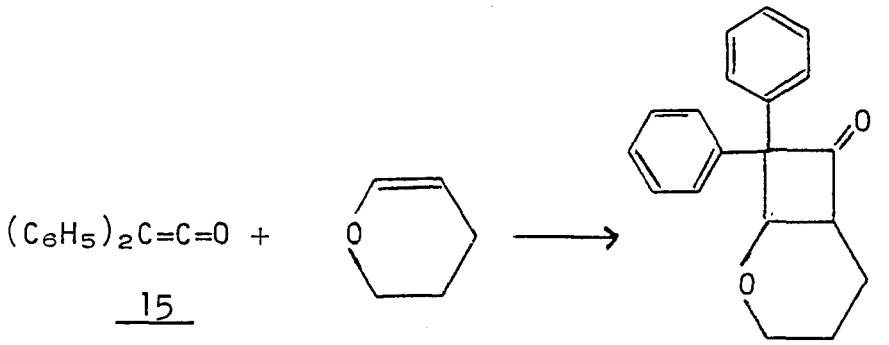
Photometric measurements at 418 nm of the ketene permitted determination of the rate of reaction with excess alkene in the absence of air and moisture. Values for the second order rate constant as k_2 (l/mole-sec) in benzonitrile at 40° were determined. The reaction was activated by the presence of phenyl group into the a position of the alkene. Alkoxy groups were still more activating but their effects were surpassed by amino functions as shown by the rate constants for a series of isobutene derivatives. The angle bridged norbornene added only 10 times more rapidly than cyclopentene. The transformation of the latter to 2,3-dihydrofuran takes place with 10^4 times increase in rate, whereas the second oxygen atom in 1,3-dioxole restricts the rate. The rate for 2,3-dihydropyran

is 340 times slower than the addition rate for 2,3-dihydrofuran. Methyl-substituted alkenes show the interplay of accelerating electronic and retarding steric effects. Electron-withdrawing substituents are so strongly deactivating that no adducts were formed with α,β-unsaturated carboxylic esters. Some reactions studied are indicated below.

Scheme 7



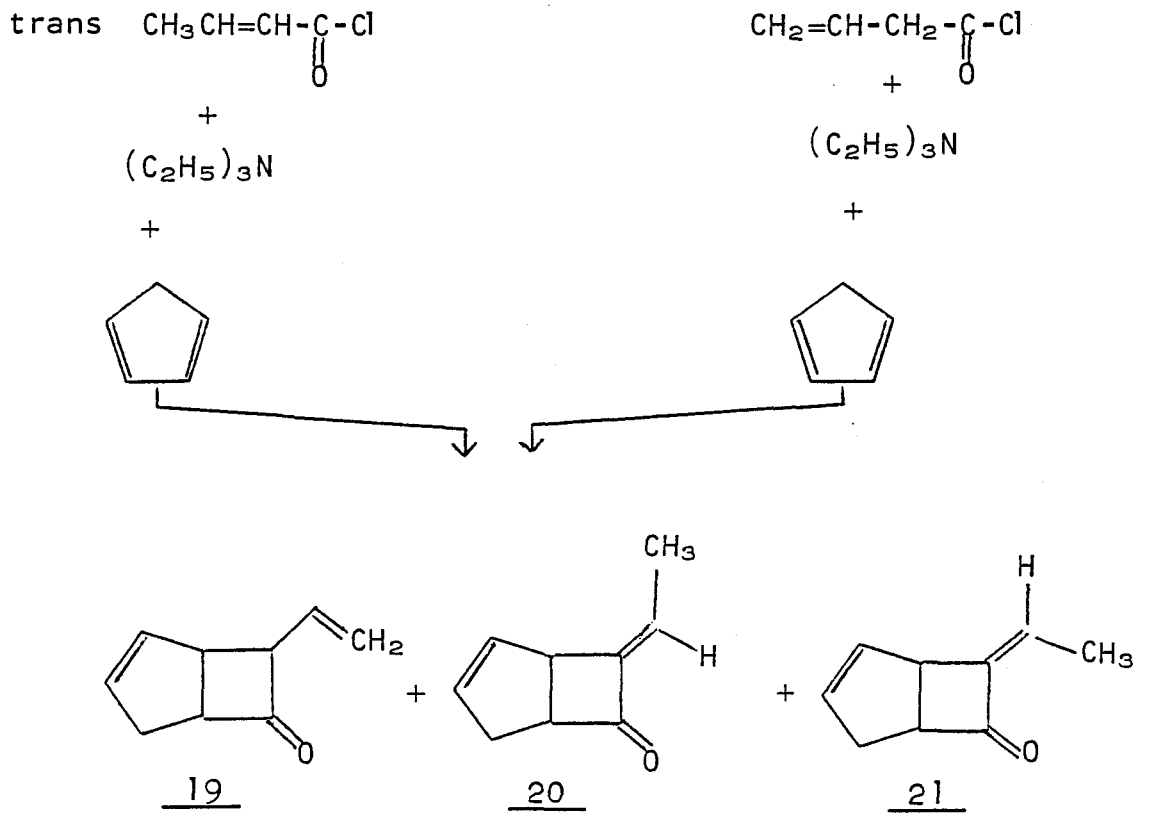
15 17



15 18

Holder, Freiman and Stefanchik demonstrated that vinyl ketene, generated from triethylamine and trans-2-butenoyl chloride, in the presence of 1,3-cyclopentadiene gave a 2 + 2 cycloaddition to form adducts below.[16]

Scheme 8



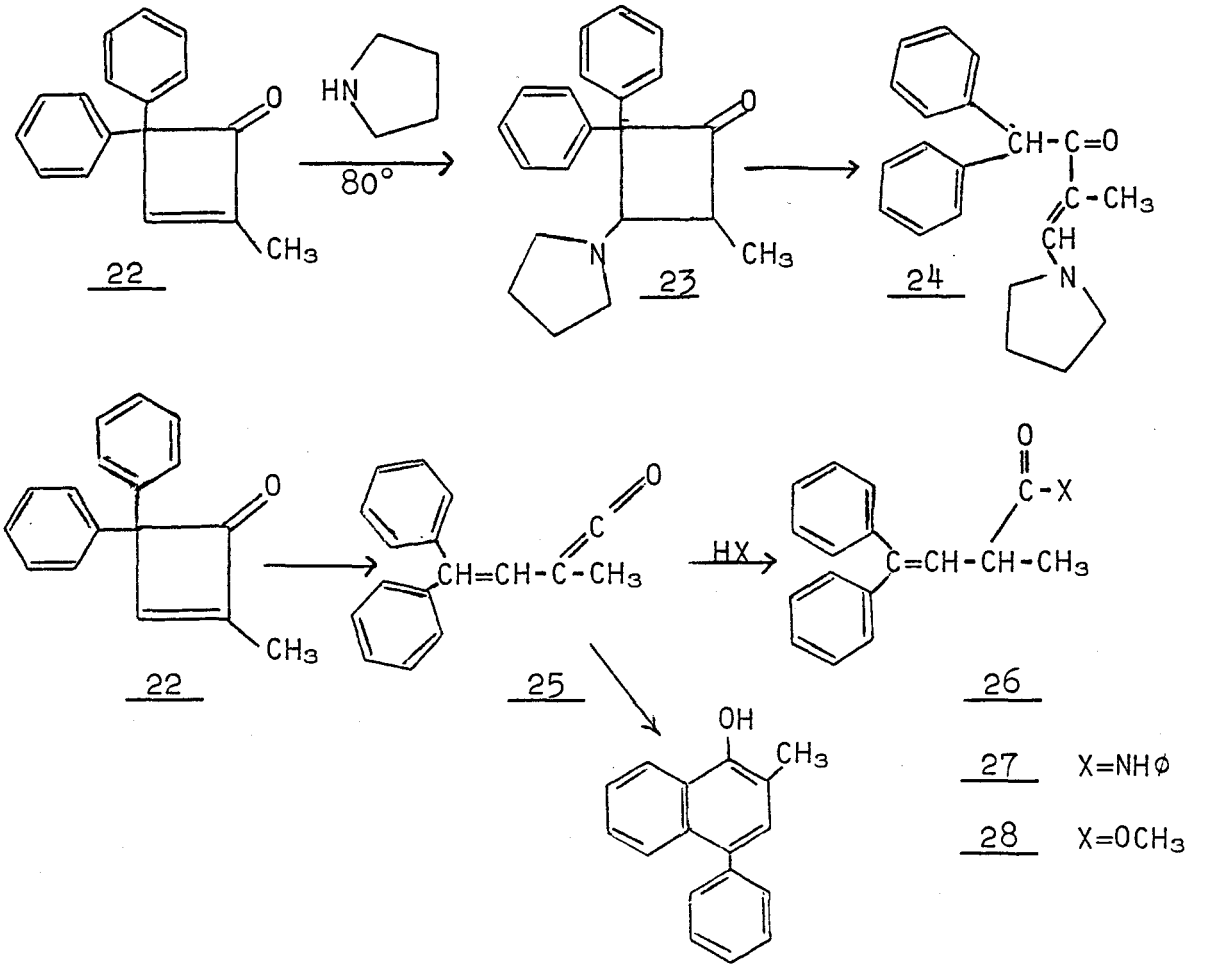
With a trace of excess triethylamine 19 isomerized chiefly to a 73:27 mixture of the trans and cis isomers 20 and 21, whose structures were accurately assigned using lanthanide induced shift nuclear magnetic resonance techniques. The possible participation of ethylideneketene ($CH_3CH=C=C=O$) was judged remote since triethylamine 3-butenoyl chloride, and 1,3-cyclopentadiene gave an identical reaction mixture.

Ring opening of cyclobutenones

It has been noted that while strong nucleophiles (e.g., $NaOCH_3$- CH_3OH) add to the endocyclic double bond of cyclobutenones, weaker nucleophiles (e.g., alcohols, aniline) interact with the vinyl ketenes which are thermally or photochemically generated from cyclobutenones.[11] The alcohol adducts show the stereochemistry of this irreversible ring opening for phenylated and alkylated cyclobutenones.

Chlorinated cyclobutenones equilibrate with small concentrations of vinyl ketenes as shown by trapping reactions with nucleophiles.[18] The products isolated from the thermolysis of 2,3-dimethyl-4-phenyl-2-cyclobuten-1-one suggested a mechanism in which an irreversible ring opening to cis-trans isomeric vinyl ketenes takes place.[18]

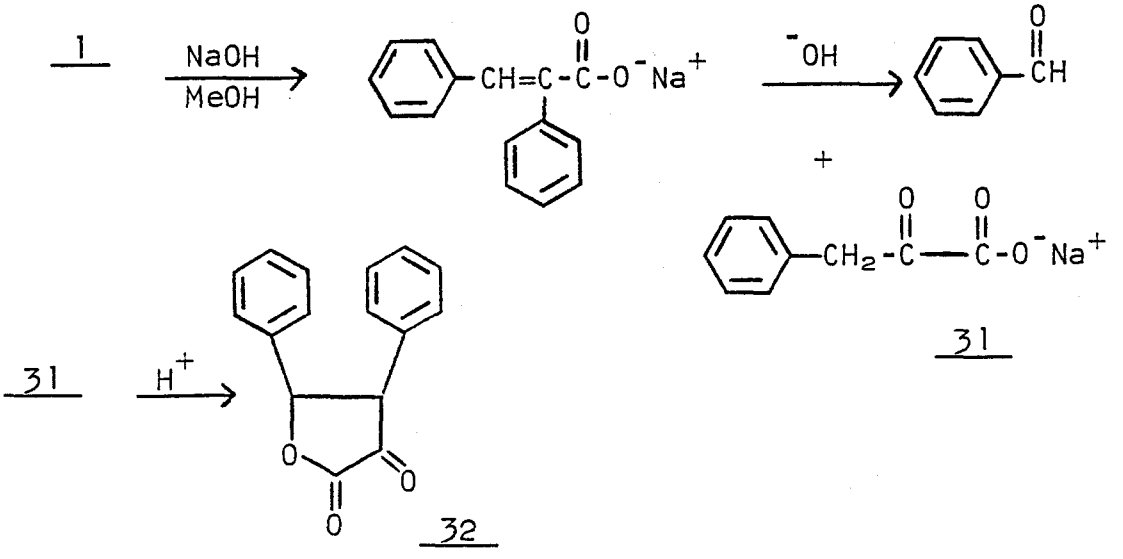
Scheme 9



As illustrated in scheme 9, the formation of 24 (64%) from the reaction of 22 with pyrrolidine in refluxing benzene suggests the intermediacy of 23 which then undergoes the base-catalysed ring opening of 3-aminocyclobutanones to 2-acylenamines.[19] The infrared absorptions at 1560 and 1622 cm^{-1} as well as the vinyl-H signal at 2.40 indicate the β-acyleneamine structure 24. Aniline at 100°C did not attack 22 but rather intercepted the vinyl ketene 25 which results from the thermal electrocyclic ring opening of 22. The anilide 27 isolated in 75% yield, is indicated to be the but-3-enoic acid derivative on the basis of its nmr spectrum [t 3.80(d $J_{2,3}$ 10 Hz, 3-H), 6.80 (doublet of quadruplets, J_2, Me 6.8 Hz, 2-H) and 8.68 (d, 2-Me)]. Also the formation of 28 from the reaction of 22 and methanol provides evidence for the intermediacy of 25. The spectra of 29 again establish the 1,2-addition of the nucleophilic reagent to the vinyl ketene 25.

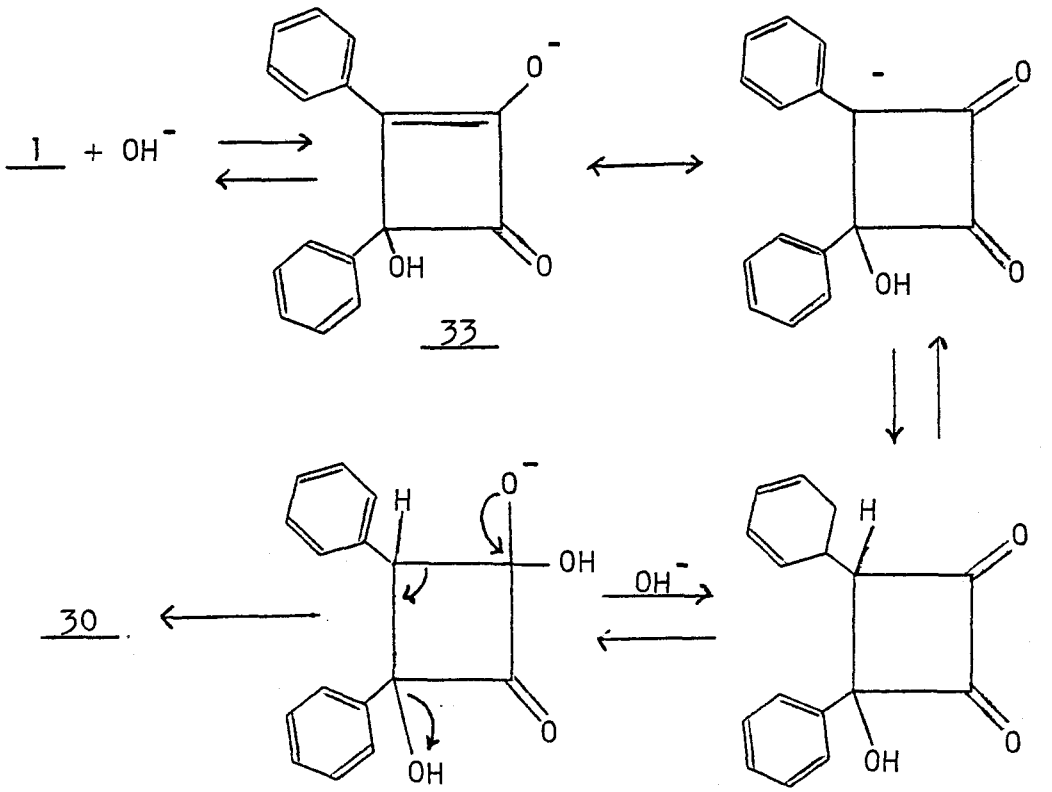
The ring opening of (1) by means of methanolic sodium hydroxide has also been studied by Bloomquist and LaLancette.[3] The products obtained together with their mode of formation are indicated below.

Scheme 10



The products actually isolated thus consist of benzaldehyde and tetrahydro-4,5-diphenyl-2,3-furandione 32. The initial formation of the sodium salt of benzilidenephenyl pyruvic acid 30 is rationalized by the mechanism shown in scheme 11. Thus, 1,4-addition of hydroxide ion to the 1,2-unsaturated ketone followed by abstraction of a proton from the reaction medium produces the intermediate 33 which upon nucleophilic attack and expulsion of hydroxide ion yields 30. A reverse aldol cleavage of 30 then accounts for the formation of benzaldehyde.

Scheme 11



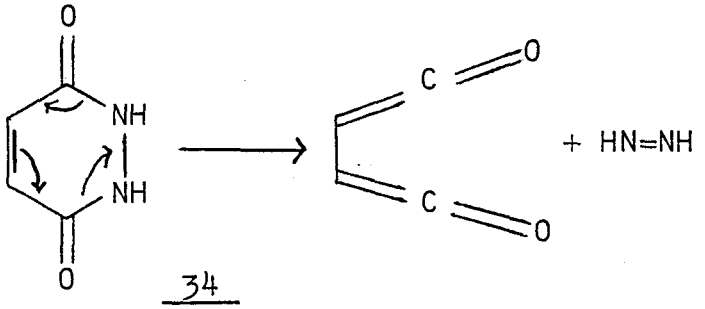
On the basis of the above mechanism, the driving force for the ring-opening of 1 with base is explained by an examination of the intermediate 33 in which the phenyl groups would be trans. Thus, the crowding of the bulky phenyl groups in the cis-stilbene system of the dione 1 is relieved.®

The chemical behavior of bis ketenes

These compounds are of interest not only because of their chemistry but also because of an implied health aspect. The thermal behavior of maleic hydrazide has been investigated due to its extensive use in U.S. tobacco fields as a sucker-inhibiting agent.[16] Clough, Kang, Johnson and Osdene described a thermally allowed mode of fragmentation of maleic hydrazide, the retro-Diels Alder reaction, which would yield diimide and bis-ketene.[20] It is suspected that the bis-ketene would be present in the tobacco smoke.

Bis-ketenes are reactive with nucleophilic agents. As mentioned previously, bis-ketenes react with alcohols to form diesters.[3] In the presence of an amine, bis-ketene reacts to form succinimide.[11]

Scheme 12

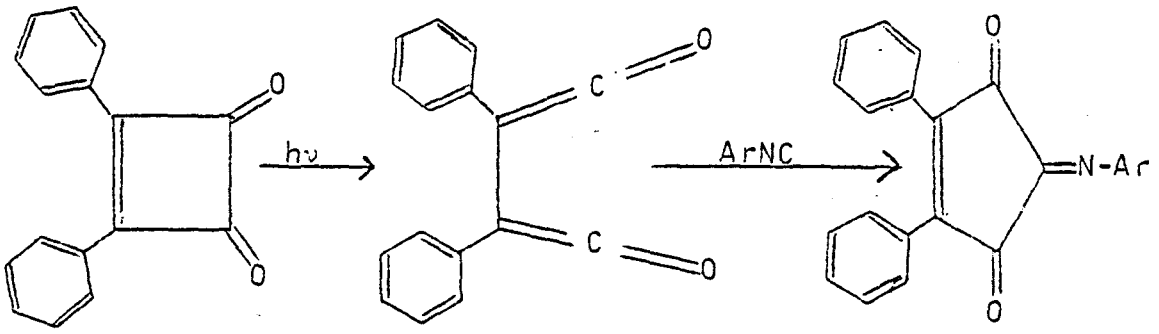


34

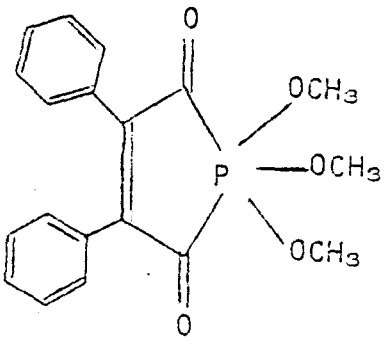
®The cyclization of 30 presumably via the free acid 28a occurred with extreme ease. Part of the 30 cyclized even under the mild conditions of neutralization.[3]

It has recently been demonstrated that on irradiation with a high pressure lamp, diphenylcyclobutenedione is efficiently converted to diketene (bis-ketene) which in the presence of an isonitrile gives adduct 35. Analogous attempts to trap the bis-ketene with trimethylphosphite in hopes of obtaining a product such as 36 below, however, were unsuccessful.[7]

Scheme 13



1 2 35



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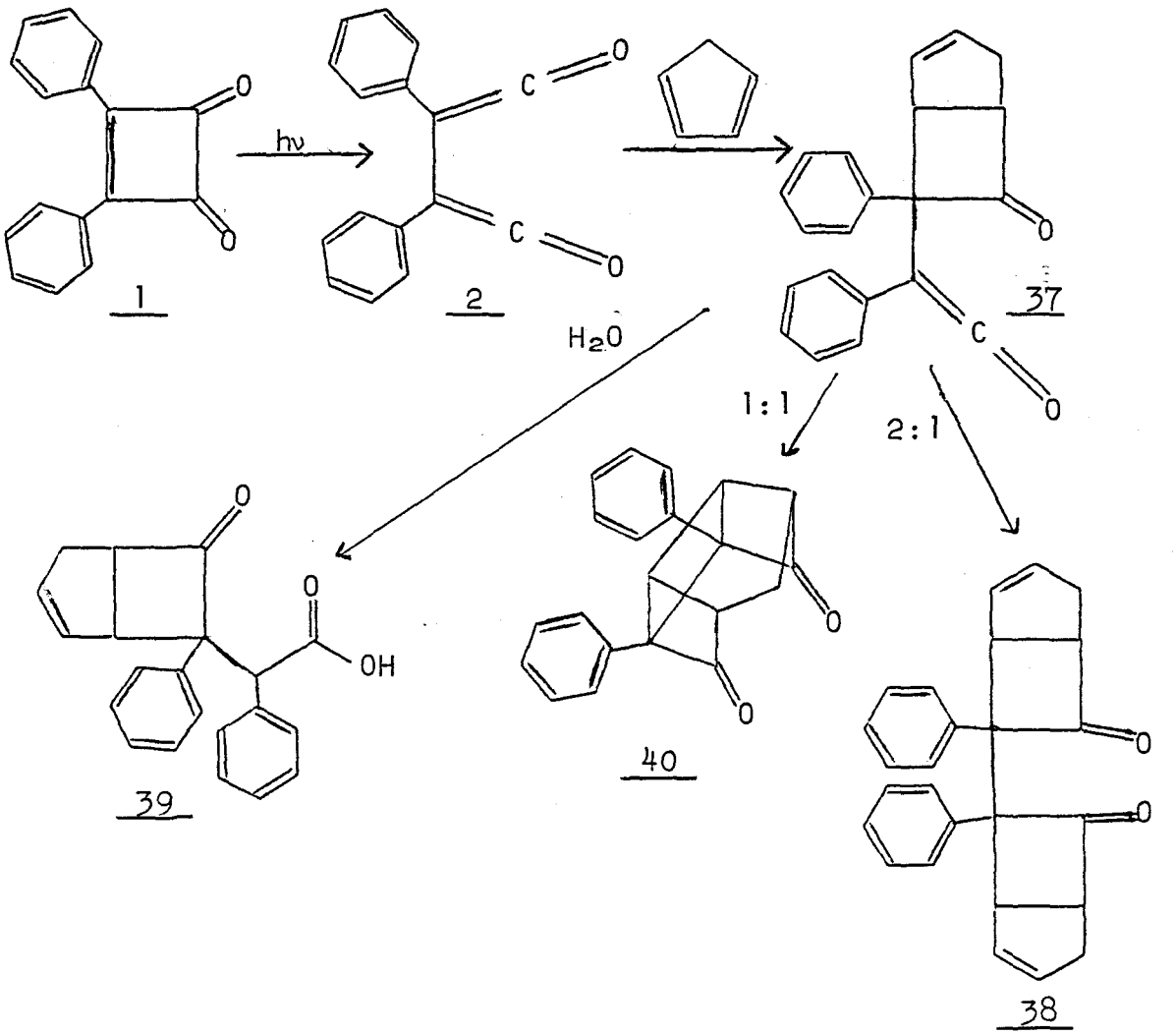
DISCUSSION OF THE RESULTS

Photochemistry of 3,4-diphenyl-3-cyclobutene-1,2-dione

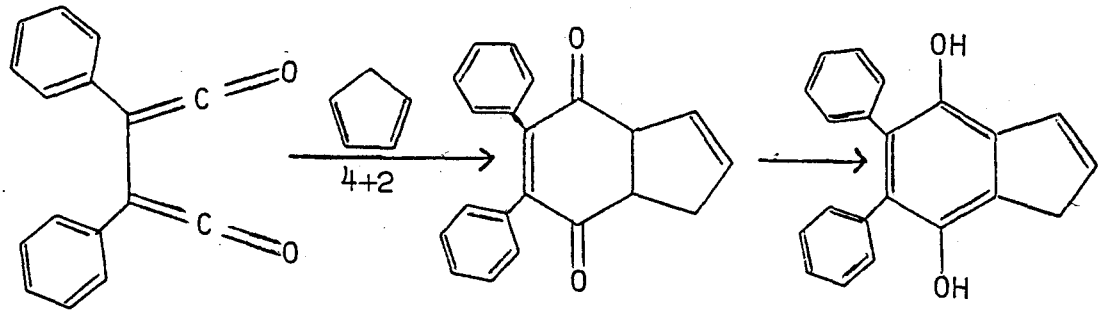
As previously stated, several workers[1,2] have shown by spectral methods that the photolysis of 1 results in the formation of 2. An attempt to substantiate this using chemical methods was initiated. Because cyclopentadiene has been shown to undergo cycloaddition with ketenes and vinyl ketenes,[21] 1 was irradiated in the presence of cyclopentadiene with the expectation that a photoadduct whose structure would require the intermediacy of 2 would be formed. For example, a 2 + 2 cycloaddition would result in a substituted cyclobutanone as indicated below.

Scheme 14



Alternatively, a 4 + 2 cycloaddition, reminiscent of the work of Hopf[21] with a bis-allene, would result in hyroquinone 41.

Scheme 15



41

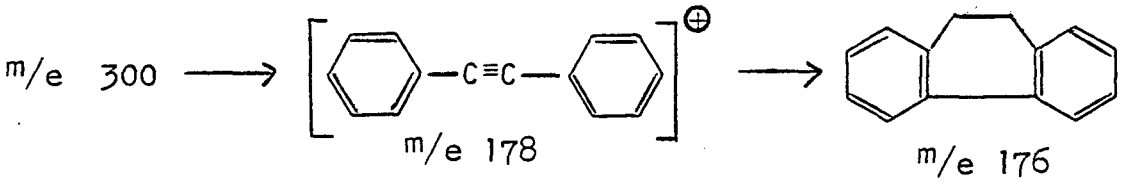
Formation of any or all of these products would require the intermediacy of 2.

Photolysis of 1 in the presence of a large excess of cyclopentadiene resulted in a 78% yield of a 1:1 adduct®. The spectral properties of this adduct do not appear compatible with any of the products suggested above or with the intermediacy of bis-phenylketene 2. The spectral properties are discussed below.

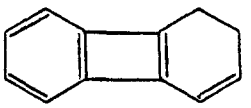
®A control experiment has shown that 1 and cyclopentadiene undergo no reaction in benzene at room temperature in the dark.

The compound showed a molecular ion in the mass spectrum at m/e 300 (52%) indicating a 1:1 adduct. The base peak appeared at m/e 178 suggesting a structure which would allow the facile elimination of diphenylacetylene (Spectrum 5).

Scheme 16



42 43

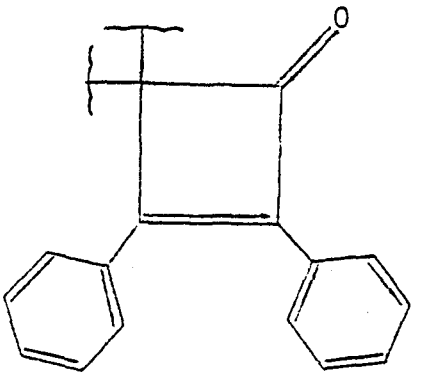


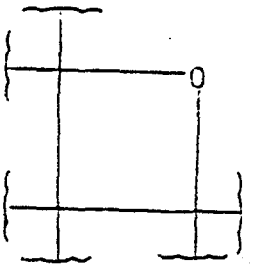
44

The structural assignment of 42 to m/e 178 is supported by the expected fragments at m/e 176 and m/e 152 which are characteristic fragments presented in the mass spectrum of diphenylacetylene.[22]

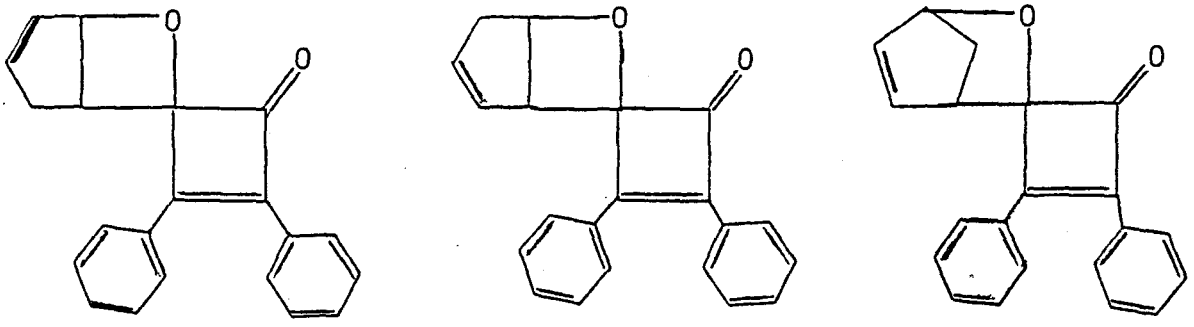
The carbonyl absorption in the infrared spectrum at 1751 cm^{-1} rules out a cyclobutanone containing 1:1 adduct. It is compatible with a cyclobutenone system.[23] Also worthy of note is the absence of any absorption in the OH stretching region which rules out any hydroquinone type system. It was also noted that bands characteristic of the C-O stretch of 4-membered cyclic ethers were present at 1022 cm^{-1} and 1032 cm^{-1} which suggest that an oxetane ring is present (Spectrum 1).

The adduct had strong absorptions in the ultraviolet spectrum at λ_1 = 292 nm and λ_2 = 240 nm (Spectrum 3). In comparing the uv spectrum of this photoadduct with the spectra of model compounds it was noted that 2-phenyl cis cinnamic acid also has two absorptions, one appearing at 274 nm (λ_1) and the other at 220 nm (λ_2).[24] Application of Woodward's correction factor of +20 nm[24] for the comparison of ketones to acids and esters results in a predicted λ max within 2 nm of that observed for the photoadduct. This observation with the ir data suggest the following partial structures.





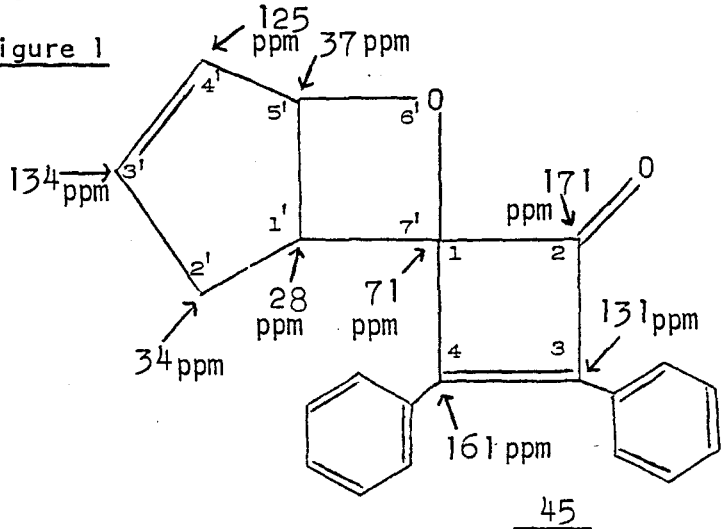
At this point three structures, 45, 46 and 47, seem reasonable although 47 is deemed less likely because it does not contain the oxetane ring suggested by the bands present in the ir spectrum. Structures 45 and 46 are simply the result of the well documented Paterno-Buchi reaction.[25]



45 46 47

The C^{13} nuclear magnetic resonance is shown in Spectrum 3. The three high field carbon atoms appear in the off resonance decoupled spectrum as a doublet (δ 28.2 Hz), a triplet (34.0 Hz) and a doublet (37.1 Hz). This is compatible with 45 and 46, but not 47. Structure 47 would show a triplet as the signal of highest field which was not observed. The C^{13} NMR assignments for structure 45 are shown in Figure 1.

Figure 1



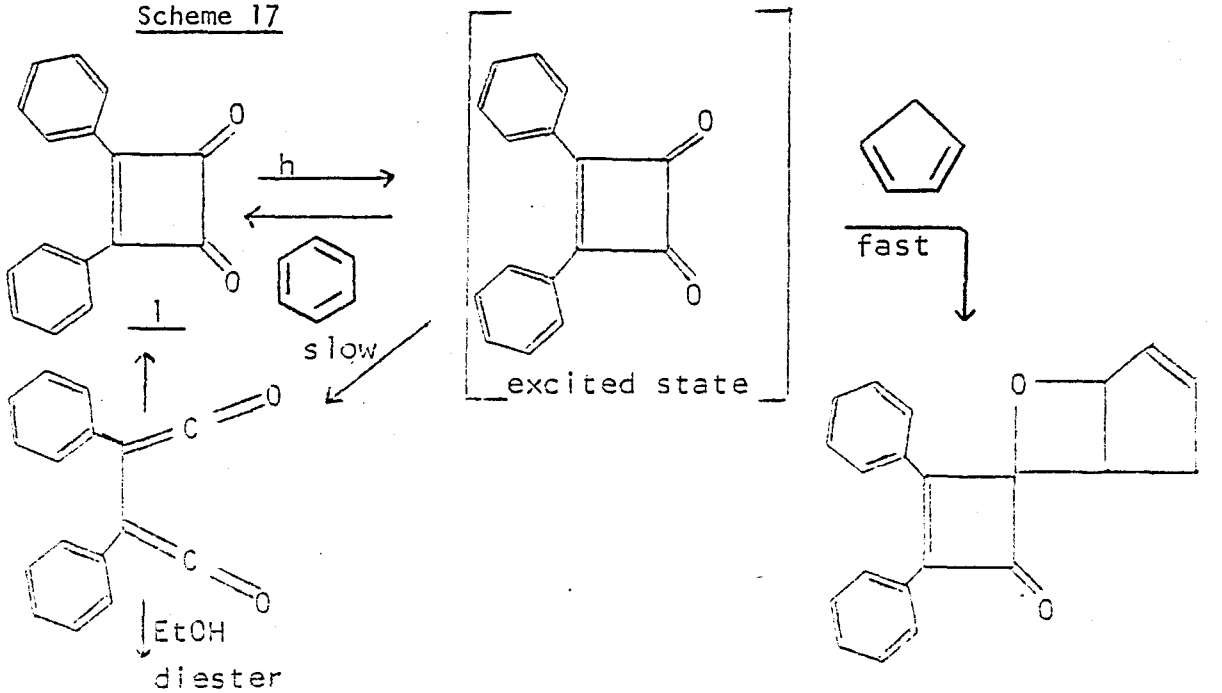
45

The proton NMR spectrum is most compatible with 45 (see Spectrum 2). The vinyl protons appear as an ABX pattern and an ABX_2 pattern at δ 6.1 and δ 5.9, respectively, as predicted for structure 45. A structure such as 47 should show two AB doublets in the vinyl region. The protons at positions 1' and 2' (see Figure 2) appeared as complex multiplets, one hydrogen at δ 2.4 and three hydrogens at δ 2.85 ppm. This is the predicted pattern for 45 but not 46 which should not show a signal at δ 2.4. Irradiation at δ 2.9 caused the complex vinyl protons to collapse to a clean AB quartet (J = 5.4 Hz). No hint of allylic coupling was observed which serves to further rule out structure 46.

Thus, the structure 45, 3,4-diphenylspiro[3-cyclobutene[1.7']-6-oxabicyclo[3.2.0]-3'-hepten]-2-one, is assigned to the photoadduct. The stereochemistry of 45 has not been determined.

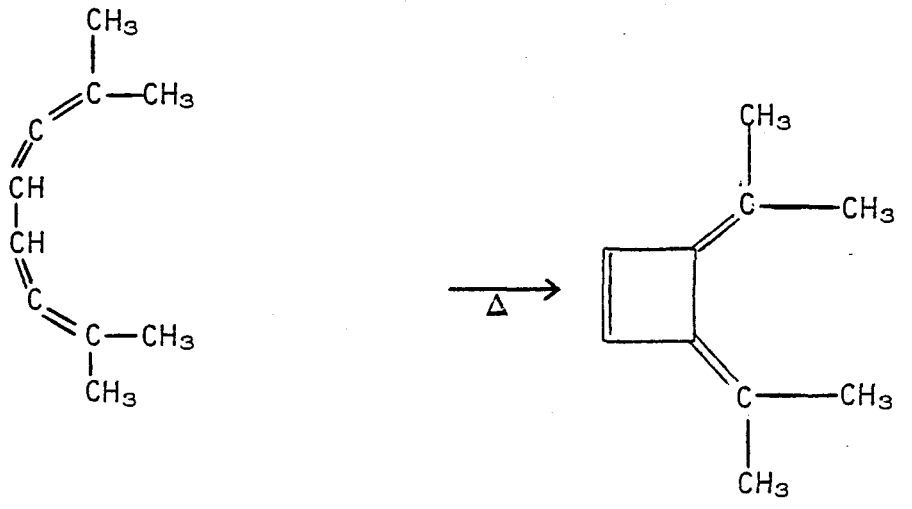
Since the formation of bis-ketene 2 has been confirmed spectrally in the photolysis of 1 it may be concluded that the transition from the excited state to the bis ketene is relatively slow compared with the 2+2 cycloaddition with cyclopentadiene (scheme 17).

Scheme 17



It was also observed that when 1 was irradiated in benzene with no cyclopentadiene present, no new products were obtained. This suggests that if the bis-ketene 2 is generated it is thermally reconverted to the starting material 1. Of interest is an experiment by Skattebol and Solomon in which a bis allene was thermally cyclized to form a cyclobutene ring.[26] This reaction is analogous to the ring closure of 2 to 1 suggesting the ring is more stable than the bis-ketene.

Scheme 18



Irradiation of 1 and tetracyanoethylene also gave no new products. This presumably is due to TCNE being more nucleophilic and therefore less reactive with the electron-rich bis-ketene.

Thermal ring opening of 3,4-diphenyl-3-cyclobutene-1,2-dione (1)

Because LaLancette has reported that 1 is converted slowly at room temperature to ester 3 in ethanol, presumably via bis phenyl ketene, this reaction was chosen as a convenient path for the determination of the energy of activation and entropy of activation for the formation of a bis-ketene. This data could be compared to similar presumed electrocyclic reactions.

However, it was found that 1 was stable in ethanol solution when stored in the dark. Thus, the reaction reported by LaLancette must have been photo-induced. It was noted that heating 1 in ethanol above 110°C did produce the diesters in quantitative yield.

The thermal ring opening of 1 was thus investigated in ethanol using the sealed tube method of Kepner, Winstein and Young.[27] The decrease in concentration of 1 was followed by ultraviolet spectroscopy at 323 nm. The ring opening followed first order kinetics, that is

$$\text{Rate} = k\,[\text{dione}]$$

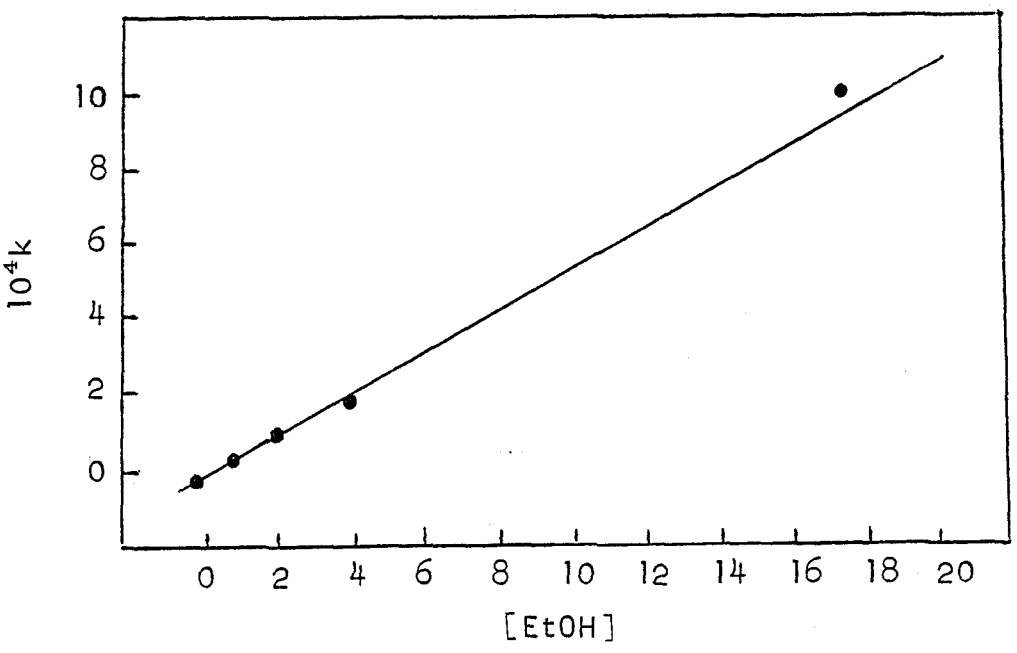
Table 1 shows k over a temperature range from 111° to 157°C for ethanol. A straight line was obtained from a least squares plot of ln k vs. 1/T showing the reaction conforms to the expression $k = Ae^{-Ea/RT}$. Ea for the reaction is approximately 31.7 kcal and $A = 1.46 \times 10^{13}\ sec^{-1}$.®

®This value compares favorably to the value of A ($1.2 \times 10^{13}\ sec^{-1}$) reported by Cooper and Walters[28] for the gas phase unimolecular ring opening of cyclobutene.

An experiment was then conducted to determine if the alcohol concentration appears in the rate expression. The ethonolysis of 1 in benzene solutions varying from 1.0M to 4.0M in ethanol and in neat ethanol was investigated.® The reaction rate was found to show first order dependence upon the dione concentration and varied linearly with the ethanol concentration (Figure 2). This dependence of the reaction rate on ethanol concentration suggests that the reaction is not unimolecular and ethanol must be included in the rate expression; thus, Rate = k [EtOH][dione].

This is an argument against the electrocyclic ring opening of 1 to form the bis-ketene 2 because this mechanism should not show a dependence on ethanol concentration.

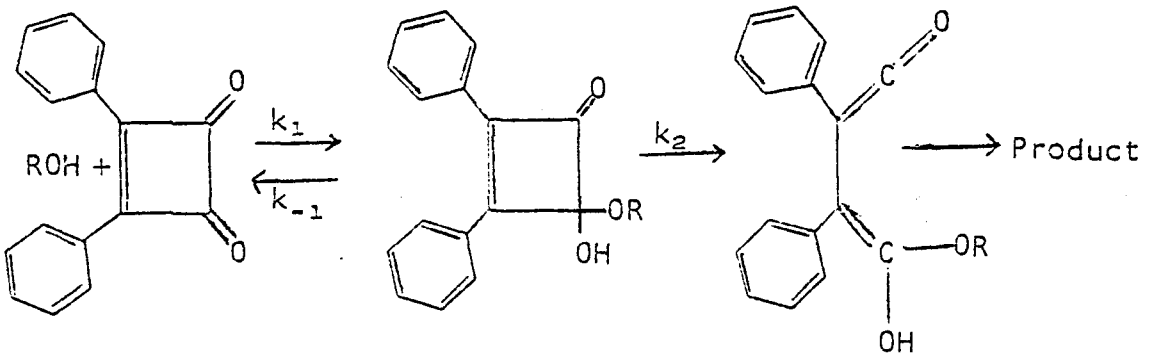
Figure 2. Pseudo first order constant k sec^{-1} vs. ethanol concentration in benzene at 157.8°C $[1]_{initial} = 10^{-3}M$.



®This work was supplemented by data obtained from the work of Clough and Coates.[15]

An alternative mechanism compatible with the observed kinetic behavior for the ring-opening of 1 in alcoholic solvent can be postulated. Nucleophilic attack at the carbonyl carbon producing a hemi-ketal 48 might precede ring opening (scheme 20). Ring opening of 48 would result in formation of a vinyl ketene 49. (It should be noted that nucleophilic attack on 1 under basic conditions usually proceeds by attack at C_3 resulting in the formation of different products[3,30] [scheme 20]). Ample documentation of the thermal conversion of cyclobutenones to vinyl ketenes has already been presented.[11,12]

Scheme 20



1 48 49

The effect of acid on the rate of this reaction was investigated because if it does indeed proceed via hemiketal formation, it might show acid catalysis.[31] Addition of either p-toluenesulfonic acid, dry HCl or benzoic acid to the reaction mixture of 1 failed to

enhance the rate of disappearance of 1 in ethanol at 158°C.[5] Because almost any nucleophilic attack on a carbonyl carbon would be acid catalyzed, the lack of acid catalysis suggests that if such an intermediate compound as 48 is present, its formation is not involved in the rate determining step. The rate constant k may well be described as $k_1k_2/(k_{-1} + k_2)$ with the ring opening step being rate limiting.

In the t-butanol alcoholysis of 1 a slight rate increase was observed with the addition of 0.1M benzoic acid to 4.0M and neat t-butanol solutions at 157.6°C (see appendix B-2). This suggests that in the mechanism indicated in scheme 20, k_1 is becoming rate limiting ($k_2 < k_1$ in ethanol, but $k_2 \geq k_1$ in t-butanol). This is compatible with acid catalysis in the t-butanol reaction but not with ethanol.

CONCLUSION

The photolysis of 3,4-diphenyl-3-cyclobutene-1,2-dione is not a good route to the bis-ketene in the presence of alkenes such as cyclopentadiene. The slow conversion from the activated state to the bis-ketene (if actually formed) cannot compete with 2 + 2 cycloadditions which proceed at faster rates.

Thermally 1 is also not a good precursor to the bis-ketene in nucleophilic solvents. This research did not show that the bis-ketene definitely was formed. The results suggest that instead of a bis-ketene formation 1 undergoes hemiketal formation followed by subsequent ring-opening to a vinyl ketene.

EXPERIMENTAL

Melting points were observed on a Hoover Capillary Melting Point Apparatus. All melting points were recorded in °C and not corrected.

The infra-red spectra were recorded on a Perkin-Elmer model 710 and a Digilab FTS 14. Absorptions indicated in wave numbers (cm^{-1}).

The nuclear magnetic resonance spectra were observed at 100 MHz with a Varian Associates XL-100 pulsed-Fourier transform or frequency swept high resolution 23.5 kg spectrophotometer. The nmr spectra at 60 MHz were obtained with a Varian Associates A-60 Recording Spectrometer. The proton nmr data are present as follows: chemical shift (splitting pattern,® number of hydrogens, coupling constant, assignment). Chemical shifts are expressed in parts per million and in deuterated chloroform are relative to internal tetramethylsilane.

Carbon-13 magnetic resonance spectra were taken at 20 MHz on a Bruker Spectrospin model spectrometer. Chemical shifts are given in parts per million for each carbon indicated.

The mass spectra were recorded on a Hitachi Perkin-Elmer spectrometer, Model RMU-6H, at 70 ev. The fragments are reported as m/e (relative intensity).

Ultraviolet spectra and data were obtained with a Beckmann Acta M-IV Spectrophotometer, using 1 cm matched quartz cells.

Irradiations were performed using a 450-watt Hanovia high pressure mercury arc lamp centered in an internal water-cooled pyrex immersion well.

®S = singlet, d = doublet

Irradiation of 3,4-diphenyl-3-cyclobutene-1,2-dione with cyclopentadiene

The dione 1 was prepared by the method of Green and Neuse.[32] Freshly distilled (from dicyclopentadiene) cyclopentadiene (6.6 g, 0.1M) was added to 150 mg (6.41×10^{-4}M) of 1 in 240 ml of dry benzene in the immersion well of the photolysis apparatus. The mixture was irradiated with the 450-watt lamp for one hour. The reaction mixture was concentrated on a rotary evaporator leaving an oil which eventually crystallized. The solid (43) was recrystallized five times from absolute ethanol, resulting in pale yellow crystals: mp 91-93°C; yield 152 mg (79%); ir (spectrum 1) ($CHCl_3$, Model FTS 14) 1751 (c = o), 1639 (c = c), 1022 and 1032 (c = o); nmr (proton) (spectrum 2) ($CDCl_3$, 80 MHz) δ 2.25 (M, 3H) δ 2.50 (M, 3H) δ 7.12-7.5 (M, 12H); nmr (C^{13}) (spectrum 3) ($CDCl_3$, 20 MHz) δ 171 (s, c = o), δ 161 (s, c =), δ 134 (d, = CH-), δ 131 (s, = C3), δ 125 (d, = CH-), δ 71 (s, c C[1.7']), δ 37 (d, CH-), δ 34 (t, $-CH_2-$), δ 28 (d, CH-); uv (spectrum 4) ($CHCl_3$) 292 nm (ε = 6.30×10^3); mass spec. (spectrum 5) m/e 300 (52%, molecular ion 45), m/e 207 (14%), m/e 178 (100%, diphenylacetylene), m/e 176 (14%, 43), m/e 152 (9%, 44).

Elemental Analysis:	Calculated for $C_{21}H_{16}O_2$	Found
C	84.00	84.02
H	5.33	5.37

Irradiation of 3,4-diphenyl-3-cyclobutene-1,2-dione (1) with tetracyanoethylene

An attempt to prepare a photoadduct of 1 and TCNE was made. Tetracyanoethylene (275 mg, 2.14×10^{-3}M) was added to 1 (100 mg, 4.27×10^{-4}M) in 240 ml dry benzene in the immersion well of the photolysis apparatus. The reaction mixture was irradiated for 1 hour with the 450-watt lamp and concentrated on a rotary evaporator. A mass spectrum of the residue revealed only starting materials and no products formed. Apparently TCNE does not intercept either the bis-ketene or 1 under these conditions.

Irradiation of 3,4-diphenyl-3-cyclobuten-1,2-dione in benzene

An experiment was performed to determine if new products would be formed in the absence of an alkene. To 240 ml of dry benzene in the immersion well of the photolysis apparatus was added 100 mg 1. The mixture was irradiated for one hour with the 450-watt lamp and concentrated on a rotary evaporator. Analysis of the residue showed only starting material.

Reaction of 3,4-diphenyl-3-cyclobutene-1,2-dione with cyclopentadiene in the absence of light

Freshly distilled (from dicyclopentadiene) cyclopentadiene[33] (3.3 g, 0.05M) was added to 75 mg (3.2×10^{-4}M) of 1 in 100 ml of dry benzene. An ultraviolet spectrum was run on a sample of the mixture. The mixture was stored in total darkness for 48 hours. Another ultraviolet spectrum was run and the absorption (λ = 322 nm) was the same as when the solution was first prepared showing no decrease in the concentration of 1.

Alcoholysis of 3,4-diphenyl-3-cyclobutene-1,2-dione

The alcoholysis of 1 was performed by preparing 10^{-3}M solutions of 1 in various concentrations of the alcohol in benzene.® The solutions were placed in 4 ml tubes, chilled and sealed. For each kinetic run, the samples were immersed in a flask of boiling solvent. A stop watch was used to determine elapsed time. Temperatures of the solvents were measured with thermometers graduated in tenths of a degree. At time intervals a vial was removed from the flask, immersed in an ice bath and kept away from light.

The decrease in concentration of 1 was followed by uv at 323 nm with a Beckmann Acta C III Spectrophotometer, using 1 cm matched quartz cells. Rate constants were obtained by a least squares plot of ln A vs. time (secs). All values are an average of three kinetic runs.

®All solutions were stored in a dark place immediately after preparation and not moved until ready for use to minimize effect by light.

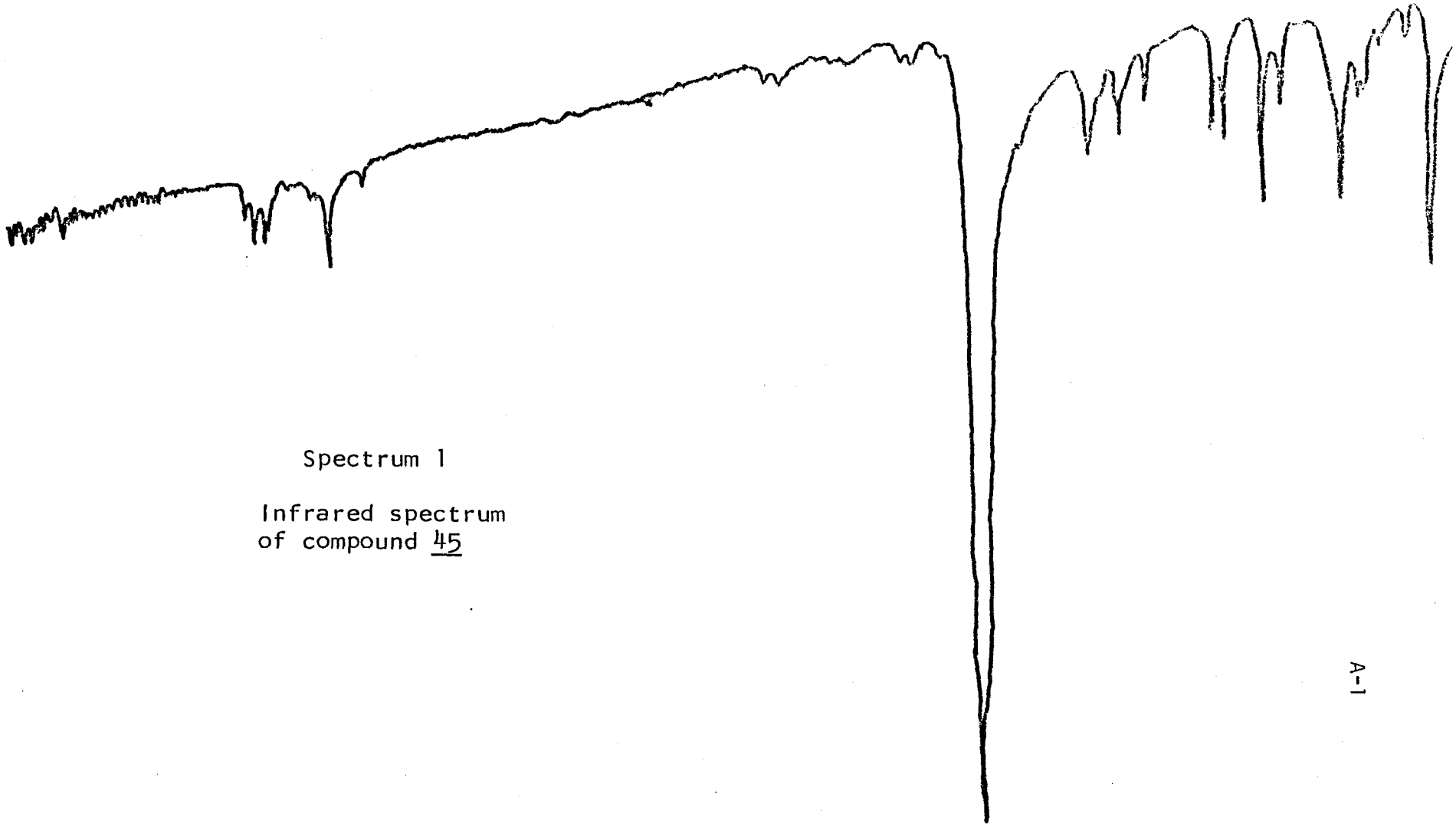
Thermal reaction of 3,4-diphenyl-3-cyclobutene-1,2-dione with tertiary butanol

Into a 20-ml ampule was placed 150 mg of 1 and 18 ml of reagent grade tertiary butanol. The ampule was sealed and placed in a 2-liter round bottom flask half full of refluxing bromobenzene (158°C). After 72 hours the reaction mixture was removed from the ampule and concentraded on a rotary evaporator resulting in 111 mg of a yellow solid material. Several attempts were made to purify the material, however, no clean product was obtained: mass spec., m/e 326 (8% molecular ion), m/e 324 (30%), m/e 300 (21%), m/e 280 (85%), m/e 246 (100%); ir ($CHCl_3$) 3050 cm^{-1} (-OH), 1695 cm^{-1} (c = 0); NMR (proton) δ 1.2 (S-3H), δ 1.35 (S-H), δ 4.2 (M, 2H), δ 7.4 (M).

Thermal reaction of crude t-butyldiphenylsuccinate with ethanol

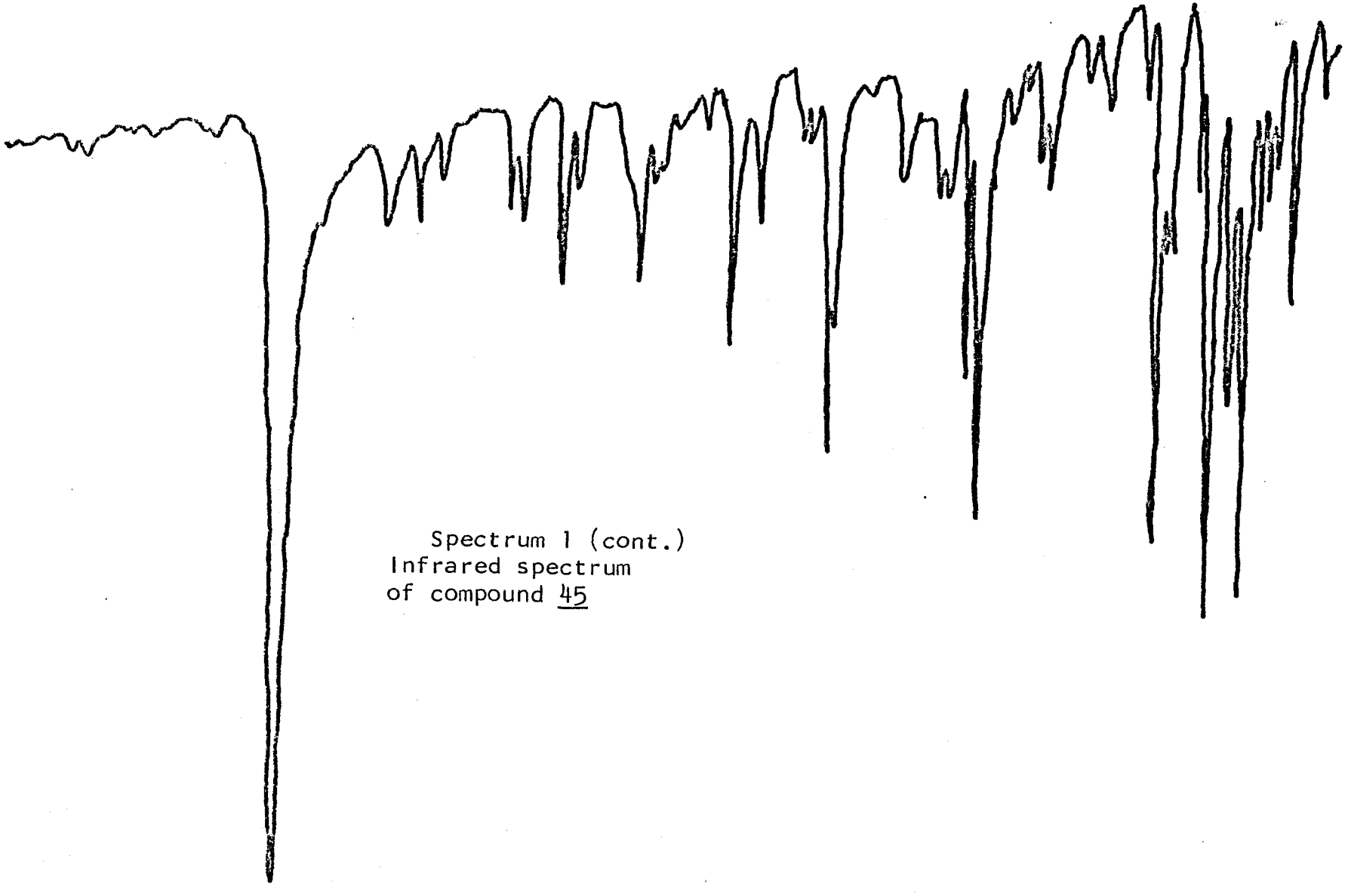
The remaining crude product, 65 mg, from the thermal reaction of 1 in t-butanol was placed in a flask with 15 ml of ethanol and 1.1 g of p-toluenesulfonic acid. The mixture was refluxed for one hour and treated with 10% aqueous $NaHCO_3$ until weakly alkaline. The mixture was extracted with chloroform, dried over $MgSO_4$ and concentrated on a rotary evaporator. Mass spectrometry showed the material to be crude diethyldiphenyl succinate. Mass spec., m/e 326 (14%, molecular ion), m/e 280 (100%), m/e 234 (21%).

APPENDIX A

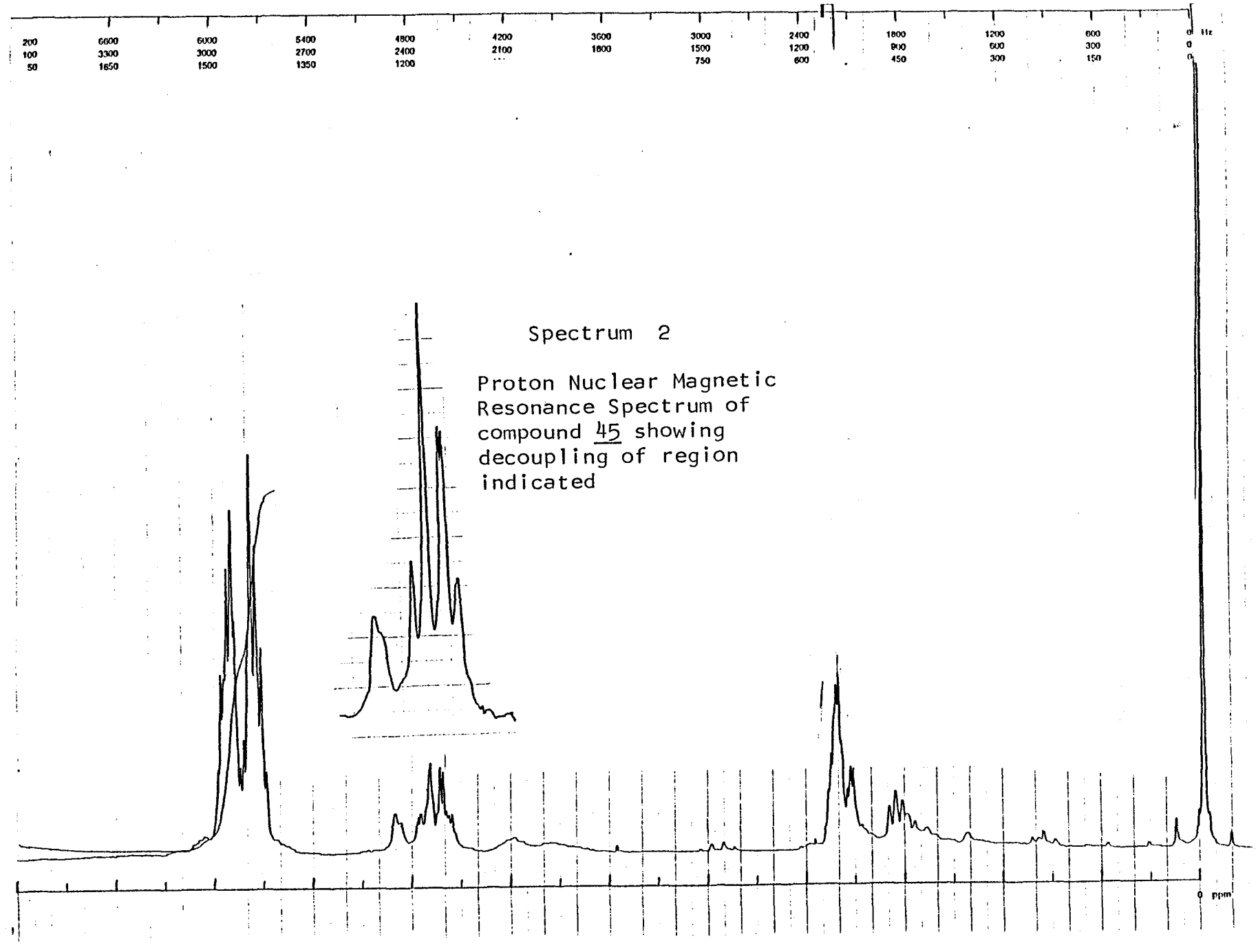


Spectrum 1

Infrared spectrum
of compound 45

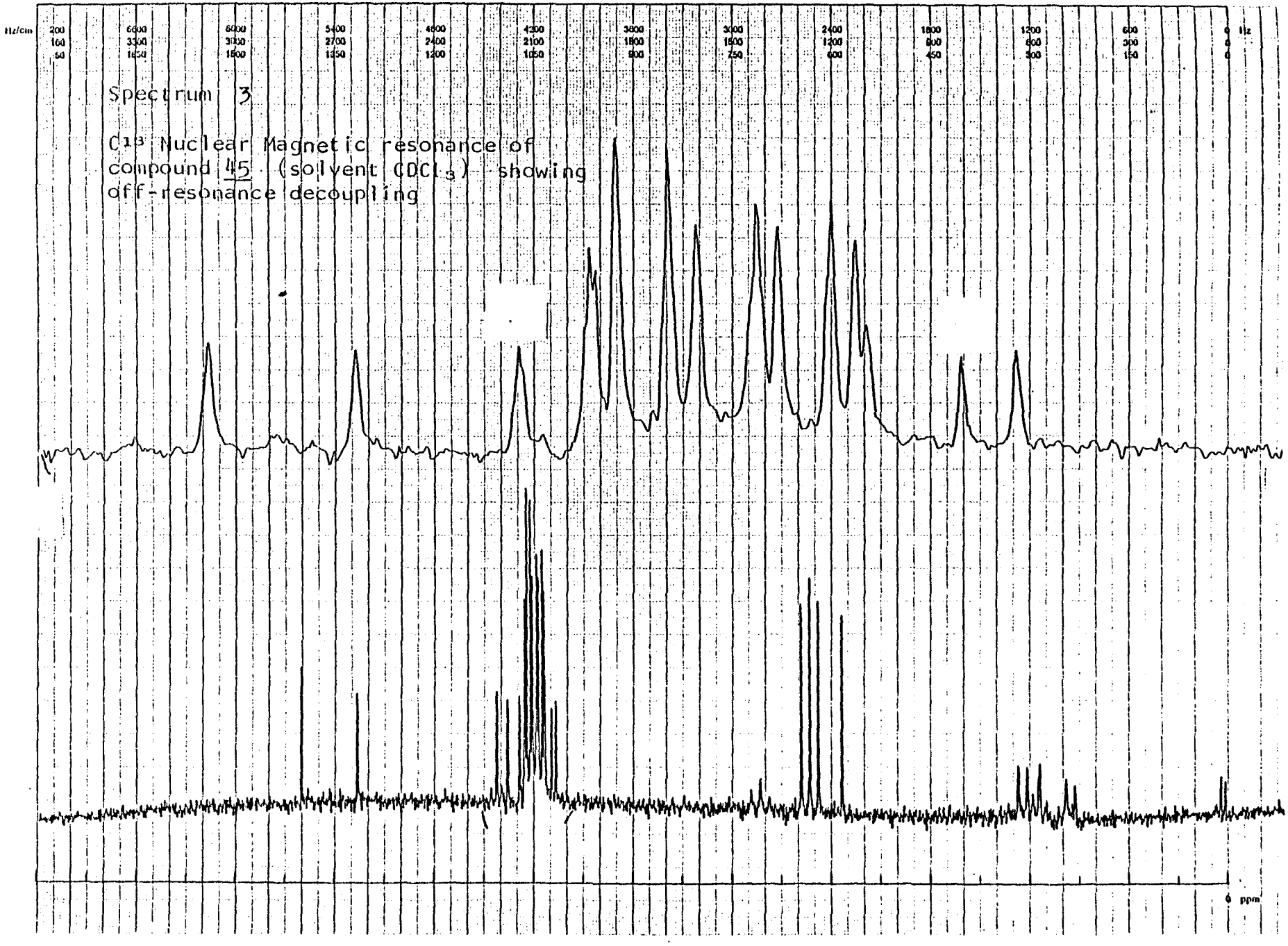


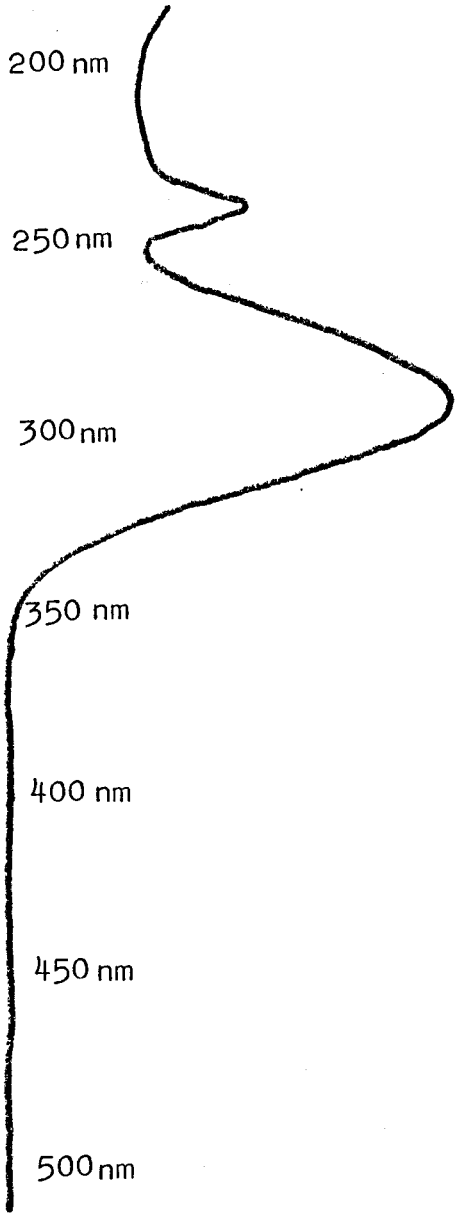
Spectrum 1 (cont.)
Infrared spectrum
of compound 45



Spectrum 2

Proton Nuclear Magnetic Resonance Spectrum of compound 45 showing decoupling of region indicated


Hz/cm
200 6600 6000 5400 4800 4200 3600 3000 2400 1800 1200 600 0 Hz
100 3300 3000 2700 2400 2100 1800 1500 1200 900 600 300 0
50 1650 1500 1350 1200 1050 900 750 600 450 300 150 0
Spectrum 3
C13 Nuclear Magnetic resonance of
compound 45 (solvent $CDCl_3$) showing
off-resonance decoupling
0 ppm

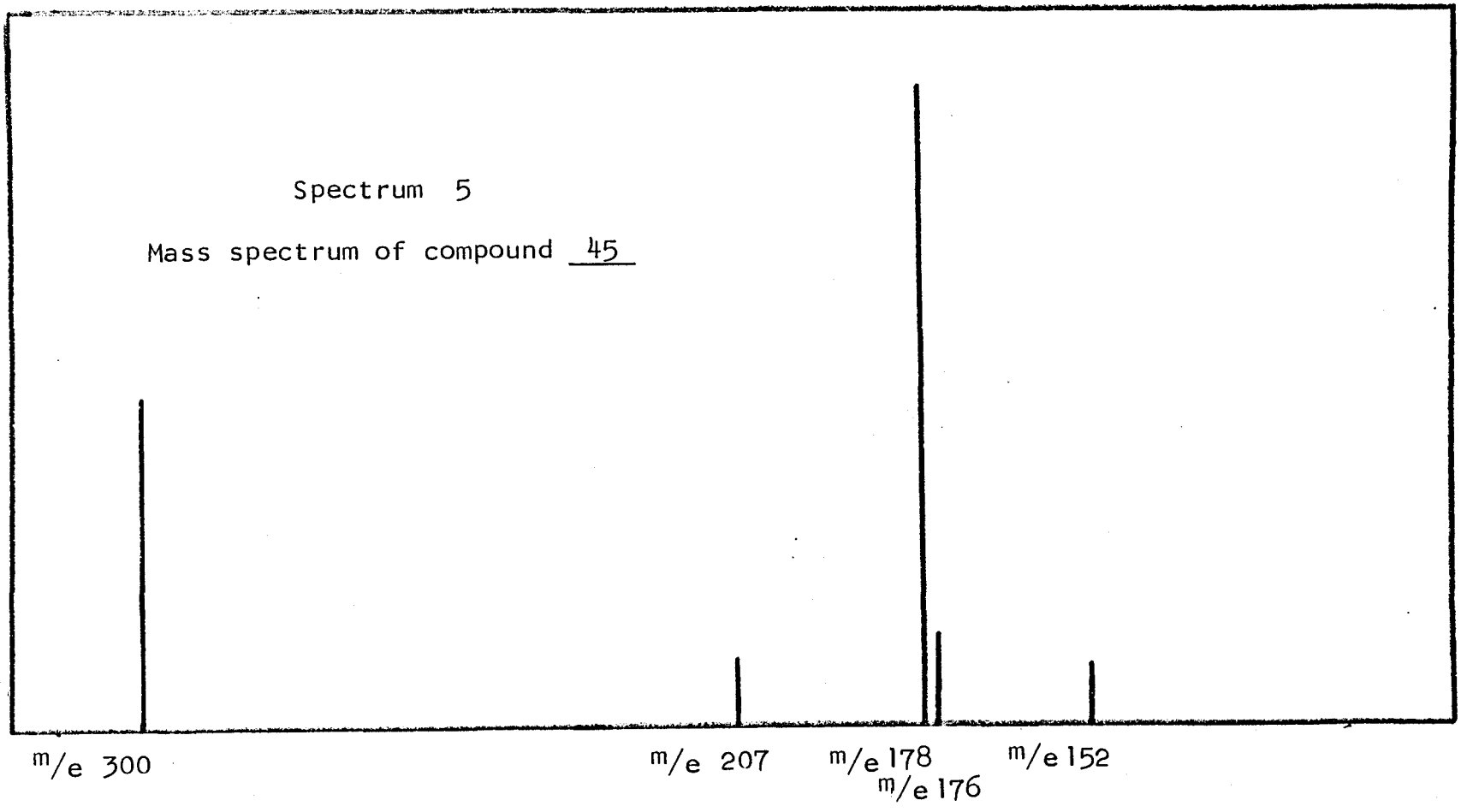


Spectrum 4

Ultraviolet spectrum
of compound 45

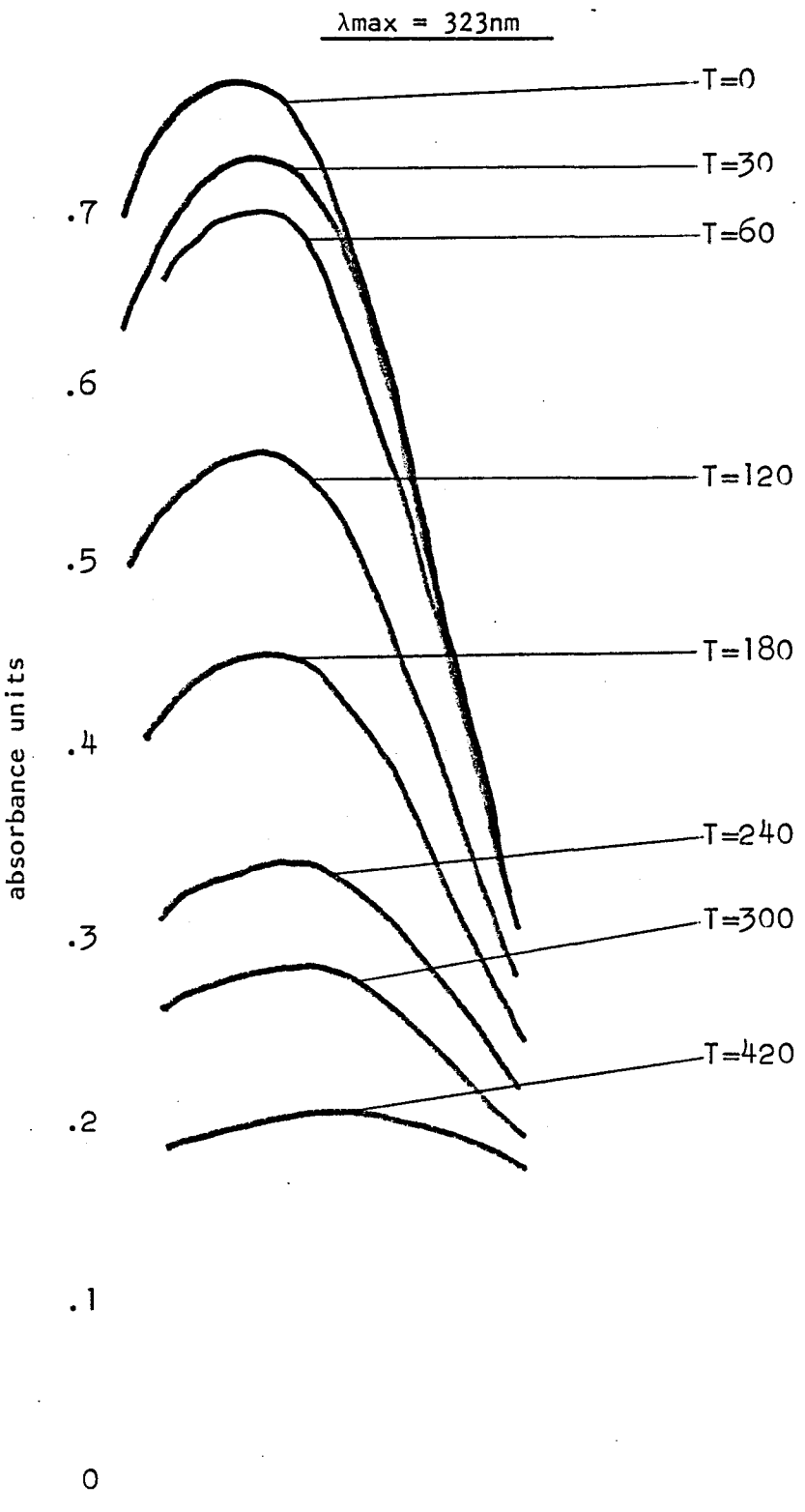
Spectrum 5

Mass spectrum of compound 45



Spectrum 6

Ultraviolet spectra of alcoholysis solution of 1 in tertiary butanol at 139.3°C. Initial concentration = 10^{-3}M. T = time in seconds.



APPENDIX B

Ethanol kinetic data

Pseudo first order Rate Constants

Molarity	Temp. (°C)	k (sec^{-1})	Average k
1M[10]	156.5	4.55×10^{-5} 3.88×10^{-5} 6.77×10^{-5}	5.0×10^{-5} sec^{-1}
2M[10]	156.5	1.17×10^{-4} 1.18×10^{-4}	1.18×10^{-4} sec^{-1}
4M	156.5	1.79×10^{-4} 1.71×10^{-4} 1.17×10^{-4}	1.56×10^{-4} sec^{-1}
8M[10]	156.5	3.54×10^{-4} 3.56×10^{-4} 3.25×10^{-4}	3.45×10^{-4} sec^{-1}
~17M	156.5	9.14×10^{-4} 13.7×10^{-4} 9.2×10^{-4} 7.91×10^{-4}	10×10^{-4} sec^{-1}
~17M	139.2	1.84×10^{-4} 1.92×10^{-4} 1.91×10^{-4}	1.89×10^{-4} sec^{-1}
~17M[10]	111	1.34×10^{-5} 1.09×10^{-5} 1.22×10^{-5}	1.22×10^{-5} sec^{-1}
4M/.15 MHCl[10]	158	1.6×10^{-4} 1.9×10^{-4}	1.75×10^{-4} sec^{-1}
4M/1MØCO$_2$H [10]	158	2.2×10^{-4} 1.74×10^{-4} 1.96×10^{-4}	1.97×10^{-4}
4M/0.1MTsOH[10]	158	1.67×10^{-4}	

Tertiary butanol kinetic data

Molarity	Temp. (°C)	k (sec^{-1})	Average k
4M	157.6	6.65×10^{-6} 6.50×10^{-6} 6.21×10^{-6}	6.45×10^{-6}
4M/0.1MØCO$_2$H	157.6	1.17×10^{-5} 1.11×10^{-5} 1.28×10^{-5}	1.18×10^{-5}
4M	165.4	7.13×10^{-6} 7.34×10^{-6} 6.88×10^{-6}	7.1×10^{-6}
4M/0.1MØCO$_2$H	165.4	1.15×10^{-5} 1.43×10^{-5} 1.55×10^{-5}	1.37×10^{-5}
4M/o.1MTsOH	157.6	5.55×10^{-5} 5.05×10^{-5} 5.95×10^{-5}	5.51×10^{-5}
10.5M	139.3	5.76×10^{-5} 5.65×10^{-5} 4.82×10^{-5}	5.41×10^{-5}
10.5M	156.7	1.35×10^{-4} 1.15×10^{-4} 1.25×10^{-4}	1.25×10^{-4}
10.5M	165.4	1.97×10^{-4} 1.70×10^{-4} 1.83×10^{-4}	1.83×10^{-4}
10.5/0.1NØCO$_2$H	157.6	1.88×10^{-4} 1.49×10^{-4} 1.71×10^{-4}	1.69×10^{-4} sec^{-1}

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VITA

John Dana Myers was born October 27, 1944, in Richmond, Virginia. He was graduated from Armstrong High School in June, 1962. The same year he enrolled at Virginia Union University where he received the degree of Bachelor of Science in 1966. Upon graduation from college he was employed by Philip Morris Co. as an assistant scientist. From 1967 to June, 1968, John Myers taught Chemistry at Maggie Walker High School. After one year of teaching he joined A. H. Robins Co., where he is presently employed. In 1971 he enrolled in the Graduate School of the University of Richmond to continue his study for the degree of Master of Science. He is a member of the American Chemical Society and the Division of Chemical Information, the Chemical Notation Association and the Drug Information Association.