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Synthesis of chromium tricarbonyl complexes of 1,3-diaryl-2-propyl methanesulfonates

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SYNTHESIS OF
CHROMIUM TRICARBONYL COMPLEXES OF
1,3-DIARYL-2-PROPYL METHANESULFONATES

A THESIS
SUBMITTED TO THE DEPARTMENT OF CHEMISTRY
OF THE GRADUATE SCHOOL OF
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MASTER OF SCIENCE

BY
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PREFACE

Various unsymmetrically substituted 1,3-diphenyl-2-propyl methanesulfonates were prepared and complexed with chromium hexacarbonyl. The major products obtained from this complexation contained one π-complexed ring and the other ring substituted with more common groups.
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HISTORICAL

Synthesis and Typical Reactions of \( \pi-(\text{Arene})\text{chromium Tricarbonyls} \)

In 1957 Fischer and Ofele reported the synthesis of \( \pi-(\text{benzene})\text{chromium tricarbonyl} \) (1) as an unexpected product from the attempted synthesis of bis-benzene chromium (2). Since the known routes to the bis complexed compound were somewhat involved and the results difficult to reproduce, Fischer and Ofele investigated the
feasibility of direct complexation of benzene with chromium hexacarbonyl. The reactants were heated in a sealed system at 220° and gave a 27% yield of the mono-complex.\(^1\) Nicholls and Whiting working independently had developed a simpler and more general method for the synthesis of the mono-complexes which involved refluxing the reactants in an inert solvent in an open system.\(^2\) Natta, Ercoli and Calderazzo soon published results describing the synthesis of similar compounds, but their reactions like Fischer's were carried out under pressure. Unlike Fischer they intermittently released the carbon monoxide generated in the reaction.\(^3\) By allowing for the escape of carbon monoxide both Nicholls and Natta recognized the significance of the equilibrium, represented by the following equation:

\[
\text{Cr(CO)}_6 + \text{C}_6\text{H}_6 \quad \overset{\rightleftharpoons}{\text{π}} \quad \text{(C}_6\text{H}_6)\text{Cr(CO)}_3 + 3 \text{CO}
\]

The products of the reaction are favored in this equilibrium only if the system is open.\(^2\) The synthesis of these mono-complexes generated extensive interest since they proved in general to be easy to synthesize, to be stable and to undergo some interesting reactions. In most cases, they
are yellow to orange solids that are stable in air and give sharp melting points.

Since the original preparative studies were published, the technique of Nicholls and Whiting has been adopted by the majority of investigators. Usually equimolar amounts of arene and chromium hexacarbonyl are refluxed in a high boiling inert solvent such as diglyme, decalin, n-butyl ether or cyclohexanol. In cases where the arene is a liquid it can be sometimes employed as the solvent. Since chromium hexacarbonyl sublimes at the boiling point of many of the solvents employed, some means of returning it to the solution is required. Nicholls and Whiting returned the sublimate mechanically to the reaction vessel. Strohmeier designed a condenser that made possible the return of sublimed chromium hexacarbonyl by condensing solvent. Since decomposition of the \( \pi \)-complex in solution is promoted by light, the reactions are generally carried out in subdued lighting or in the dark.

Several review articles have been published which catalogue the compounds that have been prepared and give
the details of the synthesis. The compounds listed in figure I illustrate the variety of the arene systems that have been used.

When the \( \pi \)-electron density of the arene is depleted by electron withdrawing substituents on the benzene ring, the arene fails to react with the chromium hexacarbonyl. Benzoic acid, benzaldehyde, nitrobenzene and benzonitrile are several substrates that do not undergo complexation. Similar electronic considerations have been proposed to explain the tendency of polynuclear aromatic compounds such as naphthalene and anthracene to form only mono-complexes. In this instance, however, the chromium tricarbonyl substituent serves as the deactivating group.

The \( \pi \)-(arene)chromium tricarbonyl has an octahedral geometrical configuration. On the basis of valence bond theory, the six electron pairs donated to the central metal ion by the ligands fill the six \( d^2sp^3 \) hybrid orbitals of the chromium. Three of these pairs are donated by the arene and the remaining pairs by the carbon monoxide molecules. From the standpoint of ligand-field theory, the six bonding orbitals from the six ligands combine with
\[ X = \text{NH}_2, \text{OH}, \text{Cl}, \text{F}, \text{CH}_3, \]

\[ \text{OCH}_3, \text{OH}, \]

\[ \text{C} = \text{C} - \text{CH} = \text{C} - \text{H} \]

\[ \text{Cr(CO)}_3 \]

\[ \text{A} - \text{CH}_2 - \text{O} \]

\[ \text{Cr(CO)}_3 \]
the six hybrid orbitals of the central metal ion to give six bonding and six anti-bonding molecular orbitals. The unused d orbitals of chromium are considered to be non-bonding. Overlap of these filled non-bonding orbitals with empty anti-bonding orbitals on the ligand accounts for a decrease in electron density on the central metal ion and the inherent stability of the complex.\textsuperscript{8,9}

The inductive effect of the chromium tricarbonyl group is considered to be similar to that of a p-nitro substituent since the ionization constants for \(\pi\)-(phenyl)chromium tricarbonyl acetic acid and p-nitrophenylacetic acid are 5.02 and 5.01, respectively. Nicholls and Whiting have suggested that the steric bulk of the chromium tricarbonyl is equal to that of a large \textit{ortho} substituent.\textsuperscript{2}

The reactions that the chromium complex undergoes could be grouped into three classifications. There are exchange reactions that involve the replacement of the arene by other organic ligands, exchange reactions that involve replacement of carbon monoxide by another inorganic ligand, and reactions of the arene system. The arene exchange reaction can be represented by the equation:
arene · Cr(CO)₃ + arene* = arene* · Cr(CO)₃ + arene

The replacement of the arene instead of carbon monoxide demonstrates the relative strength of the arene-chromium bond vs. the carbonyl-chromium bond.⁷ This reaction is useful because compounds that cannot be prepared by the normal method of refluxing the arene and chromium hexacarbonyl can be obtained by this exchange method. The formation of π-(benzaldehyde)chromium tricarbonyl (figure II) is a valid example.⁷ Several investigators have studied the exchange reaction with regard to the mechanism of the process. Ease of replacement series have been developed for many hydrocarbons.⁸

\[
\begin{align*}
\text{arene} \cdot \text{Cr(CO)}_3 &+ \text{arene}^* = \text{arene}^* \cdot \text{Cr(CO)}_3 + \text{arene} \\
\text{Cr(CO)}_3 + \text{arene} &\rightarrow \text{arene}^* \cdot \text{Cr(CO)}_3 + \text{arene} \\
\end{align*}
\]
Inorganic ligand exchange has been accomplished by treating the arene chromium tricarbonyl with such compounds as phosphine and triphenyl phosphine (3) in an inert solvent and in an inert solvent while irradiating with ultraviolet light. Other compounds such as olefins, dimethylsulfoxide and pyridine can also displace carbon monoxide from the complex. It has not been possible to generate the bis-arene complex by the substitution of an arene compound for the carbonyls.

\[
\begin{array}{c}
\text{I} \\
\text{OC} \\
\text{Cr} \\
\text{CO} \\
\end{array}
\quad + 
\begin{array}{c}
\text{PH}_3 \\
\end{array}
\quad \Leftrightarrow 
\begin{array}{c}
\text{I} \\
\text{OC} \\
\text{Cr} \\
\text{PH}_3 \\
\text{CO} \\
\end{array}
\quad + 
\begin{array}{c}
\text{CO} \\
\end{array}
\]

The chemistry of the arene system is greatly affected by the presence of the chromium tricarbonyl substituent. For example, nucleophilic aromatic substitution, a process that takes place with only a few particularly active aromatic systems, has been shown to occur with \(\pi\)-(chloro-benzene)chromium tricarbonyl. On heating the compound with
sodium methoxide at moderate temperatures, high yields of \( \pi \)-complexed anisole are produced.\(^2\) With the decrease in \( \pi \)-electron density, the electrophilic substitution of the arene should be more difficult, if not impossible. The inability of nitrobenzene to undergo a Freidel-Crafts acylation is well documented. The Freidel-Crafts acylation of \( \pi \)-complexed benzene, toluene, \( p \)-xylene and trimethylbenzene has been effected with good yields.\(^7\) Complexation of the arene can affect the ratio of the products as illustrated in figure III.\(^8\)

\[
\begin{array}{c}
\text{III} \\
\begin{array}{c}
\text{III} \\
-CH_3 \\
0,\% & m,\% & p,\% \\
8 & 0 & 92 \\
\end{array} \\
\begin{array}{c}
39 & 15 & 46 \\
\end{array}
\end{array}
\]

Reactions involving the functional group of complexed arenes are somewhat limited since acids generally decompose the complex. Such processes as base catalysed esterification, Wittig reactions, Claisen condensations and lithium
aluminum hydride reductions are possible. Attempts to oxidize an amine to a nitro group met with failure as the oxidizing agent attacks the chromium producing tetravalent chromium.7 Typical reactions of π-complexed compounds are illustrated in figure IV.
Solvolysis Studies of $\pi$-(Arene)Chromium Tricarbonyls

The first investigation that dealt extensively with the solvolysis of a $\pi$-(arene)chromium tricarbonyl system was published by Holmes, Jones and Pettit in 1965. These workers found that the rates of solvolysis of the $\pi$-chromium tricarbonyl complexes of benzyl chloride and benzhydryl chloride were five times greater than the rates of the corresponding uncomplexed compounds. They suggested that back-donation of electron density from the metal to the arene could stabilize the transition state leading to the carbonium ion formed in the solvolysis. This stabilization would result in a lower free energy of activation and a faster rate of reaction. Although the intermediate carbonium ion was not isolated in their studies, it has been observed subsequently by Trahanovsky and Wells. These workers generated the intermediate by adding an
ethanol or acetic acid solution of \( \pi \)-(benzyl alcohol) chromium tricarbonyl to concentrated sulfuric acid. The existence of the carbonium ion intermediate is ascertained by the ultraviolet-visible spectrum of the resulting solution. On the basis of acidity studies on a series of substituted \( \pi \)-complexed benzyl alcohols, they concluded that the effective positive charge on the benzylic carbon had been significantly reduced by the chromium.

R. S. Bly and co-workers have investigated the solvolysis of a series of \( \pi \)-(arene methanesulfonate)chromium tricarbonyls (4). It was hoped that the study could provide additional information about \( \pi \)-electron delocalization in the non-complexed compounds as well as about the nature of bonding in the \( \pi \)-complex. Bly's investigation was designed to parallel the work of Cram\(^{13}\) and Winstein\(^{14}\) who had studied the solvolytic behavior of a group of
diastereoisomeric substituted π-phenylethyl arenesulfonates. To explain the observed stereospecificity, the apparent reaction rate enhancement, and the rearrangements that occur during the solvolysis, Cram and Winstein had proposed the intermediacy of a phenonium ion (5). Delocalization of arising positive charge into the phenyl ring permits the formation of a lower energy transition state than would be possible if the arising positive charge were localized on the secondary carbonium ion. In the acetolysis of optically pure L-threo-3-phenyl-2-butyl-p-toluenesulfonate, it is proposed that the reaction proceeds through a symmetrical phenonium ion to give a racemic mixture of D,L-threo-3-phenyl-2-butyl acetate (figure V). Bly suggested that if the phenyl ring were complexed, the π-electron density would be somewhat depleted by the electron withdrawing chromium tricarbonyl group and would not be as effective in stabiliz-
ing the arising transition state. The solvolysis results then should differ significantly from the uncomplexed case. The solvolysis of optically pure (97%) \( L\text{-threo-3-}(\text{phenyl}) \) chromium tricarbonyl-2-butyl methanesulfonate in buffered acetic acid proceeds with retention of configuration (94%) instead of racemization. When either the pure \( L\text{-erythro} \) non-complexed or \( \pi\)-complexed sulfonates are subjected to acelolysis, an acetate with retained configuration is produced. This result is similar to the \( \text{threo} \) case, as phenyl migration in the non-complexed case does not alter the overall stereochemistry of the molecule (figure VI). The acetolysis of optically pure \( \text{erythro-2-}\pi\text{-}(\text{phenyl})\text{chromium tricarbonyl-3-pentyl methanesulfonate} \) did not proceed with rearrangement as did the acetolysis of the non-complexed tosylate. In the latter case, almost equal amounts of \( \text{erythro-3-phenyl-2-pentyl acetate} \) and \( \text{erythro-2-phenyl-3-pentyl acetate} \) were isolated (figure VII).

The amount of anchimeric assistance by the phenyl group is difficult to measure quantitatively. The observed effect of the phenyl group on the rate of solvolysis is a composite one, combining anchimeric assistance, an electron
\[-\text{OTs}^-\]
withdrawing inductive effect and a steric effect. Winstein has reported that the rates of acetolysis of 2-butyl tosylate and threo-3-phenyl-2-butyl tosylate at 50° are very close to one another.\textsuperscript{15} Bly reported that the rates of solvolysis of the similar methanesulfonates are not appreciably affected by complexation.\textsuperscript{16} When corrections are made for the electron withdrawing nature of the chromium tricarbonyl group; however, it is estimated that the rate has been enhanced 33 times for the threo and 6.8 times for the erythro-2-\textsubscript{\pi}-(phenyl)chromium tricarbonyl-3-pentyl methanesulfonates, relative to the non-complexed compounds. It is quite significant that the solvolyses of the \textsubscript{\pi}-complexed methanesulfonates proceed with retention of configuration in all butane cases. The exception was the \textsubscript{\pi}-complexed neophyl derivative (6) where complexed aryl migration can yield a more stable tertiary carbonium ion. Bly suggested that the solvolysis results could be attributed to either a decrease in phenyl participation caused by a steric and/or electron withdrawing effect of the chromium tricarbonyl group. He further postulated a possible buttressing and shielding effect by the complexed phenyl ring. Alternately the chromium could be more intimately
involved. Earlier Richards and Hill had studied the solvolysis of \(\pi\)-ferrocenyl compounds and had postulated direct interaction by the iron in displacement of the leaving group.

\[
\begin{align*}
\text{CH}_3 & \quad \text{C-CH}_2-\text{OMs} \\
\text{Cr} & \quad \text{CH}_3 \\
\text{OC} & \quad \text{CO}
\end{align*}
\]

They suggested that a filled metal d orbital could overlap with the arising empty orbital created by departure of the leaving group. This interaction is referred to as d orbital participation. Traylor and Ware had explained some similar \(\pi\)-ferrocenyl studies in terms of metal-carbon hyperconjugation (\(\pi\)-delocalization).\(^{18}\) Based on these two models, Bly proposed the mechanisms shown in figure VIII.

Lancelot and Schleyer have presented several approaches for determining the true rate enhancement of a neighboring phenyl group.\(^{19}\) One approach involves the kinetic investigation of a series of substituted 1,3-diaryl-2-propyl tosylates (7). Although both substituted phenyl rings can
\[ \text{Cr(CO)}_3 \]

\[ \text{HOAc} \xrightarrow{\text{Slow}} \]

\[ \text{HOAc} \xrightarrow{\text{Fast}} \]

\[ \text{RICHARD AND HILL MODEL} \]

\[ \text{Cr(CO)}_3 \]

\[ \text{HOAc} \xrightarrow{\text{Slow}} \]

\[ \text{HOAc} \xrightarrow{\text{Fast}} \]

\[ \text{TRAYLOR AND WARE MODEL} \]

\[ \text{VIII} \]
exert steric and inductive effects simultaneously, only one phenyl group can participate anchimerically at one instant.

As a result, direct competition exists between the two phenyl groups in their efforts to assist anchimerically. The observed solvolysis rate constant, $k_X$, for a given reaction would be a composite of the individual rate constants for the various types of phenyl involvement in solvolysis (figure IX). The $S_X S_Y$ term describes the cooperative inductive and steric effects of both substituted phenyl groups, while $x^S y$ and $y^S x$ describe participation by the phenyl groups. After the observed rate constants for a series of diaryl tosylates were determined, the rate constants were separated into the component constants by
the use of simultaneous equations. A similar analysis in the \( \pi \)-complexed methanesulfonate system could give an indication of the extent of participation by the \( \pi \)-complexed aryl group, or by the chromium tricarbonyl group.
DISCUSSION

The synthesis of the arene $\pi$-complex, ferrocene, in 1952 stimulated a great interest in the area of organo-metallic chemistry. Ever since the original synthesis was presented, many research groups have devoted their efforts to the preparation of similar sandwich compounds, and other interesting organometallic systems. This investigation concerned the preparation of a series of substituted arene $\pi$-complex chromium tricarbonyl compounds (8). More specifically, it was hoped that derivatives of the 1,3-diphenyl-2-propyl methanesulfonate system (9) could be prepared with
one \( \pi \)-complexed ring and the other ring substituted with more common groups. The synthesis of the general system could be approached by either of two routes. One path would involve the synthesis of the unsymmetrically substituted organic ligand, followed by the complexation of it with chromium hexacarbonyl. Alternately, a portion of the organic ligand could be complexed and the resulting organo-metallic compound condensed with the remaining portion of the organic system. Both routes have obvious drawbacks. When the first path is employed, there is some uncertainty as to which ring will be complexed, the substituted ring or the non-substituted one. The second path would involve a condensation reaction, for which the reaction conditions might prove destructive for the somewhat sensitive organo-metallic compound. Since the uncomplexed systems were to be used for spectral comparisons, as well as for future
kinetic work, the first path was chosen.

**Synthesis of 1,3-Diaryl-2-Propanones**

The general scheme which was developed for the synthesis of the organic ligands is outlined in figure X. The Claisen condensation provided a favorable route for the synthesis of the 1,3-diphenyl-2-propanone system, as overall yields of 60% were obtained. Unsymmetrically substituted 1,3-diphenyl-2-propanones were prepared by condensing phenylacetonitrile with ethyl phenylacetate in sodium ethoxide-ethanol, followed by hydrolysis and decarboxylation of the product. The substituent could be on either the nitrile or ester. The precursor acetates were formed by esterification of the requisite phenylacetic acids. The crude substituted diphenylacetooacetonitriles were hydrolyzed and decarboxylated by refluxing in 60% aqueous sulfuric acid until the evolution of carbon dioxide had ceased. Attempts to reproduce the results of Horning and co-workers afforded intractable tars. Instead of refluxing for 24 hrs or longer as they suggested, this research indicates that usually the reaction is complete in thirty or forty minutes and provides a minimum of polymeric residue. This route was employed success-
fully in the preparation of the unsymmetrically substituted p-Cl, p-Br, m-Cl and p-F compounds.

Numerous synthetic paths were investigated in an attempt to prepare 1-phenyl-3-(p-nitrophenyl)-2-propanone. However all efforts failed and afforded either inseparable mixtures or tarry residues. Claisen condensations with the p-nitro substituent in either the ester or the nitrile were unsuccessful. Condensation of p-nitrophenylacetamide with benzylimagnesium chloride gave an insoluble polymeric residue. The synthesis of 2-(p-aminophenyl)-4-phenylacetone-nitrile which could be hydrolyzed, decarboxylated, and then oxidized to the desired nitro compound did not proceed as anticipated. The product isolated from the reaction mixture was an amide (10).

\[
\begin{array}{c}
\text{O} \\
\text{H} \\
\text{\text{\textregistered}} \\
\text{CH}_2\text{-C-N-CH}_2\text{-C \equiv N}
\end{array}
\]

10

Coan and co-workers reported similar difficulties in introducing a nitro group into 1,3-diphenyl-2-propanone by base-catalyzed reactions. Moreover nitration of 1,3-diphenyl-
2-propanone in acidic media also provided undesirable results. Settimj\textsuperscript{23} and co-workers nitrated the ketone and obtained a variety of nitration compounds. In this research, nitration was attempted by the following chemical systems: acetic anhydride and fuming nitric acid; acetic acid and fuming nitric acid; acetic acid, fuming nitric acid and a catalytic amount of sulfuric acid. Analysis by thin layer chromatography and proton magnetic resonance spectroscopy revealed that numerous nitration products are obtained but the yield of the desired \( p\)-NO\(_2\) compound was unsuitable for further work.

Using the procedure of Elderfield and Burgess\textsuperscript{24} the condensation of \( p\)-nitrophenylacetyl chloride and benzyl cadmium chloride was attempted. The reaction was carried out twice, but in both cases no desired product could be obtained.

Lancelot has prepared 1-phenyl-3-(\( p\)-nitrophenyl)-2-propanone by the transformation of 1,3-diphenyl-1-propanone.\textsuperscript{25} The preparation is outlined in figure XI. Using the procedure of Hurd and Jenkins\textsuperscript{26} 1,3-diphenyl-1-propanone was nitrated by dissolving it in acetic anhydride and adding cupric
\[
\text{[Diagram of chemical reactions involving aromatic compounds with a nitro group substitution.]} 
\]
nitrate trihydrate. The resulting crude ortho-para nitro mixture was purified by fractional recrystallization from ether.

Another synthetic route that was investigated was the reactions of alkylolithiums with carboxylic acids to give ketones. Tegner\textsuperscript{27} used a series of free carboxylic acids, including phenylacetic acid, and methyllithium to obtain in high yields the methylketones. Gilman\textsuperscript{28} has prepared benzylolithium by the cleavage of ethers of the type $\text{C}_6\text{H}_5\text{CH}_2\text{OR}$, where R is methyl, ethyl, phenyl, and benzyl. The general synthetic scheme followed in the attempted preparation of the ketone is diagrammed in figure XII.

\[
\begin{align*}
\text{R} & \quad -\text{CH}_2\text{Cl} + \text{NaOCH}_3 \xrightarrow{\Delta} \text{R} & \quad -\text{CH}_2\text{OCH}_3 & \quad \xrightarrow{\text{Li}} & \quad \text{THF} \\
\text{R} & \quad -\text{CH}_2\text{Li} & \quad \xrightarrow{\text{C}_6\text{H}_5\text{COH}} & \quad \text{R} & \quad -\text{CH}_2\text{C}-\text{CH}_2- & \quad \text{XII}
\end{align*}
\]
Various attempts were made to prepare the ketone by using forward and reverse addition as well as cooling and refluxing the reactants; however all attempts were unsuccessful. It is believed that the benzyllithium undergoes a coupling reaction rather than reacting with the acid.

1-Phenyl-3-(o-chlorophenyl)-2-propanone was prepared by the reaction of \(\alpha,\alpha\) dichlorotoluene and phenylacetamide using the Grignard method. Sansford suggested that two conditions must exist in preparing ketones from amides and a Grignard reagent.\textsuperscript{30,31} There should be three to four equivalents of halide for each equivalent of amide and extensive heating of reactants should be maintained. The following mechanism outlined in figure XIII has been proposed:\textsuperscript{32}

\[
\begin{align*}
&\text{RC-NH}_2 + 2\text{R'}\text{MgX} \rightarrow \text{RC-R'} + \text{NHMgX} \\
&\text{RC-R'} + \text{NH}_2 \rightarrow \text{RC-R'} + \text{MgX}_2 + \text{H}_2\text{O}
\end{align*}
\]
After 44 hrs of refluxing, the mixture was hydrolyzed and afforded a 16% yield of product. Because of the low yield from this reaction, this procedure was abandoned.

**Synthesis of 1,3-Diaryl-2-Propanols**

The unsymmetrically substituted 1,3-diphenyl-2-propanones were reduced with sodium borohydride to the corresponding alcohols. A ketone was refluxed for thirty minutes in ethanol with a slight excess of sodium borohydride, and then water was added to destroy the excess hydride. Magnesium sulfate (anhydrous) was added and the resulting slurry was filtered through Celite to remove the borate salts. Celite is employed to trap "fines" of borate salts as they may pass through the filter paper. The filtrate was concentrated to give the crude, intermediate alcohol which was used without further purification. Overall yields were approximately 90% in all reductions.

**Synthesis of 1,3-Diaryl-2-Propyl Methanesulfonates**

The alcohols were converted to methanesulfonates through the procedure described by Bly. All the esters were white crystalline solids with the exception of
l-phenyl-3-(o-chlorophenyl)-2-propyl methanesulfonate which could not be induced to crystallize. These esterifications usually produced a yield in the range of 25 to 85%.

**Synthesis of Chromium Tricarbonyl Complexes of l,3-Diaryl-2-Propyl Methanesulfonates**

The \( \pi \)-arene methanesulfonate chromium tricarbonyl complexes were prepared by refluxing the methanesulfonate in freshly distilled \( n \)-butyl ether with a slight excess of chromium hexacarbonyl. The reaction is carried out in a Strohmeier apparatus in a darkened hood. The design of this piece of apparatus makes possible the return of sublimed chromium hexacarbonyl to the reaction solution. Isooctane is added to allow for refluxing when the solution is heated to 145-155°. Relatively dilute solutions were used as recommended in the literature. Various reaction times of 6, 12, 15, 24, and 54 hours were examined to establish the optimum reaction time. Analysis of the reaction mixture by thin layer chromatography indicated that by refluxing for 24 hours optimum yields could be obtained. It appeared from the chromatography results that after 54 hours the amount of by-products increases significantly.
The procedure of Bly$^{12}$ was modified for the purification of the $\pi$-complexed methanesulfonate. After filtering the hot reaction mixture through activated charcoal, the filtrate was cooled to permit precipitation of the product. Generally 400-800 mgs of crude greenish-yellow product could be isolated by filtration. The filtrate was concentrated to 10-15 ml and cooled. If no additional precipitate appeared, the solution was concentrated further and pentane was added, and the resulting solution cooled. If a precipitate was obtained, it usually contained a high concentration of the bis complexed olefins. The crude reaction product, as well as the concentrated filtrates, were analyzed by thin layer chromatography. The analyses were quite similar for all reactions investigated. The chromatograms invariably displayed five spots which have been assigned on the basis of various spectral techniques, elemental analyses and similarities between various chromatograms. A typical chromatogram is exhibited in figure XIV with the letters referring to the assigned structures.
Although fractional crystallization employing a variety of solvents proved to be unsuccessful in separating the complex reaction mixture, column chromatography gave highly successful results. The crude $\pi$-complex methanesulfonates were eluted from columns of Florisil, silica gel, and neutral alumina. Optimum separations were achieved on a neutral alumina column. The substrate was applied to the column by first concentrating a chloroform solution of complex with neutral alumina. This powdery mixture was then placed at the head of the column. The separation could be conveniently followed by observation of the series of yellow bands that resulted, as well as by thin layer chromatography. The elution of material from the column was initiated with benzene-chloroform (9:1). The first two bands were eluted rapidly and they represented the aforementioned olefinic complexes. Further elution afforded pure mono-$\pi$-complexed methanesulfonates which were recrystallized from chloroform-pentane to give pale yellow crystals. After isolation the crystals were transferred to a stoppered vial wrapped in aluminum foil and placed in the dark. Finally, elution with acetone gave in small amounts a fourth compound which corresponded in the 1,3-diphenyl-2-propyl methane-
sulfonate reaction to the bis-complexed methanesulfonate.

An investigation was made to determine the stability of the uncomplexed methanesulfonate to the complexation conditions. The same reaction method was employed, but the chromium hexacarboxyl was omitted. When the methanesulfonate was refluxed with n-butyl ether and isoctane in a flask fitted with condenser, extensive decomposition occurred after twenty-four hours. Several new compounds were shown to be present by thin layer chromatography. However, when the methanesulfonate was refluxed in a freshly cleaned Strohmeier apparatus, a nearly quantitative yield of slightly discolored methanesulfonate was recovered. When the Strohmeier apparatus was not cleaned before use, no decomposition of the methanesulfonate could be detected. It is postulated that during the course of the normal complexation reaction the mono-π-complexed methanesulfonate underwent a pyrolytic elimination to give mono-π-complexed olefin. In the case of the unsymmetrically substituted methanesulfonate, the olefin formed in abundance would probably be the one conjugated with the non-halogenated ring. This suggestion is in agreement with the work of
De Puy and Leary\textsuperscript{33} in which pyrolytic elimination proceeded in accord with the Saytzeff rule to form the more stable olefin. The \textit{bis}-complex could arise from either a di-complexation of the methanesulfonate followed by elimination, or \textit{mono}-complexation followed by elimination and then a secondary complexation. See figure XV.

An interesting observation was made with respect to the melting points of the $\pi$-complexed methanesulfonates. During the melting point analysis, some $\pi$-complexes appeared to soften over a several degree range, but true melting did not occur even when the compounds were heated to the limit of the apparatus. The o-Cl and m-Cl $\pi$-complexes do have a defined melting point. It seems probable from limited pyrolysis studies that the residue is chromium oxide.

Infrared and nuclear magnetic resonance spectroscopy were used throughout the research study as a primary means of identification. The infrared spectral data easily confirmed the reduction of the ketones to alcohols by the appearance of the hydroxyl absorption at 3500-3300 cm$^{-1}$ and the disappearance of the carbonyl absorption at 1710 cm$^{-1}$. 
\[
\begin{align*}
\text{H} \quad \text{O-CH}_2 \quad \text{~-.CH}_2 \quad \text{o~} \\
\end{align*}
\]
Formation of the methanesulfonate from the alcohols is substantiated by the appearance of absorption bonds at approximately 1350 and 1175 cm\(^{-1}\), assigned to SO\(_2\) stretching vibrations.\(^{34}\) Intense metallic carbonyl absorption frequencies at 1990, 1870, and 1860 cm\(^{-1}\) and metal-carbon stretching frequencies at 690, 670, and 530 cm\(^{-1}\) aid in the determination of \(\pi\)-complex formation. (See Appendix B, figure XVII). The three characteristic changes noted by Humphrey\(^{35}\) are observed in the infrared spectra of the \(\pi\)-complexes when they are compared to the corresponding uncomplexed methanesulfonate. These pronounced changes are as follows: a decrease in C-H stretching vibrations intensities, a shift of the C-C stretching frequencies to lower frequencies, and a disappearance of the C-H out-of-plane bending bands.

The proton magnetic resonance spectrum unequivocally established the substitution pattern for the mono-complexed methanesulfonates. In a typical spectrum (see Appendix B, figure XIX) such as that of \(p\)-Br \(\pi\)-complex, the halogen substituted ring protons gave a normal AB pattern centered at 7.35 \(\delta\) which integrated for four protons. The five
unsubstituted phenyl ring protons experience a dramatic diamagnetic shift to 5.28 ppm. This shift to higher field strength is attributed to the perturbation of the aromatic ring current by π-bond formation to the metal. The pmr spectra for all the mono-complexed methanesulfonates prepared clearly show that the chromium tricarbonyl moiety is attached to the unsubstituted phenyl ring. Based on the decrease in anisotropy of the unsaturated phenyl ring protons should also experience diamagnetic shifts. In all of the π-complexed methanesulfonates, this effect is observed. Also noteworthy is the observation that the benzyl protons undergo an increase in spin multiplicity. This effect could be attributed to either unequal conformer population or the intrinsic nonequivalence of the benzyl protons which would give an ABX spin System. The chemical shift differences of two types of benzyl protons could be associated with the two conformations the chromium tricarbonyl group can assume with the aromatic nucleus due to either electronic or steric effects.
EXPERIMENTAL

Specific procedures used for the preparation of compounds representative of a series of compounds are cited below. Example preparations are followed by tables containing a complete listing of all compounds that were synthesized in a particular series. All melting points were obtained on a Thomas-Hoover melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 621 spectrophotometer. Pmr spectra were determined on a Varian A-60 instrument. The chemical shifts are relative to TMS ($\delta$0.00). The mass spectra were obtained on a Hitachi-Perkin-Elmer RMU-6H mass spectrometer. The ionization voltage was 70 eV. Elemental analyzes were performed on a Perkin-Elmer 240 Elemental Analyzer. All chemicals used as starting materials were obtained from
Aldrich Chemical Company and were employed without further purification.

Preparation of o-Chlorobenzyl Methyl Ether. - This procedure was adapted from that described by Knowles and Norman.\textsuperscript{37}

To a warm stirred solution of sodium methoxide, prepared from 2.3 g (0.1 mol) of sodium and 750 ml of anhydrous methanol was added 16.1 g (0.1 mol) of o-chlorobenzyl chloride dissolved in 50 ml of anhydrous methanol. After refluxing overnight, the cooled solution was diluted with water, extracted with ether, the ethereal extract dried over sodium sulfate (anhydrous) and concentrated. The residual oil was distilled to give 10.0 g (70\%) of product, bp 89-93° (15 mm).\textsuperscript{28}

Attempted Preparation of 1-Phenyl-3-(o-chlorophenyl)-2-propanone. This procedure was adapted from that described by Gilman.\textsuperscript{40}

To a stirred mixture of 10.4 g (1.5 mol) of finely cut lithium wire in 60 ml of anhydrous tetrahydrofuran was
added dropwise (20 ml/min) 10 g (0.70 mol) of \( \alpha \)-chlorobenzyl methyl ether dissolved in 30 ml of anhydrous ethyl ether while maintaining a temperature of -5 to -10°. After the addition was complete, the reaction mixture was stirred for 1 hour at -10°. A positive Gilman test\(^4^1,4^2\) for the resulting benzyllithium was obtained. The reaction product was then filtered through glass wool into a dropping funnel equipped with an outer jacket containing a coolant to maintain a temperature of -10°. The benzyllithium was added dropwise (20 ml/min) to 13.5 g (0.1 mol) of phenylacetic acid dissolved in 50 ml of anhydrous ethyl ether. The solution immediately solidified and stirring ceased. After the addition was complete, the reaction was allowed to continue for 30 min. The product mixture was hydrolyzed, extracted, washed with base, and dried over sodium sulfate (anhydrous). Concentration of the extract afforded white crystals, mp 58-60°. These crystals were identified as \( \alpha \)-chlorobibenzyl, lit. mp 65°.\(^4^3\)

Preparation of Ethyl \( m \)-Chlorophenylacetate. - This procedure was adapted from that described by Coan and Becker.\(^4^4\)
A solution of 10.0 g (0.06 mol) of m-chlorophenylacetic acid dissolved in 50 ml of ethanol and 13 ml of concentrated sulfuric acid was refluxed for 4 hours. After standing overnight, the reaction mixture was poured into 300 ml of ice water, and extracted with ether. The ether layer was washed with one 100 ml portion of water, two 100 ml portions of 10% sodium bicarbonate and one 100 ml portion of water and dried over sodium sulfate (anhydrous). The extract was concentrated and the residual oil was distilled to give 10.5 g (89%) of product, bp 140-2° (15 mm), lit. bp 130° (12 mm).45

Preparation of 2-p-Nitrophenylacetamide. - This procedure was adapted from that described by Wenner.46

To 280 ml of concentrated hydrochloric acid was added 16.2 g (0.1 mol) of p-nitrophenylacetonitrile. This mixture was heated to 40-45° and allowed to stir vigorously for 1.5 hr. After the reaction mixture was cooled to 15°, 80 ml of cold water was added. The solid product was cooled in ice water for 30 min, filtered and washed with cold water. The crude solid was recrystallized from 95% ethanol to yield 12.4 g (70%) of product, mp 194-197°, lit. mp 196.5-7°.47
Preparation of 2-([p-Fluorophenyl])-2-phenylacetoacetonitrile -

This procedure was adapted from that described by Coan and Becker.44,48

Into a 250 ml three-neck flask was added 4.6 g (0.2 mol) of sodium in 75 ml of absolute ethanol. To this well-stirred and refluxing sodium ethoxide solution was added dropwise over a period of 30 min, a mixture of 13.5 g (0.1 mol) of 4-fluorophenylacetonitrile and 19.7 g (0.12 mol) ethyl phenylacetate. After the reaction mixture had refluxed for 3 hr, the solution was cooled and poured into 300 ml of ice water. The resulting mixture was extracted with ether and the organic layer discarded. The aqueous alkaline portion was acidified with cold 10% hydrochloric acid and extracted with two 100 ml portions of ether. The combined ether extracts were washed with 100 ml of water, followed by two 100 ml portions of 10% sodium bicarbonate and one 100 ml portion of water and then dried over sodium sulfate (anhydrous). Concentration of the dried solution gave 18.7 g (77%) of crude product. The impure compound was recrystallized from aqueous methanol, mp 111.0-112.5°, lit. mp 111.8-112.0°.44
Attempted Preparation of 1-Phenyl 3-(p-nitrophenyl)-2-propanone.

To a solution of 15 g (0.07 mol) of 1,3-diphenyl-2-propanone in 50 ml of acetic anhydride was slowly added at 0° a solution of 7.0 g of 90% fuming nitric acid in 15 ml of acetic anhydride. The reaction was allowed to stir at 0° for 4 hr and then overnight at room temperature. The mixture was poured into ice, extracted with ether, washed with 10% sodium bicarbonate, dried over sodium sulfate (anhydrous) and concentrated. On the basis of the pmr spectrum, the residue contained only small amounts of nitrated material. The nitration procedure was repeated using acetic acid as the solvent and fuming nitric acid mixed with a catalytic amount of concentrated sulfuric acid. Subsequent work-up afforded a mixture of nitrated products that was considered unsuitable for separation.

Preparation of p-Nitrophenylacetyl Chloride

To a 100 ml round-bottom flask equipped with a condenser was added a mixture of 15 g (0.08 mol) of p-nitrophenylacetic acid and 15.4 ml (0.22 mol) of thionyl chloride.
was removed by distillation, followed by repeated distillation of benzene from the reaction mixture. The resulting residue was placed in the freezer, where it immediately crystallized. The crude product was isolated and washed with cold petroleum ether until colorless. The yield was 4.7 g (99%), mp 44-46°, lit. mp 47-49°.

Attempted Preparation of 1-Phenyl-(p-nitrophenyl)-2-propanone. This procedure was adapted from that described by Elderfield and Burgess.

To a freshly prepared and stirred ether solution of benzyl magnesium chloride was added portions over a 15 min period, 20.5 g (0.12 mol) of anhydrous cadmium chloride. The Grignard reagent was prepared from 3.42 g (0.14 mol) of magnesium, 18.04 g (0.14 mol) of benzyl chloride and 200 ml of ether. After the Grignard reagent was diluted to approximately 0.2 mol per 300 ml, it was transferred to the reaction flask through glass wool.

During the addition of the cadmium chloride to the transferred Grignard reagent, the temperature was maintained at 0° during the course of the reaction. After it
had stirred for 2 hr, the solution gave a negative Gilman test\textsuperscript{41,42} and was almost colorless.

To this organocadmium reagent was added over a 5 min period 11.0 g (0.55 mol) of \(p\)-nitrophenylacetyl chloride in 30 ml of absolute ether. The solution immediately solidified although vigorous stirring broke up the solid. After the reaction mixture had stirred for 6 hr at near \(0^\circ\), it was poured into 300 ml of ice, and 20 ml of 20\% sulfuric acid was added. Two immiscible layers were formed with an insoluble substance at the interface. Subsequent work-up of the ether layer provided a gummy oil. The interfacial solid was isolated by filtration. On the basis of the spectral data, none of the anticipated product was present.

\underline{Preparation of 1-Phenyl-3-(\(p\)-chlorophenyl)-2-propanone. (Method I)} - This procedure was adapted from that described by Jenkins.\textsuperscript{30,31}

In a dry and nitrogen purged 500 ml flask equipped with stirrer, condenser, and dropping funnel were placed 9.7 g (0.4 mol) of magnesium and a small volume of anhydrous ether. To the dropping funnel was added a solution of
70.8 g (0.44 mol) of α, o-dichlorotoluene in 10 ml of anhydrous ether. When a small portion of the chloride solution was allowed to enter the flask, it reacted immediately causing the ether to reflux and become cloudy. The α, o-dichlorotoluene was then diluted with 200 ml of anhydrous ether and added dropwise at a rate corresponding to the rate of ether reflux. After the addition was complete, the reaction was allowed to reflux for an additional 15 min. To this Grignard reagent was added in portions 3.5 g (0.1 mol) of phenylacetonitrile, the rate of addition determined by the vigour of the reaction. After the mixture had refluxed 44 hr, it was cooled and poured into 400 ml of 10% sulfuric acid, extracted with ether, washed with 10% sodium carbonate solution, and concentrated. The resulting oil was distilled depending on the purity to give 4 g (16%) of product, bp 140-145° (0.5 mm), mp 37-39°, lit. bp 184-188° (3-4 mm)50 lit. mp 38-39.5°.50

Preparation of 1-Phenyl-3-(p-bromophenyl)-2-propanone.

(Method II)

A mixture of 19.8 g (0.063 mol) of crude 2-p-bromophenyl)-4-phenyl-acetoacetonitrile in 60 ml of 60%
### TABLE I

**SUBSTITUTED DIPHENYLACETOACETONITRILES**

<table>
<thead>
<tr>
<th>Acetoacetonitriles</th>
<th>Formula</th>
<th>% Yield</th>
<th>Calcd., %</th>
<th>Found, %</th>
<th>Mp, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-(p-Bromophenyl)-4-phenyl</td>
<td>C₁₈H₁₂BrNO</td>
<td>95</td>
<td>61.17</td>
<td>3.85</td>
<td>4.46</td>
</tr>
<tr>
<td>2-(m-Chlorophenyl)-4-phenyl</td>
<td>C₁₈H₁₂ClNO</td>
<td>60</td>
<td>71.25</td>
<td>4.48</td>
<td>5.19</td>
</tr>
<tr>
<td>2-(p-Chlorophenyl)-4-phenyl</td>
<td>C₁₈H₁₂ClNO</td>
<td>77</td>
<td>71.25</td>
<td>4.48</td>
<td>5.19</td>
</tr>
<tr>
<td>2-(p-Fluorophenyl)-4-phenyl</td>
<td>C₁₈H₁₂FNO</td>
<td>80</td>
<td>75.87</td>
<td>4.77</td>
<td>5.53</td>
</tr>
<tr>
<td>2-(Phenyl)-4-(m-chlorophenyl)d</td>
<td>C₁₈H₁₂ClNO</td>
<td>62</td>
<td>71.25</td>
<td>4.48</td>
<td>5.19</td>
</tr>
</tbody>
</table>

* a Lit. mp 131.0-131.2° 44
* b Lit. mp 127.0° 52
* c Lit. mp 111.8-112.0° 44
* d Not isolated
sulfuric acid was stirred and refluxed until evolution of carbon dioxide ceased (approximately 30 to 40 min). The solution was cooled, poured into 150 ml of ice water, and extracted with ether. The ether layer was washed with 10% sodium carbonate and then with water, dried over sodium sulfate (anhdyrous) and concentrated. The residue constituted 8.3 g (46%) of crude product. The oil was recrystallized from cold petroleum ether - chloroform, mp 52-54°, lit. mp 53.8-54.2°. 44

Preparation of 1-Phenyl-3-(o-chlorophenyl)-2-propanol.

To a stirred solution of 4.0 g (0.017 mol) of 1-phenyl-3-(o-chlorophenyl)-2-propanone in 50 ml of absolute ethanol was added in portions 1.3 g (0.034 mol) of sodium borohydride with the rate of addition determined by the vigour of the reaction. The solution then was refluxed for 30 min. After the reaction mixture was cooled, water was added until the precipitation of borate salts occurred. Magnesium sulfate was added, and the mixture was filtered through Celite. The organic layer was concentrated to give 3.8 g (90%) of an oil.
<table>
<thead>
<tr>
<th>2-Propanones</th>
<th>Formula</th>
<th>% Yield</th>
<th>Calcd., %</th>
<th>Found, %</th>
<th>Mp, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Phenyl-3-(p-bromophenyl)-</td>
<td>C₁₅H₁₃BrO</td>
<td>46</td>
<td>62.30</td>
<td>62.26</td>
<td>52-54a</td>
</tr>
<tr>
<td>1-Phenyl-3-(o-chlorophenyl)-</td>
<td>C₁₅H₁₃ClO</td>
<td>16</td>
<td>73.62</td>
<td>73.41</td>
<td>37-39b</td>
</tr>
<tr>
<td>1-Phenyl-3-(m-chlorophenyl)-</td>
<td>C₁₅H₁₃ClO</td>
<td>62</td>
<td>73.62</td>
<td>72.03</td>
<td>011c</td>
</tr>
<tr>
<td>1-Phenyl-3-(p-chlorophenyl)-</td>
<td>C₁₅H₁₃ClO</td>
<td>88</td>
<td>73.62</td>
<td>73.77</td>
<td>39-41d,e</td>
</tr>
<tr>
<td>1-Phenyl-3-(p-fluorophenyl)-</td>
<td>C₁₅H₁₃FO</td>
<td>67</td>
<td>78.93</td>
<td>78.22</td>
<td>011f</td>
</tr>
</tbody>
</table>

a Lit. mp 53.8-54.2°
b Lit. mp 39.0-39.7°
c See ref 24, p 1976
d Lit. mp 35.9-36.5°
e Lit. mp 40.5-41.0°
f Lit. mp 36.0-36.5°
<table>
<thead>
<tr>
<th>2-Propanols</th>
<th>Formula</th>
<th>% Yield</th>
<th>Calcd., %</th>
<th>Found, %</th>
<th>Appearance(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,3-Diphenyl-</td>
<td>C(<em>{15})H(</em>{15})O</td>
<td>96</td>
<td>84.87</td>
<td>84.50</td>
<td>011</td>
</tr>
<tr>
<td>1-Phenyl-3-((p)-bromophenyl))-</td>
<td>C(<em>{15})H(</em>{15})BrO</td>
<td>95</td>
<td>61.87</td>
<td>61.69</td>
<td>011</td>
</tr>
<tr>
<td>1-Phenyl-3-((o)-chlorophenyl))-</td>
<td>C(<em>{15})H(</em>{15})ClO</td>
<td>90</td>
<td>73.02</td>
<td>73.13</td>
<td>011</td>
</tr>
<tr>
<td>1-Phenyl-3-((m)-chlorophenyl))-</td>
<td>C(<em>{15})H(</em>{15})ClO</td>
<td>90</td>
<td>73.02</td>
<td>72.70</td>
<td>011</td>
</tr>
<tr>
<td>1-Phenyl-3-((p)-chlorophenyl))-</td>
<td>C(<em>{15})H(</em>{15})ClO</td>
<td>95</td>
<td>73.02</td>
<td>72.55</td>
<td>011</td>
</tr>
<tr>
<td>1-Phenyl-3-((p)-fluorophenyl))-</td>
<td>C(<em>{15})H(</em>{15})FO</td>
<td>87</td>
<td>78.24</td>
<td>78.26</td>
<td>011</td>
</tr>
</tbody>
</table>

\(^a\) All analytical samples were either chromatographed or purified by molecular distillation.
Preparation of 1,3-Diphenyl-2-propyl Methanesulfonate

Into a 100 ml flask containing a solution of 5.0 g (0.024 mol) of 1,3-diphenyl-2-propanol in 30 ml of dry pyridine was added in portions 3.16 ml (0.048 mol) of methanesulfonyl chloride. The reaction mixture then was poured into a separatory funnel containing approximately 100 ml of ice water. Any material remaining in the flask was washed into the separatory funnel with two 20 ml portions of chloroform. An additional 50 ml of chloroform was added to the separatory funnel. The chloroform layer was isolated and washed twice with 50 ml of cold 10% hydrochloric acid, once with 100 ml of cold 10% hydrochloric acid, twice with cold 10% sodium bicarbonate, and once with 100 ml of cold water. The organic layer was dried over magnesium sulfate (anhydrous), filtered, and concentrated to yield 6 g (85%) of an off-white solid. The product was recrystallized from chloroform petroleum ether (30-80°), mp 77-79°.

Preparation of 1-[π-(Phenyl)chromium tricarbonyl]-3-(o-chlorophenyl)-2-propyl Methanesulfonate. - This procedure was adapted from that described by Bly.¹²,⁵¹
TABLE IV
SUBSTITUTED 1,3-DIPHENYL-2-PROPYL METHANESULFONATES

<table>
<thead>
<tr>
<th>2-Propyl Methanesulfonates</th>
<th>Formula</th>
<th>% Yield</th>
<th>Calcd., %</th>
<th>Found, %</th>
<th>Mp, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,3-Diphenyl-</td>
<td>C_{18}H_{18}SO_3</td>
<td>85</td>
<td>66.18</td>
<td>6.25</td>
<td>66.17</td>
</tr>
<tr>
<td>1-Phenyl-3-(p-bromophenyl)-</td>
<td>C_{18}H_{17}BrSO_3</td>
<td>52</td>
<td>52.04</td>
<td>4.64</td>
<td>52.06</td>
</tr>
<tr>
<td>1-Phenyl-3-(o-chlorophenyl)-</td>
<td>C_{18}H_{17}ClSO_3</td>
<td>43.4</td>
<td>59.16</td>
<td>5.28</td>
<td>59.63</td>
</tr>
<tr>
<td>1-Phenyl-3-(m-chlorophenyl)-</td>
<td>C_{18}H_{17}ClSO_3</td>
<td>38.4</td>
<td>59.16</td>
<td>5.28</td>
<td>59.14</td>
</tr>
<tr>
<td>1-Phenyl-3-(p-chlorophenyl)-</td>
<td>C_{18}H_{17}ClSO_3</td>
<td>25.6</td>
<td>59.16</td>
<td>5.28</td>
<td>59.23</td>
</tr>
<tr>
<td>1-Phenyl-3-(p-fluorophenyl)-</td>
<td>C_{18}H_{17}FSO_3</td>
<td>56.1</td>
<td>62.32</td>
<td>5.56</td>
<td>62.23</td>
</tr>
</tbody>
</table>
To 100 ml of n-butyl ether (freshly distilled from sodium) and 20 ml of distilled isoctane was added 1.0 g (0.0038 mol) of 1-phenyl-3-(o-chlorophenyl)-2-propyl methanesulfonate and 0.75 g (0.00345 mol) of chromium hexacarbonyl. Using a Strohmeier apparatus the reaction mixture was refluxed in the dark for a period of 24 hr. The solution was filtered while hot through activated charcoal into two 100 ml flasks and the flasks cooled in an ice water bath. After 30 min to 1 hr, the material that had precipitated was collected to give 436 mg of fine crystals. The reaction product was analyzed by thin layer chromatograph (Silica gel; benzene-chloroform, 9:1) and was shown to be predominantly one component. A second crop of crystals, 150 mg, was obtained when the filtrate was cooled in the freezer overnight. The filtrate was concentrated to 10-15 ml and cooled for 1 hr. If no additional precipitate appeared, 25 ml of pentane was added and the solution was cooled. Any solid that appeared was collected, and the solution was concentrated and cooled. Providing no additional crystallization occurred, the small amount of residue was analyzed and discarded.
The combined crude product (586 mg, 42%) was dissolved in chloroform and mixed with a small amount of neutral alumina (80-200 mesh). The solvent was removed and the residue was placed on a prepared alumina column (30-40 x 1.5 mm i. d.). Two fast moving bands were eluted with 9:1 benzene-chloroform. Based on infrared analyses, these compounds were tentatively identified as 1-[(\pi-phenyl)chromium tricarbonyl]-3-[(\pi-o-chlorophenyl)chromium tricarbonyl]-2-propene and 1-[(\pi-(phenyl)chromium tricarbonyl]-3-[(\pi-(o-chlorophenyl)chromium tricarbonyl]-1-propene. Both of these components were present in small amounts.

Further elution gave a third compound which was identified by elemental and spectral analyses as 1-[(\pi-phenyl)chromium tricarbonyl]-3-(o-chlorophenyl)-2-propyl methanesulfonate. Finally, elution with acetone gave 1-[(\pi-(phenyl)chromium tricarbonyl]-3-[(o-(o-chlorophenyl)chromium tricarbonyl)-2-propyl methanesulfonate. This fourth component constituted only a small percentage of the reaction mixture. The desired mono-\pi-complex was redissolved in chloroform, filtered through activated charcoal and reprecipitated with
<table>
<thead>
<tr>
<th>π-Complexed-2-propyl Methanesulfonates</th>
<th>Formula</th>
<th>% Yield</th>
<th>Calcd., %</th>
<th>Found, %</th>
<th>Mp, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-[[π-(Phenyl)chromium tricarbonyl]-3-(phenyl)]</td>
<td>C_{19}H_{18}SO_{6}Cr</td>
<td>18.2</td>
<td>53.52</td>
<td>4.26</td>
<td>53.52</td>
</tr>
<tr>
<td>1-[[π-(Phenyl)chromium tricarbonyl]-3-(p-bromophenyl)]</td>
<td>C_{18}H_{17}BrSO_{6}Cr</td>
<td>17.5</td>
<td>45.16</td>
<td>3.39</td>
<td>45.42</td>
</tr>
<tr>
<td>1-[[π-(Phenyl)chromium tricarbonyl]-3-(o-chlorophenyl)]</td>
<td>C_{19}H_{17}ClSO_{6}Cr</td>
<td>23.3</td>
<td>49.52</td>
<td>3.72</td>
<td>49.39</td>
</tr>
<tr>
<td>1-[[π-(Phenyl)chromium tricarbonyl]-3-(m-chlorophenyl)]</td>
<td>C_{19}H_{17}ClSO_{6}Cr</td>
<td>24</td>
<td>49.52</td>
<td>3.72</td>
<td>49.39</td>
</tr>
<tr>
<td>1-[[π-(Phenyl)chromium tricarbonyl]-3-(p-chlorophenyl)]</td>
<td>C_{19}H_{17}ClSO_{6}Cr</td>
<td>14.5</td>
<td>49.52</td>
<td>3.72</td>
<td>49.50</td>
</tr>
<tr>
<td>1-[[π-(Phenyl)chromium tricarbonyl]-3-(p-fluorophenyl)]</td>
<td>C_{18}H_{17}FSO_{6}Cr</td>
<td>13.7</td>
<td>51.35</td>
<td>3.86</td>
<td>50.97</td>
</tr>
<tr>
<td>1,3-[[π-(Phenyl)chromium tricarbonyl]-propene]</td>
<td>C_{22}H_{18}SO_{6}Cr_{2}</td>
<td>7.6</td>
<td>46.98</td>
<td>3.23</td>
<td>46.82</td>
</tr>
<tr>
<td>1,3-[[π-(Phenyl)chromium tricarbonyl]-propene]</td>
<td>C_{21}H_{14}O_{6}Cr_{2}</td>
<td>1.3</td>
<td>54.09</td>
<td>3.23</td>
<td>53.90</td>
</tr>
</tbody>
</table>

The melting point corresponds to the temperature at which crystals begin to liquify. The compound does not completely melt, but leaves a green residue, probably CrO₃.
pentane. The yellow crystals were collected to give 328 mg (23.3%), mp 128-132°.

**Preparation of 1,3-[π-(phenyl)chromium tricarbonyl]-2-propyl methanesulfonate and 1,3-[π-(phenyl)chromium tricarbonyl]-propene.**

Using the previously described procedure 1.0 g (0.00345 mol) of 1,3-diphenyl-2-propyl methanesulfonate and 2.25 g (0.01035 mol) of chromium hexacarbonyl were allowed to react for 24 hr. While the reaction solution was being filtered through activated charcoal, crystallization of some material occurred in the funnel. Recrystallization of this solid from chloroform gave 147 mg (7.6%) of 1,3-[π-(phenyl)chromium tricarbonyl]-2-propyl methanesulfonate that was identified by elemental and spectral analysis, mp 177-179°.

The filtrate was cooled and additional solid, corresponding to 1-[π-(phenyl)chromium tricarbonyl]-3-(phenyl)-2-propyl methanesulfonate, was recovered. When the filtrate was concentrated and pentane added to ensure complete recrystallization, a dark yellow solid precipitated.
These crystals were collected to give according to elemental and spectral analysis 21 mg (1.3%) of 1,3-[[\pi- (phenyl)chromium tricarbonyl]]-propene, mp 121-124°.
APPENDIX A
ir (KBr) 3030(w) [CH phenyl]; 2960(w), 2940(w) [CH aliphatic]; 1605(w), 1590(w), 1490(m), 1458(w), 1446(w), 1410(m), 1370(s), 1272(w), 1220(w); 1345(vs) and 1172(vs) [OSO₂]; 1310(w), 1285(w), 1270(m), 1015(m); 972(m) and 905(vs) [CO]; 880(m), 848(m), 810(w), 800(m), 780(m), 750(m), [di-substituted phenyl]; 730(w), 719(w); 701(s) [mono-substituted phenyl]; 650(m), 550(m), 540(m), 530(m), 500(s), 480(m), 440(w) cm⁻¹. nmr (DCCl₃) δ 7.33, AB multiplet (4 BrC₆H₄); 7.32, singlet (5 C₆H₅); 4.95, pentet (1 CH methine); 2.97, doublet of doublets (4 CH₂C₆H₅); 2.30 singlet (3 OSO₂CH₃). m/e 368⁺.

ir (KBr) 3090(w), 3070(m), 3040(m), 3020(w) [CH phenyl]; 2960(w), 2440(m) [CH aliphatic]; 1950(w), 1880(w), 1820(w); 1730(w) [mono-substituted phenyl]; 1605(m), 1590(w), 1498(m), 1455(s), 1445(w), 1430(w), 1415(w), 1369(m), 1270(w), 1220(w); 1249(vs) and 1172(vs) [OSO₂]; 1092(w) 1080(m), 1050(w), 1030 (w), 995(m); 972(s) and 898(vs)[CO]; 880(s), 825(w), 800(m), 790(m), 755(s); 701(vs) [mono-substituted phenyl]; 650(s), 550(s), 530(s), 505(s), 490(s), 470(m), 420(w) cm⁻¹. nmr (DCCl₃) δ 7.33, singlet (10 C₆H₅); 4.95, pentet (1 CH methine); 3.01, doublet (4 CH₂C₆H₅); 2.20, singlet (OSO₂CH₃). m/e 290⁺.


\[ \text{Ir (Neat) } 3095(w), 3065(w), 3030(m) \ [\text{CH phenyl}]; 2940(m), 2860(w) \ [\text{CH aliphatic}]; 1601(w), 1570(w), 1495(m), 1475(m), 1455(m), 1410(w), 1351(vs) \text{ and } 1175(s) \ [\text{OSO}_2]; 1080(w), 1051(m), 1040(w), 1030(w), 1020(w); 970(m), 960(m), and 910(vs) \ [\text{CO}] ; 875(w), 790(m); 750(s) \ [\text{di-substituted phenyl}]; 700(s) \ [\text{mono-substituted phenyl}]; 680(w) \ \text{cm}^{-1}. \ \text{nmr (DCCl}_3) \ 6 7.32, \text{ broad singlet (9 Cl}_{\text{C}_6\text{H}_4}, {\text{C}_6\text{H}_5}); 5.10, \text{ pentet, (1 CH methine)}; 3.10, \text{ multiplet (4 CH}_2{\text{C}_6\text{H}_5}); 2.22 \text{ singlet (3 \text{OSO}_2{\text{CH}_3}). m/e 324}^+.

\[ \text{Ir (KBr) } 3100(w), 3070(w), 3040(w), 3010(w) \ [\text{CH phenyl}]; 2960(w), 2940(w) \ [\text{CH aliphatic}]; 1603(m), 1575(m), 1500(m), 1480(m), 1460(m), 1430(m), 1460(w), 1370(s), 1338(s), 1272(w), 1210(w); 1351(vs) \text{ and } 1175(vs) \ [\text{OSO}_2]; 1110(w), 1090(m), 1080(m), 1058(w), 1030(w), 998(m); 970(m) \text{ and } 900(vs) \ [\text{CO}]; 830(w), 796(m), 785(s); 750(s) \ [\text{di-substituted phenyl}]; 703(s) \ [\text{mono-substituted phenyl}]; 690(m), 649(w), 550(m), 532(s), 500(m), 480(w), 445(m), 420(w) \ \text{cm}^{-1}. \ \text{nmr (DCCl}_3) \ 6
7.31, multiplet (9 ClC₆H₄,C₆H₅); 4.95 pentet (1 CH methine);
2.99, doublet (4 CH₂C₆H₅); 2.30, singlet (3 O₅₀₂CH₃). m/e 324⁺.

\[
\begin{align*}
\text{Cl-} & \quad \text{CH}_2-\text{C-CH}_2-\text{OMs} \\
\text{OS}_2 & \\
15
\end{align*}
\]

ir (KBr) 3100(w), 3080(w), 3045(m), 3035(m) [CH phenyl];
2960(w), 2950(m) [CH aliphatic]; 1601(w), 1498(s), 1460(m),
1450(w), 1440(w), 1415(m), 1372(s), 1275(w), 1220(w); 1350(vs)
and 1178(vs) [OSO₂]; 1112(m), 1095(s), 1058(w), 1032(w), 1022
(m), 1005(w); 980(s) and 910(vs) [C=O]; 888(m), 850(m), 819(m),
805(s); 790(m), 750(s) [di-substituted phenyl]; 741(w), 725(w),
7705(s) [mono-substituted phenyl]; 680(w), 661(m), 619(w),
550(s), 535(m), 529(m), 505(s), 488(m), 441(m) cm⁻¹. nmr
(DCCl₃) & 7.31, broad singlet (9 ClC₆H₄C₆H₅); 4.95, pentet
(1 CH methine); 2.98, doublet of doublet (4 CH₂C₆H₅); 2.30,
singlet (3 O₅₀₂CH₃). m/e 324⁺.

\[
\begin{align*}
\text{F-} & \quad \text{CH}_2-\text{C-CH}_2-\text{OMs} \\
\text{OS}_2 & \\
16
\end{align*}
\]

ir (KBr) 3100(w), 3070(w), 3070(w), 3040(w), 3020(w) [CH phenyl];
2970(w), 2940(w) [CH aliphatic]; 1601(m), 1550(m), 1515(s),
1480(m), 1450(w), 1420(w), 1410(w), 1370(m), 1225(s); 1350(vs)
and 1175(vs) [OSO₂]; 1100(m), 1078(w), 1100(w), 975(s) and
903(vs) [C=O]; 850(w), 830(m), 820(w), 750(vs) [di-substituted
phenyl]; 700(s) [mono-substituted phenyl]; 640(m), 565(w),
550(m), 540(m), 530(m), 500(s) cm⁻¹. nmr (DCCl₃) & 7.32 sing-
glet (5 C₆H₅); 7.15, broad-multiplet (4 F-C₆H₄); 4.93, pentet
(1 CH methine); 2.98, doublet of doublets (4 CH$_2$C$_6$H$_5$); 2.28, singlet (3 OSO$_2$CH$_3$) . m/e 308$^+$. 

![Chemical Structure](image1)

ir (KBr) 3080(w), 3030(w) [CH aliphatic]; 2950(w) [CH aliphatic]; 1980(vs), 1990(vs), 1870(vs), 1860(vs) [C=O]; 1540 (w), 1500(w), 1460(m), 1440(w), 1425(w), 1410(m); 1335(s) and 1179(s) [OSO$_2$]; 1050(m), 990(w), 972(s) and 920(s) [CO]; 845(w), 820(w), 798(s), 755(m); 700(s) [mono-substituted-phenyl]; 690(w), 670(s), 635(s), 530(s) [CrC]; 495(m), 480(w) cm$^{-1}$. nmr(DCCl$_3$) $\delta$ 7.36, broad singlet (5 C$_6$H$_5$); 5.31, broad multiplet (5 Cr(CO)$_3$C$_6$H$_5$); 4.90, broad multiplet (1 CH methine); 3.03, doublet (2 CH$_2$C$_6$H$_5$); 2.72, multiplet (2 CH$_2$Cr(CO)$_3$C$_6$H$_5$); 2.42, singlet (3 OSO$_2$CH$_3$). m/e 424$^+$. 

![Chemical Structure](image2)

ir (KBr) 3090(w), 3030(w) [CH phenyl]; 2930(w) [CH aliphatic]; 1985(vs), 1990(vs), 1872(vs), 1862(vs) [C=O]; 1490(w), 1460(w), 1440(w), 1420(w), 1410(w), 1260(w); 1335(s) and 1172(s) [OSO$_2$]; 1100(w), 1070(w), 1050(w), 1015(w); 960(m) 910(s) [CO]; 850(w), 910(m), 790(w), 720(w); 670(s), 632(s), 530(s) [CrC] cm$^{-1}$. nmr DCCl$_3$ $\delta$ 7.33 AB, doublet (2 Br-C$_6$H$_4$); 7.17 AB, doublet (2 Br-C$_6$H$_4$); 5.28, broad multiplet (5 Cr(CO)$_3$C$_6$H$_5$); 5.00,
broad multiplet (1 CH methine); 3.01, doublet (2 CH₂ C₆H₅); 2.72, multiplet (2 CH₂Cr(CO)₃C₆H₅); 2.53, singlet (3 OSO₂CH₃). m/e 502⁺.

\[
\begin{align*}
\text{H} & \quad \text{Cl} \\
\text{OM₅} & \quad \text{Cr(CO)₃} \\
\end{align*}
\]

ir (KBr) 3100(w), 3020(w) [CH phenyl]; 2970(w), 2940(w) [CH aliphatic]; 1960(vs), 1880(vs), 1860(vs) [C=O]; 1570(w), 1470(w), 1460(w), 1450(w), 1425(w), 1410(w); 1352(s) and 1172(s) [OSO₂]; 1150(m), 1075(w), 1050(m), 1015(w), 990(w); 960(s) and 907(s) [CO]; 890(w), 865(w), 840(w), 800(m), 715(w), 705(w), 680(w); 670(s), 631(s), 525(s) [CrC]; 470(m), 450(w) cm⁻¹. nmr(DCCl₃) & 7.33 broad singlet (4 ClC₆H₄); 5.33, broad multiplet superimposed on phenyl protons (1 CH multiplet); 3.17, multiplet (2 CH₂C₆H₅); 2.80, multiplet (2 CH₂Cr(CO)₃C₆H₅); 2.45, singlet (3 OSO₂CH₃). m/e 458⁺.

\[
\begin{align*}
\text{H} & \quad \text{Cl} \\
\text{OM₅} & \quad \text{Cr(CO)₃} \\
\end{align*}
\]

ir (KBr) 3110(w), 3040(w), 3010(w) [CH phenyl]; 2970(w), 2940(w), [CH aliphatic]; 1970(vs), 1895(vs), 1850(vs) [C=O]; 1610(m), 1575(w), 1480(m), 1460(m), 1410(w); 1370(s) and 1172(s) [OSO₂]; 1345(s), 1760(w), 1080(w), 1040(w), 990(w), 975(m); 962(s)
and 915(s) [CO]; 890(s), 880(m), 868(w), 825(w), 795(s), 785(s), 720(m), 708(s), 685(m), 665(s), 635(s), 530(s); [CrC] cm$^{-1}$.

nmr(DCCl$_3$) & 7.28, broad singlet (4 ClC$_6$H$_4$),
5.26, broad multiplet with another multiplet superimposed
(6 Cr(CO)$_3$C$_6$H$_5$ and CH methine); 3.03 doublet (2 CH$_2$C$_6$H$_5$);
2.71 multiplet (2 CH$_2$Cr(CO)$_3$C$_6$H$_5$); 2.51, singlet (3 OSO$_2$CH$_3$).

m/e 458+.

\[
\text{Cl-} \begin{array}{c}
\text{OMs} \\
\text{H}
\end{array}
\begin{array}{c}
\text{C-CH$_2$-} \\
\text{H}
\end{array}
\begin{array}{c}
\text{Cr(CO)$_3$} \\
\text{F-} \begin{array}{c}
\text{OMs} \\
\text{H}
\end{array}
\begin{array}{c}
\text{C-CH$_2$-} \\
\text{H}
\end{array}
\begin{array}{c}
\text{Cr(CO)$_3$}
\end{array}
\]

21

ir (KBr) 3090(w), 3030(w) [CH phenyl]; 2950(w) [CH aliphatic];
1985(vs), 1890(vs), 1870(vs) [C=O]; 1495(s), 1462(m), 1445(w),
1425(w), 1410(w); 1337(s) and 1175(s) [OSO$_2$]; 1100(m), 1070(w),
1050(m), 1020(m); 970(m) and 912(s) [CO]; 850(w), 830(w),
815(m), 795(m), 722(w), 690(w); 668(s), 532(s), 532(s) [CrC];
500(m), 490(w), 460(w) cm$^{-1}$. nmr(DCCl$_3$) & 7.30, AB multiplet
(4 ClC$_6$H$_4$); 5.30, broad multiplet (5 Cr(CO)$_3$C$_6$H$_5$) with superimposed
multiplet at 5.00, 1 CH methine); 3.17, doublet (2 CH$_2$
C$_6$H$_5$); 2.70 multiplet (2 CH$_2$Cr(CO)$_3$C$_6$H$_5$); 2.51, singlet
(3 OSO$_2$CH$_3$). m/e 458+.

22

ir (KBr) 3080(w), 3030(w) [CH phenyl]; 2950(w) [CH aliphatic];
1980(vs), 1870(vs) [C=O]; 1600(w), 1515(s), 1460(m), 1440(w);
1420(w), 1140(m), 1130(m); 1337(s) and 1180(s) [OSO$_2$];
1100(w), 1050(w); 970(m) and 920(s) [CO]; 838(m), 820(w),
795(m), 760(w), 720(w), 668(s), 632(s), 532(s) [CrC];
510(w) cm$^{-1}$. nmr(DCCl$_3$) $\delta$ 7.20, broad multiplet (4 C$_6$H$_4$);
5.30, broad multiplet (5 Cr(CO)$_3$C$_6$H$_5$); 4.95, broad multiplet
(1 CH methine); 3.02 doublet (2 CH$_2$ F$_2$C$_6$H$_4$); 2.72, multiplet
(2 CH$_2$Cr(CO)$_3$C$_6$H$_5$); 2.51, singlet (OSO$_2$CH$_3$). m/e 442$^+$.  

\[
\begin{align*}
&\text{H} \\
&\text{Cr(CO)$_3$} - \text{CH$_2$} - \text{C-CH$_2$} - \text{OMs} \\
&\text{Cr(CO)$_3$}
\end{align*}
\]

ir (KBr) 3100(w) [CH phenyl]; 2930(w) [CH aliphatic]; 1965(vs),
1890(vs) [C=O]; 1460(m), 1420(m); 1365(s) and 1172, [OSO$_2$];
1350(s), 1070(w), 1020(w), 1000(w), 990(w); 970(m), 960(m),
920(s) [CO]; 840(w), 790(w), 730(w), 710(w), 690(w); 662(s),
630(s), 530(s) [CrC]; 490(w), 480(m) cm$^{-1}$. nmr(DCCl$_3$) $\delta$ 5.46,
broad multiplet (112 Cr(CO)$_3$C$_6$H$_5$ and CH methine); 2.80, singlet
(3 OSO$_2$CH$_3$) superimposed on a broad complex multiplet, 2.602.85,
(4 CH$_2$ Cr(CO)$_3$C$_6$H$_5$). m/e 558$^+$.  

\[
\begin{align*}
&\text{Cr(CO)$_3$} - \text{C=C-CH$_2$} - \text{Cr(CO)$_3$}
\end{align*}
\]

23

24
ir (KBr) 2920(w) [CH aliphatic]; 1980(vs) 1970(vs), 1885(vs) [C=O]; 1455(w), 1415(w), 1260(w), 1150(w); 990(w), 955(w) [trans C=C olefin]; 8.20(w); 660(s), 630(s), and 530(s) [CrC] cm$^{-1}$. m/e 462+. 
Infrared Spectrum of 1-Phenyl-3-(p-bromophenyl)-2-propyl Methanesulfonate (KBr)

Figure XVI
Infrared Spectrum of 1-[π-(Phenyl)chromium tricarbonyl]-3-(p-bromophenyl)-2-propyl Methanesulfonate (KBr)

Figure XVII
Proton Magnetic Resonance Spectrum of 1-Phenyl-3-(p-bromophenyl)-2-propyl Methanesulfonate in DCCl₃

Figure XVIII
Proton Magnetic Resonance Spectrum of 1-[\(\pi\)-(Phenyl)chromium tricarbonyl]-3-(\(p\)-bromophenyl)-2-propyl Methanesulfonate in DCCl\(_3\)

Figure XIX
Proton Magnetic Resonance Spectrum of 1,3-Diphenyl-2-propyl Methanesulfonate in DCCl₃

Figure XX
Proton Magnetic Resonance Spectrum of 1,3-[\pi-(Phenyl)chromium tricarbonyl]-2-propyl Methanesulfonate in DCCl₃

Figure XXI
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51. For the purpose of this thesis, we have used the nomenclature of Bly in naming the complexes.
The author was born in Gordonsville, Virginia on June 19, 1943 and attended the secondary schools of Orange County, Virginia. Upon graduation in June, 1961, he entered the University of Richmond, Virginia and achieved his B.S. degree in June, 1965. From then until the present, he has been employed at A. H. Robins, Co., Inc. as a chemist.