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REARRANGEMENTS IN CARBENOID DECOMPOSITION OF
2,2,2-TRIARYLDIAZOETHANES

DISSERTATION
Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By
Peter Barry Sargeant, B.S.

* * * * * *

The Ohio State University
1962

Approved by

[Signature]
Adviser
Department of Chemistry
Dedicated to my wife, Patricia Marie, whose patience, understanding, and sacrifices helped make this possible.
ACKNOWLEDGMENT

I would like to express my appreciation to Professor Harold Shechter for his inception of this study, for his guidance and suggestions throughout the investigation, for many stimulating discussions, and for his assistance in the preparation of this dissertation.

I would also like to thank Professors W. N. White and P. G. Gassman for helpful discussions and advice.

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INTRODUCTION AND HISTORICAL

Divalent carbon chemistry (1) has been a subject of

(1) Confusion and ambiguity exists regarding the nomenclature of gem-divalent radicals. The term "carbene" will be used in this study to denote the family of divalent carbon compounds in general. The first member of this homologous series will be named methylene (H₂C:); all other gem-divalent radicals will be named by adding "-idene" to the name of the corresponding univalent radical [International Union of Pure and Applied Chemistry Report on Nomenclature, J. Am. Chem. Soc., 82, 5545 (1960); R. S. Shank, Ph.D. Dissertation, The Ohio State University, 1961].

renewed interest in the past decade. New syntheses of divalent carbon intermediates have been devised and evidence of the presence of carbenes in numerous reactions has been found (2-5).

(2) For reviews of the chemistry of divalent carbon see: W. Kirmse, Angew. Chem., 73, 161 (1961); 71, 537 (1959);
(3) J. Leitich, Osterr. Chemiker-Ztg., No. 6, 164 (1960);
(4) R. Huisgen, Angew Chem., 67, 439 (1955); and

Any discussion of divalent carbon must include consideration of the multiplicity of these species. The two unshared electrons may be unpaired and formally considered to occupy two 2p orbitals resulting in a triplet, or they
may be paired and formally considered to occupy a \( sp^2 \)
orbital with a \( 2p \) orbital vacant resulting in a singlet molecule.

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H}
\end{align*}
\]

**Triplet**

**Singlet**

Skell and Woodworth (6) suggested that singlet

---

(6) P. S. Skell and R. C. Woodworth, J. Am. Chem. Soc., 78, 4496 (1956);

methylenne should react stereospecifically with olefins, whereas triplet methylene should not, and therefore assigned the singlet state to methylene produced from photolysis of diazomethane on the basis of its stereospecific addition to cis- and trans-2-butene. Extensions (8-12) of this idea

---

(8) R. M. Etter, H. S. Skovronek and P. S. Skell, J. Am. Chem. Soc., 81, 1009 (1959);
(9) P. S. Skell and J. Klebe, J. Am. Chem. Soc., 82, 247 (1960);
(10) P. S. Skell and A. Y. Garner, J. Am. Chem. Soc., 78, 5430 (1956);
(11) P. S. Skell and R. M. Etter, Chem. and Ind., 624 (1958);

were the basis for the assignment of the singlet state to
dibromomethylene (10), dichloromethylene (10), propyldiene (9),
carbethoxymethylene (11), and 2-ketopropylidene (9), and the
triplet state to diphenylmethylenè (8) and propargylidene (9).

Detailed quantum mechanical calculations (13-15) for

(13) G. A. Gallup, J. Chem. Phys., 26, 716 (1957);
(14) A. Padgett and M. Kraus, J. Chem. Phys., 32, 189
(1960);
(15) J. M. Foster and S. F. Boys, Rev. Mod. Phys.,
32, 305 (1960).

methylene indicate a triplet ground state and a close-lying
singlet excited state. These calculations are in satisfac-
tory agreement with the report (16) of spectroscopic evidence

(16) G. Herzberg and J. Shoosmith, Nature, 183, 1801
(1959); G. Herzberg, Proc. Roy. Soc. (London), Ser. A., 262,

that the vapor phase photolysis of diazomethane produces
singlet methylene which decays to the triplet state in the
presence of inert gas at high pressures. This result indi-
cates that the ground state of methylene must be triplet.
Chemical evidence has been obtained for the singlet-triplet
decay of methylene in the gas phase in the presence of argon
at high pressures (17) in that triplet methylene reacts with


cis-2-butene non-stereospecifically. Triplet methylene has
been generated (18) in solution by photosensitized

(18) K. R. Kopecky, G. S. Hammond and P. A. Leermakers,
decomposition of diazomethane. Triplet methylene did indeed react non-stereospecifically with \textit{cis-} and \textit{trans-}2-butenes as predicted (3) and as observed in the vapor phase (17). Thermal decomposition of diazomethane also produces singlet methylene.

Application of electron paramagnetic resonance measurements to detect the triplet state of carbenes was at first unsuccessful (19,20); however electron paramagnetic resonance of diphenylmethylene has recently been observed (21), thus indicating its triplet ground state as predicted (8).

From these observations and the fact that methylene is highly reactive (22), it is reasonable to conclude that thermal or direct photolytic decomposition of diazomethane produces excited singlet methylene which undergoes reaction much more rapidly than spin inversion to its triplet ground state. This situation should be generally true for carbenes except when certain structural features (6-11) either facilitate spin inversion to the triplet state or allow direct formation of a triplet carbene from a triplet precursor.

---

There are several types of bimolecular reactions which carbenoid systems undergo. The ability of carbenes to react with unsaturated centers has been known for many years and provides the basis for many useful syntheses (23).

(23) For a review of the literature to 1950 see M. Gordon, Chem. Rev., 50, 127 (1952). Reviews covering more recent literature are listed in references (2-5).

Furthermore, carbenes readily insert across saturated covalent bonds (24-31).

(24) W. von E. Doering and L. H. Knox, J. Am. Chem. Soc., 78, 4947 (1958);
(26) V. Franzen and L. Fikentscher, Ann., 617, 1 (1958);
(27) L. Friedman and H. Shechter, J. Am. Chem. Soc., 81, 5512 (1959);
(28) L. Friedman and H. Shechter, J. Am. Chem. Soc., 82, 1002 (1960);
(29) L. Friedman and H. Shechter, J. Am. Chem. Soc., 83, 3159 (1961);

In any system with \(\alpha\)- or \(\beta\)-hydrogens, the predominant intramolecular reactions are \(\alpha\)-hydrogen migration (1,2-insertion) to form olefins and 1,3-insertion between \(\beta\)-carbon-hydrogen bonds to form cyclopropanes (27).

Examples of 1,4- (31-32), 1,5- (33-36), 1,6- (36) and

(33) D. B. Denney and P. P. Klemchuk, J. Am. Chem. Soc., 80, 3289 (1958);
1,7-insertions (36) between carbon-hydrogen bonds have also been observed. Transannular insertion reactions of the 1,3-, 1,5-, and 1,6- type occur in reactions of C7 through C10 cycloalkylidenes (37-38).

Carbon-skeleton rearrangements (39) do not occur extensively in carbenoid systems of the neopentyl type (27); however such rearrangements are major reactions in thermal decomposition of diazocyclopropane (29), diazocyclobutane (28) and cyclopropylidiazomethane (28). Migration of alkyl and aryl groups is the basis of the Wolff rearrangement of α-diazoketones (40). Phenyl migrates faster than methyl (10:1) in thermal decomposition of 2-methyl-2-phenyldiazopropane (41). A tentative order of


migration in rearrangements of 2,2-diphenylethylidene and 2-phenylpropylidene is $H \phi \rightarrow \mathrm{Me}$ (42). Phenyl migration has

(42) Private communication from G. Kauffman of this laboratory.

also been observed in thermal rearrangement of 2,2,2-triphenylidazoethane (43).


A singlet carbene atom has a free pair of electrons, and at the same time, is electron deficient. Considerable data have shown that carbenes exhibit electrophilic character (2-5). Recently a nucleophilic carbene (I) has been described (44);

\[
\begin{align*}
\phi & \quad \mathrm{N} \\
H_2\mathrm{C} & \quad \mathrm{C}\vdash \\
H_2\mathrm{C} & \quad \mathrm{N} \\
\phi & \quad \mathrm{I}
\end{align*}
\]


apparently this molecule has sufficient resonance stabilization by participation of the electrons on the nitrogen atoms with the vacant $2p$ orbital of the carbene to allow isolation.
In view of the indicated electrophilic character of carbenes, and the tendency for structural rearrangements only in selected systems, the present research was designed to study a general system in which rearrangement will allow quantitative measure of the electrical character of a carbenic process. Determination of migratory aptitudes is a classical method for evaluating electrical effects in skeletal rearrangement reactions (45-48).

(46) Ann. Repts. Chem. Soc. (London), 27, 114 (1930); 30, 18 (1933); 36, 195 (1939);
(47) W. E. Bachman and H. R. Steinberger, J. Am. Chem. Soc., 56, 170 (1934);

To this end selected 2,2,2-triaryldiazoethanes were prepared and decomposed in situ (Eq. 1, 2, and 3) by base-catalyzed thermal decomposition of their respective p-toluenesulfonylhydrazones in diethyl Carbitol, a process known to proceed via a carbene mechanism (49,50). The

(49) L. Friedman, Ph.D. Dissertation, The Ohio State University, 1959;

products were triarylethylenes. The triarylethylenes were oxidized

$$\text{Ar}_3\text{CCH}=\text{NNHO}_2\text{SC}_7\text{H}_7 \rightarrow \text{B}^- \rightarrow \text{Ar}_3\text{CCHN}_2 + ^-\text{O}_2\text{SC}_7\text{H}_7 + \text{BH}$$

(1)
\[
\text{Ar}_3\text{CCHN}_2 \xrightarrow{} \text{Ar}_3\text{CCH:} + \text{N}_2 \quad (2)
\]
\[
\text{Ar}_3\text{CCH:} \xrightarrow{} \text{Ar}_2\text{C=CHAR} \quad (3)
\]

to their respective diaryl ketones and substituted benzoic acids (Eq. 4). The acids were separated and esterified;
\[
\text{Ar}_2\text{C=CHAR} \xrightarrow{\text{KMnO}_4} \text{Ar}_2\text{C}=\text{O} + \text{ArCO}_2\text{H} \quad (4)
\]
gas chromatographic analysis provided a quantitative measure of the migration aptitudes of the substituted aromatic groups.
DISCUSSION

The major task in the successful solution of the present study was the development of synthetic routes to the desired triarylacetaldehydes. Many pathways may be visualized; in practice only certain of those attempted proved satisfactory and were capable of generalization.

The reaction between orthoformic esters and Grignard reagents is a practical method for preparation of aldehydes (51-52). The reaction between triphenylmethylmagnesium chloride and triethyl orthoformate produced triphenylmethyl peroxide and was not investigated further.

Attempts were made to synthesize 2,2,2-triphenylethanol which would then be oxidized to triphenylacetaldehyde. The reaction between Grignard reagents and formaldehyde is a classical method for preparing primary alcohols (53,54), and

reaction between triphenylmethylsodium and formaldehyde is
reported to yield 2,2,2-triphenylethanol (55). In the


present study the primary product from the reaction of triphenylmethylmagnesium chloride and formaldehyde was triphenylmethane (71% yield); similarly, the reaction between triphenylmethyl lithium (56) and formaldehyde yielded


triphenylmethyl peroxide as the major product.

Acid-catalyzed dehydration of the proper triarylethylene glycol has been used to prepare triphenylacetaldehyde (57), p-anisyldiphenylacetaldehyde (58),

(57) S. Danilov, J. Russ. Phys. Chem. Soc., 49, 282 (1917);
(58) H. Orechow and M. Tiffeneau, Compt. rend., 171, 475 (1920);

diphenyl-o-tolylacetaldehyde (59), and
diphenyl-p-tolylacetaldehyde (59). Study of the acid-catalyzed dehydration of triarylethylene glycols (60)

(60) See C. J. Collins, Quart. Rev., 14, 357 (1960) for a review and references of this study.

indicates the products of reaction can be controlled by the judicious selection of solvents and temperature. Formic
acid (98%) at room temperature or below seemed to be the solvent of choice for the preparation of aldehydes.

It has been presently found that the dehydration of 1-α-anisyl-2,2-diphenylethylene glycol yielded α-α-anisyl-α-phenylacetophenone, α,α-diphenyl-α-methoxyacetophenone and a small amount of p-anisyldiphenylacetaldehyde (Eq. 5);

\[
\text{CH}_3\text{O} - \text{C}_6\text{H}_4\text{OH} - \text{CH} - \phi_2 \rightarrow \text{CH}_3\text{O} - \text{C}_6\text{H}_4\phi - \phi_2\text{CH} - \text{C}_6\text{H}_4\text{OCH}_3 + \phi_2\text{CCHO} \tag{5}
\]

1-α-anisyl-1,2-diphenylethylene glycol gave α-α-anisyl-α-phenylacetophenone as the major product (Eq. 6)

\[
\text{CH}_3\text{O} - \text{C}_6\text{H}_4\phi - \phi_2\text{CH} - \phi \rightarrow \text{CH}_3\text{O} - \text{C}_6\text{H}_4\phi - \phi_2\text{CH} - \phi \tag{6}
\]

and 1-p-chlorophenyl-1,2-diphenylethylene glycol formed a half-formate which underwent further reaction to produce a small amount of p-chlorophenyldiphenylacetaldehyde and α,α-diphenyl-p-chloroacetophenone (tentative) (Eq. 7).

\[
\text{Cl} - \text{C}_6\text{H}_4\phi - \phi_2\text{CH} - \phi \rightarrow \text{Cl} - \text{C}_6\text{H}_4\phi - \phi_2\text{CH} - \phi + \phi_2\text{CCHO} \tag{7}
\]
Reaction temperatures of 0-30° and reaction times of 1-24 hours did not materially change the product ratios. It is apparent hydrogen migration occurs in preference to aryl migration in the cases studied.

Nitriles have been reduced to aldehydes with an equivalent amount of lithium aluminum hydride at -70° (61, 62), excess lithium tri-t-butoxyaluminum hydride (63), and hydrochloric acid and stannous chloride, the Stephen reduction (64, 65). In the present study, each reagent had no effect on triphenylacetonitrile; starting material was recovered.

2,2,2-Triphenyldiazoethane has been isolated from reaction of ethyl-N-nitroso-N-\(\beta,\beta,\beta\)-triphenylethyl carbamate and sodium methoxide (66). This method was of possible use instead of that involving tosylhydrazones. Examination of the reaction between lithium aluminum hydride and triarylacetonitriles appeared desirable. However, triphenylacetonitrile is not reduced by lithium aluminum
hydride at 25° (67). It was found that reduction of triphenylacetonitrile with excess lithium aluminum hydride at -70° in ether gave triphenylmethane (17% yield) and unreacted triphenylacetonitrile (31% recovery), but in refluxing ether the product was 2,2,2-triphenylethylamine in good yield.

Extension of this reaction to other triarylacetonitriles produced surprising results. The reduction of diphenyl-0-tolylacetonitrile gave diphenyl-0-tolylmethane (87% yield); the reduction of p-anisyldiphenylacetonitrile produced p-anisyldiphenylmethane (29% yield); and the reduction of p-bromophenylidiphenylacetonitrile resulted in triphenylmethane (31% yield). Similar results have been found in the reduction of diphenyl-0-tolylacetonitrile with lithium aluminum hydride (68). Reduction of triphenylacetonitrile with sodium and alcohol yielded triphenylmethane and hydrogen cyanide (69), and phenyl-di-p-tolylacetonitrile, sodium and


alcohol yield phenyl-di-p-tolylmethane and hydrogen cyanide (70).

(70) J. Hoch, Compt. rend., 197, 770 (1933).

The results of reduction of triarylacetonitriles with lithium aluminum hydride may be rationalized if the following mechanism is important:

\[
\begin{align*}
\text{Ar}_3\text{CCN} + \text{LiAlH}_4 &\rightarrow \text{Ar}_3\text{CC}=\text{NA}1\text{H}_3\text{Li}^+ \quad \text{(8)} \\
\text{Ar}_3\text{CC}=\text{NA}1\text{H}_3\text{Li}^+ + \text{H} &\rightarrow \text{Ar}_3\text{CLi}^+ + \text{HCN} + \text{AlH}_3 \quad \text{(9)} \\
\text{Ar}_3\text{C}^- + \text{H}^+ &\rightarrow \text{Ar}_3\text{CH} \quad \text{(10)}
\end{align*}
\]

Experimental evidence supporting this mechanism is the appearance of a deep-red color during the addition of nitrile to lithium aluminum hydride. The color persists until hydrolysis; triphenylmethysodium and triphenylmethyllithium are both deep-red. Therefore, the color developed in the reduction of triarylacetonitriles may be reasonably attributed to the presence of the triarylmethyl anion.

Since no amines were isolated from these reactions, it appears that cleavage occurs more readily than addition of the second hydride required for reduction to an amine. The successful reduction of triphenylacetonitrile in contrast to the cleavage reaction exhibited by the other triarylacetonitriles examined is consistent with the sequence indicated (Eq. 8, 9 and 10). On the basis of the electron-
withdrawing inductive effects of \( \text{p-methoxy} \) and \( \text{p-bromo} \) substituents, it is expected that the carbon-carbon bond between the substituted triarylmethyl group and the imino carbon (Eq. 8) will be broken anionically more easily than that of triphenylacetonitrile.

The effect of the \( \text{o-methyl} \) group in causing cleavage rather than reduction of diphenyl-\( \text{o-tolylacetonitrile} \) may be attributed to steric hindrance to addition of the second hydride required in the reduction to amine, and also to steric strain making the diphenyl-\( \text{o-tolylmethyl} \) anion a better leaving group than is the triphenylmethylide ion.

The unusual temperature effect observed in the reduction of triphenylacetonitrile cannot be simply explained, although it may be the result of different structures of lithium aluminum hydride in solution (71).

(71) N. G. Gaylord, "Reduction with Complex Metal Hydrides," Interscience Publishers, Inc., New York, New York, 1956, pp. 9-13, reports that the active reducing agent in lithium aluminum hydride seems to be a function of solvent and temperature.

The loss of bromine from the aromatic nucleus in reduction of \( \text{p-bromophenyl} \)-diphenylacetonitrile is probably the result of a secondary nucleophilic substitution reaction by lithium aluminum hydride, possibly on the \( \text{p-bromophenyl} \)-diphenylmethylide ion. There are a few cases (72)

where prolonged refluxing of an aromatic halide in tetrahydrofuran with excess lithium aluminum hydride produces the hydrogenolyzed product in low yields. For example, 1-chloro-2-iodobenzene with excess lithium aluminum hydride in tetrahydrofuran (73) yields chlorobenzene (40% yield) and starting material (38%; recovery); p-bromotoluene with lithium aluminum hydride and lithium hydride in tetrahydrofuran (74) gives toluene (14% yield).

Four synthetic procedures were subsequently developed for the successful preparation of triarylacetaldehydes.

The Grignard reagent prepared from magnesium and triphenylchloromethane was carbonated and converted by thionyl chloride to triphenylacetyl chloride; the acid chloride was reduced to 2,2,2-triphenylethanol with lithium aluminum hydride in ether, and the alcohol was oxidized with chromium trioxide-pyridine to triphenylacetaldehyde (Chart 1).

Preparation of p-anisylidiphenylacetic acid by carbonation of the Grignard reagent failed. However, the acid was successfully prepared by condensation of benzilic acid with anisole in a mixture of sulfuric and acetic acids (1:1). The acid was converted to the acid chloride; the acid chloride was reduced with lithium aluminum hydride to
2-p-anisyl-2,2-diphenylethanol and the alcohol was oxidized with chromium trioxide-pyridine to p-anisylidiphenylacetaldehyde (Chart 2).

**Chart 1**

\[
\begin{align*}
\phi_3\text{CCl} + \text{Mg} & \rightarrow \phi_3\text{CMgCl} \\
& \xrightarrow{1.\text{CO}_2} \phi_3\text{CCO}_2\text{H} \\
& \xrightarrow{2.\text{H}^+} \phi_3\text{CCO}_2\text{H} \\
& 92\%
\end{align*}
\]

\[
\begin{align*}
\text{SOCl}_2 & \rightarrow \phi_3\text{CCOCl} \\
& \xrightarrow{\text{LiAlH}_4} \phi_3\text{CCH}_2\text{OH} \\
& 88\% \\
& 91\%
\end{align*}
\]

\[
\begin{align*}
\text{CrO}_3 & \rightarrow \phi_3\text{CCHO} \\
& 88\%
\end{align*}
\]
As previously mentioned the acid-catalyzed rearrangement of 1,2-diphenyl-1-o-tolylethylene glycol produced diphenyl-o-tolylacetaldehyde. The glycol was prepared from o-tolylmagnesium bromide and benzoin (Chart 3).
The fourth method utilized reduction of triarylacetonitriles with diborane, followed by hydrolysis of the alkylideneamino borane intermediate (Chart 4). This sequence was used in the synthesis of diphenyl-$p$-tolyl-, phenyl-$d$-$p$-tolyl-, $p$-chlorophenyl$2$phenyl-, and $p$-nitrophenvldiphenylacetaldehydes.

![Chart 4]

It has been reported (75,76) that reduction of nitriles with diborane yields amines. Winternitz and Spillane (77) claim a process for preparing aliphatic substituted hexahydro-$s$-triazaaborines from nitriles and diborane. In view of these reports, the isolation of dimeric...
alkylideneamino boranes from reduction of triarylacetonitriles was unexpected.

Although the structures for the amino boranes were not completely established, those proposed (Chart 4) are the most reasonable interpretation of the data. The triphenyl- and p-chlorophenylidiphenylethylideneamino boranes were examined in greatest detail. Their molecular weights indicated that they were dimers. Their infrared spectra indicated quarternery-boron hydrogens and imino (C=N) groups. Peroxide oxidation (Eq. 11) produced oximes; basic hydrolysis (Eq. 12) yielded amines and acid hydrolysis (Eq. 13) gave aldehydes.

\[
\phi_3\text{CCH}=\text{N} + \phi_3\text{CH}=\text{N} + \text{H}_2\text{O} + \text{NaOH} \xrightarrow{\text{diglyme}} \phi_3\text{CCH}=\text{N} + \phi_3\text{CCH}_{2}\text{NH}_2
\]
Finally, synthesis (78) of several aryl- and alkylideneamino t-butylboranes (II) from nitriles and t-butylborane has been reported. The infrared absorptions reported for boron-hydrogen and for C=N agree with those found in the present study; the molecular weights and nuclear magnetic resonance spectra indicate dimers, and acid hydrolysis of benzylideneamino t-butylborane yielded benzaldehyde.

Additional products of reaction of triarylacetonitriles and diborane are the corresponding triarylethylamines (Eq. 14). Triphenylacetonitrile gave 2,2,2-triphenylethylamine (41 to 62% yield);
diphenyl-\(\pi\)-tolylacetonitrile gave
2,2-diphenyl-2-\(\pi\)-tolylethylamine (37\% yield); phenyl-di-\(\pi\)-tolylacetonitrile produced
2-phenyl-2,2-di-\(\pi\)-tolylethylamine (20\% yield); \(\pi\)-chlorophenylidiphenylacetonitrile yielded
2-\(\pi\)-chlorophenyl-2,2-diphenylethylamine (27\% yield); and \(\pi\)-anisyldiphenylacetonitrile gave
2-\(\pi\)-anisy1-2,2-diphenylethylamine (32\% yield).

\[
\begin{align*}
\text{Ar}_3\text{CCN} + \text{B}_2\text{H}_6 & \rightarrow \text{Ar}_3\text{CC\equivN:BH}_3 \rightarrow \text{Ar}_3\text{CCH=NBH}_2 \\
\text{Ar}_3\text{CCH}_2\text{NBH} & \rightarrow \text{Ar}_3\text{CCH}_2\text{NH}_2 \rightarrow \text{Ar}_3\text{CCH}_2\text{NH}_2 + \text{H}_3\text{BO}_3
\end{align*}
\]

Preliminary experiments indicate that decreasing the amount of diglyme as solvent and temperatures of 0-10\(^\circ\) result in an increase in the yield of alkylideneamino borane. It is believed that the yield of amines would be increased if a larger amount of diglyme and higher temperatures were used.

These reduction results may be explained if the reaction proceeds through a stepwise addition of BH\(_3\) to the carbon-nitrogen triple bond followed by hydride transfer from boron to carbon producing an alkylamino borane (Eq. 14). In a minimum amount of solvent and at low temperatures the alkylideneamino borane may precipitate as the dimer rather than rearrange. After consideration of the results of the
present work and Hawthornes' data, in contrast to that of Brown and Subba Rao (75), it is also possible that the reason for the isolation of alkylideneamino boranes or \(t\)-butylboranes is steric in nature. In order for complete reduction to amine, two hydride shifts must occur (Eq. 14). In one case the \(t\)-butyl group (III) and in the other the triaryl group (IV) might act to prevent the second hydride addition to the carbon-nitrogen double bond.

It is also necessary to consider whether the products of acid-hydrolysis of the alkylideneamino boranes are ketones rather than aldehydes. The carbonyl compounds synthesized in the present research were previously unknown; aldehydes are known to be isomerized to ketones by strong acids.

\(p\)-Anisyldiphenylacetaldehyde, prepared by the unambiguous procedure previously discussed, was converted to the tosylhydrazone. The tosylhydrazone obtained via hydrolysis of \(p\)-anisyldiphenylethylideneamino borane was identical to this compound. The oxidation of
triphenylacetaldehyde tosylhydrazone with aqueous buffered potassium permanganate (79) gave triphenylacetic acid; and

(79) The same oxidation procedure was used in the analysis of rearrangement products and is fully discussed in that section.

the oxidation of phenyl-di-p-tolylacetaldehyde tosylhydrazone produced phenyl-di-p-tolylacetic acid. Further, all tosylhydrazones prepared in this study exhibited a characteristic infrared spectrum (Table 1). The N-H absorption appears at 3300-3125 cm\(^{-1}\). The \(\text{SO}_2\)- group has two bands, one at 1330-1280 cm\(^{-1}\) and the other at 1170-1161 cm\(^{-1}\) (80). Two very important weak bands appear


(81) pp. 156-157. Bands from 2900-2700 cm\(^{-1}\) and in some cases two bands, one at 2820 cm\(^{-1}\) and the other at 2720 cm\(^{-1}\), are attributed to C-H stretching vibrations of the carbonyl carbon atom in aldehydes.

(82) p. 268.

at 2900-2885 cm\(^{-1}\) and 2825-2775 cm\(^{-1}\). These absorptions are attributed to the C-H stretching vibrations of the imino group (81). These bands are absent in the infrared spectrum of phenylacetone tosylhydrazone and dibenzyl ketone tosylhydrazone. Since these bands are present it is apparent that rearrangement has not occurred.

The C=N absorption usually found at 1690-1640 cm\(^{-1}\) (82) for imines and at 1650 cm\(^{-1}\) for phenylacetone
<table>
<thead>
<tr>
<th>Tosylhydrazone</th>
<th>Absorption Frequency cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triphenylacetaldehyde</td>
<td>3300 2900 2775 1320 1160</td>
</tr>
<tr>
<td>Diphenyl-o-tolylacetaldehyde</td>
<td>3200 2900 2800 1320 1165</td>
</tr>
<tr>
<td>Diphenyl-p-tolylacetaldehyde</td>
<td>3180 2900 2800 1320 1161</td>
</tr>
<tr>
<td>Phenyl-di-p-tolylacetaldehyde</td>
<td>3200 2900 2800 1330 1165</td>
</tr>
<tr>
<td>p-Anisylidiphenylacetaldehyde</td>
<td>3125 2885 2795 1280 1170</td>
</tr>
<tr>
<td>p-Chlorophenyldiphenylacetaldehyde</td>
<td>3180 2900 2825 1320 1165</td>
</tr>
<tr>
<td>p-Nitrophenyldiphenylacetaldehyde</td>
<td>3200 2900 2800 1320 1165</td>
</tr>
</tbody>
</table>
tosylhydrazone and 1640 cm$^{-1}$ for dibenzyl ketone
tosylhydrazone is absent in the tosylhydrazones prepared in
the present study.

The decomposition of 2,2,2-triphenyldiazoethane has
been studied under a variety of conditions (67). In a
desiccator at 5$^\circ$ for two months followed by storage at room
temperature for one week, or in ether solution containing
copper powder or a crystal of iodine, the product was
triphenylethylene. In water at 100$^\circ$ the major product was
triphenylethylene; the minor product was
triphenylacetaldazine (V). The decomposition of

\[ \text{CCH} - \text{N} - \text{N} - \text{CHC} \]
\[ \text{V} \]

2-methyl-2-phenyldiazopropene (83) in hexane at 59$^\circ$ produced

\[ \text{(83)} \text{ H. Phillips and J. Keating, Tetrahedron Letters, 15, 523 (1961).} \]

dimethylphenylacetaldazine (50%), $\beta$, $\beta$-dimethylstyrene,
$\alpha$, $\beta$-dimethylstyrene and 1-methyl-1-phenylcyclopropane
(total hydrocarbon yield 35%, ratio 51:9:40) (Eq. 15).
In order to understand better the rearrangement of 2,2,2-triaryldiazoethanes it was decided to independently synthesize, isolate and rearrange 2,2,2-triphenyldiazoethane. In the present study 2,2,2-triphenyldiazoethane was stirred in benzene at 60°. The decomposition was smooth and the evolution of nitrogen complete in 10 hours. The only product isolated was triphenylethylene (74% yield) (Eq. 16).

\[
\Phi_3\text{CCHN}_2 \rightarrow \Phi\text{CCH}=\text{N-N=CHF} + \Phi\text{CH}=\text{C(CH}_3)_2
\]

+ \text{CH}_3\text{CH}=\text{CCH}_3 + \Phi

(15)

The base-catalyzed decomposition of triphenylacetalddehyde tosylhydrazone in diethyl Carbitol with a molar equivalent of sodium methoxide effected by slowly increasing the temperature to 160° was also examined for products other than triphenylethylene. None were found and triphenylethylene was isolated in greater than 90% yield. Thus, in this reaction rearrangement of an aryl
group occurs to the exclusion of any other process (Eqs. 17, 18 and 19).

\[
\begin{align*}
\phi_3\text{CCH}=\text{NNHO}_2\text{SC}_7\text{H}_7 & \xrightarrow{\text{NaOCH}_3} \phi_3\text{CCHN}_2 + \text{NaO}_2\text{SC}_7\text{H}_7 \quad (17) \\
\phi_3\text{CCHN}_2 & \rightarrow \phi_3\text{CCH}: + \text{N}_2. \quad (18) \\
\phi_3\text{CCH}: & \rightarrow \phi_2\text{C}=\text{CH}\phi \quad (19)
\end{align*}
\]

The tosylhydrazone decompositions proceed smoothly with physical changes similar to those previously observed (84). Visible evolution of nitrogen occurred at about 90° and was complete at 140-150°. Evolution was quite vigorous at 120°. Decompositions were effected by sodium methoxide or sodium amide and in molar ratios from 1:1 to 3:1 with no change in product composition.

Isothermal experiments in which the rate of nitrogen evolution was observed indicate decomposition is complete in 15-20 min. at 90°, and in less than 5 min. at 125°, and that evolution of nitrogen occurs via a first-order reaction.
The analysis procedure involved oxidation of the triarylethylenes in buffered aqueous acetone with potassium permanganate to diaryl ketones and benzoic and/or substituted benzoic acids. Radiochemical analysis (c¹⁴) of this reaction shows that approximately 1% phenyl migration occurs during the oxidation; such rearrangement thus does not significantly affect the oxidation reaction as an analytical method (85).


It was possible to isolate benzoic acid in 85% yield from oxidation of triphenylethylene.

The acids obtained from the substituted triphenylethylenes were separated from the ketones and esterified. The esters were analyzed by vapor phase chromatography. In the initial analytical method, esterification was effected with methanol using 2,2-dimethoxypropane in order to insure a quantitative reaction. For each mole of water formed during esterification, two moles of methanol are subsequently obtained by hydrolysis of 2,2-dimethoxypropane. The esterification thus is driven to completion by removing water from the reaction medium. This procedure has been useful for esterification of aliphatic acids (86), but not previously recommended for

aromatic acids (87). It was found in the present work that

(87) Private communication from Dr. J. Little of the Dow Chemical Co., Midland, Michigan.

excess methanol and slightly more than molar equivalents of 2,2-dimethoxypropane gave quantitative esterification upon refluxing the reaction mixture 14 hours. Further, it was found that known mixtures of benzoic and o-toluic acids analyzed with a precision of +3%.

Nevertheless, because of the time involved in esterification, and because the acetone produced from hydrolysis of 2,2-dimethoxypropane formed condensation products such as phorone, isophorone, etc., which might interfere with the gas chromatographic analyses, the acids were esterified with diazomethane. The analysis data based on use of methanol and 2,2-dimethoxypropane are believed to be less reliable than those using diazomethane.

The results of the base-catalyzed decomposition of substituted triarylacetaldehyde tosylhydrazones are listed in Table 2. It is apparent that the migratory aptitudes of the aryl groups are independent of the base and insensitive to changes in the temperature of decomposition. Because the decomposition is complete in less than 20 minutes, slowly increasing the temperature of reaction should allow decomposition and rearrangement at the lowest possible temperature, and presumably with the greatest selectivity.
<table>
<thead>
<tr>
<th>Substituents</th>
<th>Temp. °C</th>
<th>Base</th>
<th>Analysis</th>
<th>% CO₂ Me</th>
<th>Migration Aptitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-Me, H, H&lt;sup&gt;e&lt;/sup&gt;</td>
<td>V&lt;sup&gt;b&lt;/sup&gt;</td>
<td>NaOCH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>DMP&lt;sup&gt;c&lt;/sup&gt;</td>
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<td>NaOCH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>DMP</td>
<td>35.4</td>
<td>3.65</td>
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<tr>
<td>o-Me, H, H&lt;sup&gt;e&lt;/sup&gt;</td>
<td>V</td>
<td>NaOCH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>DMP</td>
<td>35.4</td>
<td>3.65</td>
</tr>
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<td>NaNH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>DM&lt;sup&gt;d&lt;/sup&gt;</td>
<td>33.7</td>
<td>3.93</td>
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<td>o-Me, H, H&lt;sup&gt;f&lt;/sup&gt;</td>
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<td>DMP</td>
<td>59.8</td>
<td>1.34</td>
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<td>1.35</td>
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<td>1.10</td>
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<tr>
<td>p-Me, p-Me, H&lt;sup&gt;f&lt;/sup&gt;</td>
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<td>p-Me, p-Me, H&lt;sup&gt;f&lt;/sup&gt;</td>
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<td>1.17</td>
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<td>DM</td>
<td>63.8</td>
<td>1.13</td>
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<tr>
<td>p-Cl, H, H&lt;sup&gt;h&lt;/sup&gt;</td>
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<td>NaNH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>DM</td>
<td>63.3</td>
<td>1.16</td>
</tr>
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TABLE 2 (cont.)

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<tr>
<th>Substituents</th>
<th>Temp.°</th>
<th>Base</th>
<th>Analysisa</th>
<th>%CO₂Me</th>
<th>Migration Aptitude</th>
</tr>
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<tbody>
<tr>
<td>p-Cl, H, H⁵</td>
<td>90</td>
<td>NaNH₂</td>
<td>DM</td>
<td>63.2</td>
<td>1.16</td>
</tr>
<tr>
<td>p-MeO, H, H⁵</td>
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<td>NaNH₂</td>
<td>DM</td>
<td>54.1</td>
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<td>p-MeO, H, H⁵</td>
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<td>NaNH₂</td>
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<td>54.3</td>
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<tr>
<td>p-MeO, H, H⁵</td>
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<td>NaNH₂</td>
<td>DM</td>
<td>55.5</td>
<td>1.61</td>
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<td>p-NO₂, H, H¹</td>
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<td>NaNH₂</td>
<td>DM</td>
<td>76.7</td>
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<tr>
<td>p-NO₂, H, H¹</td>
<td>90</td>
<td>NaNH₂</td>
<td>DM</td>
<td>77.5</td>
<td>0.58</td>
</tr>
</tbody>
</table>

(a) Method of esterification. (b) Temperature slowly increased to 160°. (c) 2,2-Dimethoxypropane. (d) Diazomethane. (e) 1.00 g. run. (f) 0.50 g. run. (g) 0.050 g. run. (h) 0.25 g. run. (i) 0.070 g. run.
Since the rearrangement reaction did not show significant differences in migration aptitude as a function of temperature, it may be concluded that the transition state is too energetic to reflect changes in temperature over the range studied. An alternative explanation requires the isokinetic temperature to be near the temperatures at which the reactions were examined. Unfortunately, the data of the present study do not allow determination of the isokinetic temperature.

In considering the role of substituents on the migratory aptitude of an aryl group, the most striking fact is their very small effect (Table 2). The migration aptitude at 90° of \( o \)-tolyl is 4.00; \( p \)-anisyl, 1.67; \( p \)-tolyl, 1.36; \( p \)-chlorophenyl, 1.15; phenyl, 1.00; \( p \)-nitrophenyl, 0.60.

In the acid-catalyzed rearrangement of symmetrical aromatic pinacols to their pinacolones, a carbonium ion process, the migratory aptitudes are: \( p \)-anisyl, 500; \( p \)-tolyl, 15.7; \( p \)-chloro, 0.70 (88). In the carbenic rearrangement of 2-methyl-2-phenylpropylidene (Eq. 20) the

\[
\begin{align*}
\Phi C\text{CH}: & \rightarrow \Phi C=\text{CHCH}_3 + \Phi CH=\text{C(CH}_3)_2 + \\
\text{CH}_3 & \quad 9 \quad 51 \quad 40
\end{align*}
\]

phenyl:methyl migration ratio is 10:1 (83), and in the thermal rearrangement of triarylmethyl azides (89), a reaction postulated to proceed via the nitrogen analog of a carbene, the migration aptitudes are: p-anisyl, 2.5; p-tolyl, 1.8; p-chlorophenyl, 0.39; p-nitrophenyl, 0.20.

The lack of large substituent effects on the carbenoid reactions in contrast to the results of the piancol rearrangement are not surprising. If the carbene is a highly reactive species, as previously discussed, it will show little selectivity in its reactions. That is, if the free energy difference between the reactant and the transition state is small, the reaction will be relatively insensitive to minor structural changes.

The relative rates of migration are in the order expected for migration to an electron deficient center. Thus, VI is a more reasonable picture of the transition state of rearrangement than is VII.

\[
\begin{align*}
\phi_2C & \rightarrow CO_2H \\
\phi_2C & \rightarrow +CO_2H \\
\text{VI} & \\
\text{VII}
\end{align*}
\]
The migratory aptitude of the $p$-chlorophenyl group was initially surprising. The $p$-chloro substituent normally decreases the rate of an electrophilic reaction (90), for example, in electrophilic aromatic substitution. However, if the system is highly electron deficient, the non-bonded electrons on the chlorine atom may be utilized to provide resonance stabilization of the transition state (VIII), and

\[
\begin{array}{c}
\phi_2C\text{CH} \\
\text{Cl}
\end{array}
\quad 
\begin{array}{c}
\phi_2C\text{CH} \\
\text{Cl}
\end{array}
\]

thus facilitate $p$-chlorophenyl migration with respect to that of phenyl.

In an attempt to correlate the ability of the ring substituent to stabilize the transition state through resonance interaction with the electron deficient center, the relationship of the migration aptitudes to the Hammett equation (91,92) was determined. The data were compared with

\[
\begin{array}{c}
\end{array}
\]
relationship exists between the migration aptitude and the \( \sigma_p^+ \) substituent constants (Figure 1). The correlation coefficient was found by the usual statistical method \( (94) \)


to be 0.97. The correlation coefficient of migration aptitudes with the \( \sigma_p^- \) substituent constants (Figure 2) was 0.94, which is slightly less than satisfactory \( (95) \).


The correlation of the migratory aptitudes with \( \sigma_p^+ \) allows certain conclusions to be drawn. Correlation of the migratory aptitude with \( \sigma_p^+ \) substituent constants indicates that positive charge is transmitted into the aromatic ring of the migrating group, and that there is strong resonance interaction between this charge and the \( p \)-substituent of the ring. Further, the value of \( \rho = -0.28 \) obtained from the slope of the regression line indicates that the reaction proceeds through an electron deficient
Figure 1

Hammett Correlation of Migration Aptitudes with $\sigma^*$. Substituent Constants.

Correlation Coefficient = 0.97

$\rho = -0.28$
Figure 2

Hammet Correlation of Migration Aptitudes with $\sigma'_p$ Substituent Constants.

Correlation Coefficient = 0.94
$\rho = -0.37$
transition state, and that the substituents have a minor
effect on the reaction (96).

(96) If the isokinetic temperature is close to the
experimental temperature, is small and the interpretations
presented are invalid.

The migration aptitude of the \( p \)-tolyl group in
2,2-diphenyl-2-\( p \)-tolylethylidene is 1.36, and in
2-phenyl-2,2-di-\( p \)-tolylethylidene, 1.10. The rearrangement
in the di-\( p \)-tolyl system is not correlated by either the
\( \sigma_P \) or \( \sigma_P^+ \) relationship. It might be expected that the
migration aptitude of a group is independent of their number.
Nevertheless, it is possible to rationalize the differences
in migration aptitude in an explanation consistent with the
previously discussed data. If on the basis of the reaction
sequence in Chart 5, it is postulated that the transition
state for aryl migration reflects the structure of \( X \), the
\( \sigma_P^+ \) correlation requiring the development of a positive
center in the migrating group is explained. If the transition

\[ \begin{align*}
\Phi-C-\ddot{C}-H & \rightarrow \Phi-C \quad \text{IX} \\
\Phi-C \quad \text{X} & \rightarrow \Phi-C=\ddot{C}-H \quad \text{XI} \\
\Phi-C=\ddot{C}-H & \rightarrow \Phi-C \quad \text{XII}
\end{align*} \]
state also reflects the structure of XI, the positive character at the migration origin affects the ability of a group to move. If this is true, then XIII is a reasonable representation of the transition state. Therefore, when the substituent on the migrating group is electron-donating, and when the substituents on the non-migrating groups are electron-donating, the transition state is stabilized. These opposing effects can explain the difference observed in migratory aptitudes of \( \text{p-tolyl} \) groups in the two systems. In rearrangement of 2-phenyl-2,2-di-p-tolylethylidene, the two \( \text{p-tolyl} \) groups must stabilize transition state XIII to such an extent that phenyl migration is relatively greater than in the 2,2-diphenyl-2-p-tolylethylidene system.

The minor substituent effects in rearrangement of 2,2,2-triarylethylidenes support the interpretation that transition state XIII reflects the structures X and XI. The opposing requirements of the migration origin and the migrating group level the effect of any substituent by requiring migration of an electron-rich group (\( \text{X} \)), and
simultaneously providing transition state stabilization if the non-migrating group is electron-donating (XI).

To test the validity of this explanation it would be desirable to observe the rearrangement in systems such as 2,2-di-\(p\)-anisyl-2-phenylethylidene. It is predicted the \(p\)-anisyl group will have a migration aptitude less than 1.67.

The migration aptitude of the \(o\)-tolyl group is 4.00 and thus is larger than any of the other groups studied. Therefore, in addition to the favorable electrical effect of the \(o\)-methyl group (97), the release of steric compression about (97) The \(o\)-methyl group will stabilize the electron-deficiency developed in the migrating ring, and further, such stabilization through a structure of extended conjugation such as XIV may be more important than stabilization from a \(p\)-substituent.

\[
\begin{align*}
\phi & \quad \phi-C \quad \overline{C-H} \\
\phi-\mathbf{C} & \quad \overline{C-H} \\
& \quad \mathbf{CH}_3
\end{align*}
\]

XIV

the migration origin must be important in this system. This is not unexpected since the crowding of three aromatic rings about a central carbon atom would be seriously increased by the \(o\)-methyl group and greatly relieved by the migration of an \(o\)-tolyl radical.
The conclusions concerning the rearrangement of 2,2,2-triaryl diazoethanes drawn from this study are as follows:

1. The effects of temperature and substituents on migration aptitude are small. These results indicate that the free energy difference between reactant and transition state is small and agrees with the reports that carbenic intermediates are highly reactive.

2. The migration aptitudes have a linear free energy relationship with $\sigma_p^+$ substituent constants. The rearrangement thus proceeds through an electron deficient transition state which is stabilized by resonance contribution of electron-donating substituents on the migrating group. The results also support the contention that carbenes are electrophilic.

3. The difference in the migration aptitude of $p$-tolyl groups in rearrangements of 2,2-diphenyl-2-$p$-tolylethylidene and 2-phenyl-2,2-di-$p$-tolylethylidene indicate that the stability of the transition state reflects the development of positive charge in the migrating group and incipient positive character at the migration origin.

4. In systems such as 2,2-diphenyl-2-$o$-tolylethylidene the rearrangement reaction can be controlled by the relief of steric compression at the migration origin. Study of
molecular models indicates relief of the steric compression existing in any 2,2,2-triarylethylidene caused by three aryl groups bonded to a single carbon may contribute a large degree of the driving force for rearrangement, and thus partially account for the small substituent effects observed.
EXPERIMENTAL

General Information

Melting points. Melting points were determined on a Fisher melting point block and are uncorrected unless otherwise noted. Corrected melting points were determined with a Hershberg melting point apparatus utilizing calibrated thermometers.

Infrared spectra. The infrared spectra of compounds prepared in this research were obtained with a Baird Associates, model B, recording infrared spectrophotometer, a Perkin-Elmer, model 21, recording infrared spectrophotometer, and a Perkin-Elmer, model 137, Infracord, recording infrared spectrophotometer. All instruments were standardized by a polystyrene calibration.

Solvents. Anhydrous ether, Mallinckrodt analytical reagent, was used directly without additional drying or purification when necessary. Tetrahydrofuran was purified by storage over potassium hydroxide followed by distillation from calcium hydride.

Microanalyses. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee unless otherwise noted.
Intermediates

Triphenylacetic Acid ••• Chlorotriphenylmethane (40.95 g., 0.147 mole, recrystallized from benzene and 20% acetyl chloride) was added, all at once, to a stirred mixture of powdered magnesium (7.55 g., 0.31 mole, 80-200 mesh), iodine (4.65 g., 0.037 mole) and ether (380 ml., purified by distillation from calcium hydride) under nitrogen. The mixture was heated with a flame until reaction began and then refluxed using a heating mantle for 3.5 hr. The stirred mixture was cooled to 0° and carbon dioxide (produced from Dry Ice and passed through sulfuric acid and anhydrous calcium sulfate) was added at a rate of @ 0.5 liters per minute. After 3.5 hr. the mixture was poured into 20% hydrochloric acid (200 ml.) and the ether removed by evaporation. The solid was collected, digested with dilute sodium hydroxide and filtered; the filtrate was acidified with dilute hydrochloric acid. After filtering and drying, triphenylacetic acid [39.0 g., 0.135 mole, 92% yield, m.p. 263-271°, lit. (98) m.p. 264-265°] was obtained.

(98) J. Schmidlin, Ber., 39, 628 (1906).

Triphenylacetyl Chloride ••• Triphenylacetic acid (38.93 g., 0.135 mole) was added to thionyl chloride (130 ml.); the mixture was refluxed 15 min. after gas evolution ceased. Most of the thionyl chloride was removed by distillation and
the residue was poured over ice (150 g.). Triphenylacetyl chloride was crystallized from benzene–Skellysolve B [36.61 g., 0.120 mole, 88% yield, m.p. 126-128°, lit. (99) m.p. 127°].


2,2,2-Triphenylethanol ⋯ Triphenylacetyl chloride (24.01 g., 0.0783 mole) in ether (100 ml.) and benzene (50 ml.) was added slowly to a slurry of lithium aluminum hydride (4.0 g., 0.105 mole) in ether (100 ml.) under nitrogen. The reaction was refluxed 3 hr.; ethyl acetate was added to destroy the excess hydride and hydrolysis was completed by adding 20% hydrochloric acid (150 ml.). The layers were separated; the aqueous layer was extracted with ether; the organic layers were combined and washed with aqueous saturated sodium bicarbonate. The ether was removed by evaporation and 2,2,2-triphenylethanol [19.53 g., 0.0714 mole, 91% yield, m.p. 101-102°, lit. (100) m.p. 106-107°] was crystallized from Skellysolve B.


Triphenylacetaldehyde ⋯ Chromium trioxide (7.0 g., 0.07 mole) was cautiously added to pyridine (70 ml.) keeping the stirred mixture at 15-20°. After the yellow complex had formed, 2,2,2-triphenylethanol (6.79 g., 0.0247 mole) in
pyridine (70 ml.) was added with stirring, and the mixture stored overnight. The reaction mixture was poured into water (100 ml.) and extracted with ether (3x150 ml.). The ether portions were combined; the ether was removed under reduced pressure and triphenylacetaldehyde [5.89 g., 0.0216 mole, 88% yield, m.p. 106-108°, lit. (101, 102)]

(101) S. Danilov, J. Russ. Phys. Chem. Soc., 49, 282 (1917);

m.p. 105°] was crystallized from ethanol.

Triphenylacetaldehyde phenylhydrazone was prepared [m.p. 140-142°, lit. (101) m.p. 142°] from phenylhydrazine in acetic acid.

Triphenylacetaldehyde tosylhydrazone ••• Triphenylacetaldehyde (5.00 g., 0.0184 mole) and p-toluenesulfonyl hydrazide (tosyl hydrazide, 3.24 g., 0.019 mole), were refluxed with ethanol (175 ml.) for 5 hr. The ethanol (150 ml.) was removed by distillation; after cooling, triphenylacetaldehyde tosylhydrazone [7.18 g., 0.0163 mole, 89% yield, m.p. 210.7-211.7° (corr.)] was collected by filtration.

Anal. Calcd. for C_{27}H_{24}N_{2}O_{2}S: C, 73.61; H, 5.49; N, 6.36.
Found: C, 73.60; H, 5.30; N, 6.55.

1,2-Diphenyl-1-o-tolylethyleneglycol ••• o-Bromotoluene (25.0 g., 0.146 mole) was added to magnesium (3.51 g., 0.146 mole) in ether under nitrogen and stirred at room
temperature until most of the magnesium had reacted. Benzoin (10 g., 0.047 mole) was added; as soon as the initial reaction subsided, tetrahydrofuran (200 ml.) was added and the ether removed by distillation. The reaction was refluxed 14 hr., cooled, poured over ice and hydrochloric acid and the layers were separated; the solvent was removed by evaporation and 1,2-diphenyl-1-0-tolylethylene glycol [7.11 g., 0.023 mole, 50% yield, m.p. 154-155°, lit. (103)


m.p. 154-155°] was crystallized from ethanol.

Diphenyl-o-tolylacetaldehyde ••• 1,2-Diphenyl-1-0-tolylethylene glycol (7.11 g., 0.023 mole) was added to 98% formic acid (118 ml.) and stirred 16 hr. The mixture was cooled, filtered, and washed with cold 90% ethanol to yield diphenyl-o-tolylacetaldehyde [4.00 g., 0.014 mole, 61% yield, m.p. 162-163°, lit. (103) m.p. 163-164°].

Diphenyl-o-tolylacetaldehyde Tosylhydrazone •••
Diphenyl-o-tolylacetaldehyde (2.00 g., 0.007 mole) was dissolved in absolute ethanol (100 ml.) and added to p-tosyl hydrazide (1.40 g., 0.0075 mole) in absolute ethanol (25 ml.) and conc. hydrochloric acid (1 ml.). The solution was refluxed 5 hr. and part of the ethanol (75 ml.) was removed by distillation. The solution was cooled and
diphenyl-o-tolylacetaldehyde tosylhydrazone [2.94 g., 0.0065 mole, 92% yield, m.p. 202.0-203.6° (corr.)] was collected by filtration.

**Anal.** Calcd. for C_{28}H_{26}N_{2}O_{2}: C, 73.98; H, 5.76; N, 6.16. 
Found: C, 73.84; H, 5.56; N, 5.99.

**Triphenylacetonitrile** ... Triphenylchloromethane (10.46 g., 0.0365 mole) was powdered and mixed with cuprous cyanide (8.0 g.) and heated at 150-170° for 1 hr. The fused mass was extracted with benzene; the benzene was filtered and removed under reduced pressure. Triphenylacetonitrile [9.17 g., 0.034 mole, 93% yield, m.p. 126-127.5°, lit. (104)]


m.p. 127.5°] was crystallized from ethanol.

**2,2,2-Triphenylethylamine** ... Lithium aluminum hydride (3.80 g., 0.10 mole) was slurried in ether (50 ml.) under nitrogen. Triphenylacetonitrile (22.41 g., 0.083 mole) in ether (150 ml.) and benzene (75 ml.) was added slowly to the refluxing mixture. The mixture was refluxed overnight (12 hr.) and the excess hydride destroyed with water (15 ml.). The mixture was poured into 20% aqueous sodium potassium tartrate (900 ml.); the layers were separated; the aqueous portion was filtered, extracted with benzene, and the organic portions were combined and removed under reduced pressure.
2,2,2-Triphenylethylamine [19.41 g., 0.071 mole, 86% yield, m.p. 130-131°, lit. (105) m.p. 132°] was crystallized from benzene-petroleum ether (65-110°).

Ethyl N-β,β,β-Triphenylethyl Carbamate
(2,2,2-Triphenylethylurethane) ... Sodium carbonate (4.0 g., 0.038 mole) and ethyl chloroformate (3.4 g., 0.031 mole) were added to an aqueous (75 ml.) suspension of 2,2,2-triphenylethylamine (8.24 g., 0.03 mole) in an Erlenmeyer flask. The reaction mixture was swirled and the granular precipitate thoroughly triturated. The mixture was swirled with excess sodium carbonate, filtered, and washed with water. The solid was triturated with warm dilute hydrochloric acid, collected and dried. 2,2,2-Triphenylethylamine (1.30 g., 0.0046 mole) was recovered from the acid wash; the 2,2,2-triphenylethylurethane [7.33 g., 0.21 mole, 69% yield, m.p. 93-93.5°, lit. (106) m.p. 94°] was recrystallized from petroleum ether (65-110°).
Ethyl N-Nitroso-N-β,β,β-triphenylethyl Carbamate
(N-carbethoxy-N-nitroso-2,2,2-triphenylethylamine) ...

2,2,2-Triphenylethylurethane (4.5 g., 0.013 mole) was dissolved in dry ether (150 ml.); anhydrous sodium sulfate (9.5 g., freshly heated and cooled over phosphorus pentoxide) was added and the mixture was cooled in an ice bath. The gases produced by the action of 80% sulfuric acid on sodium nitrite and dried by passage through two calcium sulfate towers were swept into the vigorously stirred mixture by a stream of nitrogen. When the reaction mixture turned green (1.5 hr.), it was filtered to remove sodium sulfate, washing with ether. The solution was protected from the atmosphere and the ether was partially removed in a stream of dry air. The solution was then cooled in an ice-salt bath and filtered to collect N-carbethoxy-N-nitroso-2,2,2-triphenylethylamine [3.73 g., 0.01 mole, 77% yield, m.p. 111.5-112.5°, lit. (106) m.p. 114°].

2,2,2-Triphenyldiazoethane ... Sodium methoxide (0.60 g., 0.011 mole) in methanol (4 ml.) was added to N-carbethoxy-N-nitroso-2,2,2-triphenylethylamine (2.19 g., 0.00585 mole) in ether (60 ml.) and maintained at -20° (methanol-ice bath) for 3 hr. The ether was removed in a stream of dry air, maintaining the mixture at -15°. The yellow solid was triturated with ice-water, filtered, washed with ice-water, and dried over phosphorous pentoxide in an
evacuated desiccator at $0^\circ$. 2,2,2-Triphenyldiazoethane [1.46 g., 0.00515 mole, 88% yield, decomposition pt. 73-75$^\circ$, lit. (106) dec. pt. 75$^\circ$, infrared absorption at 5.0 $\mu$] decomposes slowly above $0^\circ$.

Diphenyl-$p$-tolylmethanol $\cdots$ $p$-Bromotoluene (20 g., 0.117 mole) was reacted with magnesium (2.80 g., 0.115 mole) in tetrahydrofuran under nitrogen. Upon completion of the reaction, benzophenone (20.8 g., 0.114 mole) in tetrahydrofuran was added and the mixture was refluxed 14 hr. The mixture was hydrolyzed with concentrated hydrochloric acid (35 ml.); the layers were separated and the aqueous layer was extracted with ether (3 x 100 ml.). The ether extracts were washed with saturated sodium chloride solution (1 x 100 ml.); the organic portions were combined, concentrated, and steam-distilled. Diphenyl-$p$-tolylmethanol [22.40 g., 0.082 mole, 71% yield, m.p. 73-74$^\circ$, lit. (107) (107) S. F. Acree, Ber., 37, 990 (1904). m.p. 73-74$^\circ$] was crystallized from petroleum ether (30-60$^\circ$).

Phenyl-di-$p$-tolylmethanol $\cdots$ Methyl benzoate (20 g., 0.147 mole) in tetrahydrofuran was added to the Grignard reagent prepared from magnesium (8.95 g., 0.368 mole) and $p$-bromotoluene (63 g., 0.368 mole) in tetrahydrofuran under nitrogen. The reaction mixture was refluxed 15 hr.; the product was hydrolyzed with 20% hydrochloric acid (70 ml.)
and the layers were separated. The aqueous portion was extracted with ether (3x100 ml.) and the ether extracts were washed with saturated sodium chloride solution (1x100 ml.). The combined organic portions were concentrated and then steam-distilled to yield a yellow oil. The oil was dissolved in ether and dried over magnesium sulfate, and the ether was removed under reduced pressure.

Phenyl-di-p-tolylmethanol [9.92 g., 0.0034 mole, 23% yield, m.p. 74.5-75.5°, lit. (108) m.p. 76.5-77.5°] was crystallized twice from petroleum ether (30-60°).

p-Chlorophenyldiphenylmethanol ... Benzophenone (94.0 g., 0.515 mole) in benzene (125 ml.) was added to the Grignard reagent prepared from magnesium (12.65 g., 0.522 mole) and p-bromochlorobenzene (100 g., 0.522 mole) in benzene. The mixture was refluxed 10 hr. and then hydrolyzed with dilute sulfuric acid. The layers were separated and the benzene solution was washed with 10% sulfuric acid (1x200 ml.) and saturated sodium chloride solution (1x200 ml.). The benzene extract was steam-distilled to yield a yellow oil which solidified on two days standing. p-Chlorophenyldiphenylmethanol [47.57 g., 0.161 mole, 31% yield, m.p. 82.5-83°, lit. (109) m.p. 85°] was crystallized from Skellysolve B.

(108) A. Kliegl, Ber., 38, 84 (1905).

(109) M. Gomberg and L. H. Cone, Ber., 39, 3274 (1906).
Diphenyl-p-tolylchloromethane (110) ⋯


Diphenyl-p-tolylmethanol (54.34 g., 0.198 mole) was dissolved in a minimum amount of benzene and heated to reflux. Acetyl chloride (50 ml.) was added and the mixture refluxed 15 min.; additional acetyl chloride (50 ml.) was added in 10 ml. portions over 15 min. The mixture was refluxed 1 hr., cooled, and diluted with petroleum ether (30-60°). On standing the precipitated diphenyl-p-tolylchloromethane [53.86 g., 0.184 mole, 93% yield, m.p. 91-93°, lit. (111) m.p. 99°] was collected.

Phenyl-di-p-tolylchloromethane ⋯ Phenyl-di-p-tolylmethanol (93.75 g., 0.325 mole) was treated in the same manner as diphenyl-p-tolylmethanol (page 55) to yield phenyl-di-p-tolylchloromethane [83.57 g., 0.272 mole, 84% yield, m.p. 94-100°, lit. (112) m.p. 106-107°].

(111) A. Bistrzycki and J. Gyr, Ber., 37, 655 (1904).

(112) M. Gomberg, Ber., 37, 1626 (1904).

p-Chlorophenyldiphenylchloromethane ⋯
p-Chlorophenyldiphenylmethanol (47.57 g., 0.161 mole) was treated in the same manner as diphenyl-p-tolylmethanol
(page 55) to give \textit{p}-chlorophenyldiphenylchloromethane

\[[48.54 \text{ g.}, 0.155 \text{ mole}, 93\% \text{ yield, m.p. } 86-87^\circ, \text{ lit. (113)}\]

\footnotesize


m.p. 88-89\(^\circ\}].

\textbf{Diphenyl-\textit{p}-tolylacetonitrile ...}

Diphenyl-\textit{p}-tolylchloromethane (53.86 g., 0.172 mole) was
heated with cuprous cyanide (50 g.) as was
triphenylchloromethane (page 50) to yield
diphenyl-\textit{p}-tolylacetonitrile \[[43.79 \text{ g.}, 0.155 \text{ mole}, 90\% \text{ yield, m.p. } 111-111.7^\circ \text{ (corr.), lit. (114) m.p. } 111^\circ\].

\footnotesize

(114) J. Hoch, Compt. rend., \textit{197}, 770 (1933).

\textbf{Anal. Calcd. for C}_{20}\text{H}_{17}\text{N: C, 89.01; H, 6.05; N, 4.94.}

\footnotesize

\textbf{Found: C, 88.85; H, 6.16; N, 5.01.}

\textbf{Phenyl-di-\textit{p}-tolylacetonitrile ...}

Phenyl-di-\textit{p}-tolylchloromethane (83.57 g., 0.272 mole) was
heated with cuprous cyanide (85 g.,) to give
phenyl-di-\textit{p}-tolylacetonitrile \[[76.14 \text{ g.}, 0.256 \text{ mole}, 94\% \text{ yield, m.p. } 131.8-132.7^\circ \text{ (corr.), lit. (115,116) m.p. } 132-133^\circ\].

\footnotesize

(115) D. Vorlander, \textit{Ber.}, \textit{44}, 2469 (1911);

Anal. Calcd. for C_{22}H_{19}N: C, 88.85; H, 6.44; N, 4.71.
Found: C, 86.97, 87.23; H, 6.20, 6.22; N, 4.90.

p-Chlorophenyldiphenylacetanitride ...

p-Chlorophenyldiphenylchloromethane (48.54 g., 0.155 mole) was heated with cuprous cyanide (50 g.) in the same manner as triphenylchloromethane (page 50) to give p-chlorophenyldiphenylacetanitride [40.56 g., 0.134 mole, 86% yield, m.p. 99.1-99.9° (corr.)].

Anal. Calcd. for C_{21}H_{14}ClN:
C, 79.07; H, 4.64; Cl, 11.67; N, 4.61.
Found: C, 79.12; H, 4.76; Cl, 11.55; N, 4.82.

Diphenyl-p-tolylacetaldehyde Tosylhydrazone ...

Boron trifluoride etherate (117) (70.8 g., 0.50 mole) in diglyme (25 ml.) was added slowly (1.5 hr.) to a stirred solution of diphenyl-p-tolylacetanitride (42.58 g., 0.15 mole) and sodium borohydride (14.18 g., 0.375 mole) in diglyme (117) under nitrogen. After a white precipitate formed, stirring was stopped and the mixture stored 16 hr. The mixture was hydrolyzed with water (50 ml.) followed by 20% hydrochloric acid (300 ml.) and stirred 3 hr. The precipitate was
filtered and washed with 10% hydrochloric acid and ether (118). The precipitate, presumably dimeric

After neutralization, extraction with ether, and crystallization from Skellysolve B, the acidic solution yielded 2,2-diphenyl-2-p-tolylethylamine [15.88 g., 0.055 mole, 37% yield, m.p. 92.0-92.5° (corr.)].

Anal. Calcd. for C_{21}H_{21}N: C, 87.76; H, 7.37; N, 4.87.
Found: C, 87.90; H, 7.33; N, 5.01.

The ether wash yielded an organoboron compound [22.07 g., white, crystalline solid, melting over a wide range (80-120°)]. The infrared spectrum of this material showed B-H absorption at 2260, 2340, and 2450 cm.\(^{-1}\), and weak imine absorption at 1640 cm.\(^{-1}\). The hydrolysis of this material (22.0 g.) with boiling diglyme and hydrochloric acid (This procedure is described in detail below for 2,2-diphenyl-2-p-tolylethylideneamino borane.) yielded 2,2-diphenyl-2-p-tolylethylamine (6.16 g.) and an oil (1.75 g.) which was converted to diphenyl-p-tolylacetaldehyde tosylhydrazone (0.63 g.).

2,2-diphenyl-2-p-tolylethylideneamino borane (21.15 g., 0.03 mole, 47% yield) (119) was dried, suspended in diglyme

(119) The general properties of these alkylideneamino boranes are discussed on page 77.

(200 ml.) and 10% hydrochloric acid (40 ml.), and refluxed until the amino borane dissolved and a fluffy white precipitate appeared. The mixture was cooled; the precipitate was dissolved by adding a little water; the solution was acidified with 20% hydrochloric acid and stored overnight. The products were extracted in ether; the ether extract was washed with water (5x100 ml.) and saturated sodium chloride solution (1x100 ml.). Removal of the ether under reduced
pressure yielded a colorless oil (19.03 g.). Its infrared spectrum shows carbonyl and imine absorption; it is believed to be a mixture of diphenyl-\(p\)-tolylacetaldehyde and diphenyl-\(p\)-tolylacetaldehyde imine. The oil was dissolved in ethanol; tosyl hydrazide (14.0 g.) and 20% hydrochloric acid (20 drops) were added. The solution was refluxed and concentrated to yield diphenyl-\(p\)-tolylacetaldehyde tosylhydrazone [12.77 g., 0.0282 mole, 39% yield, m.p. 190.0-190.6\(^\circ\) (corr.)].

**Anal.** Calcd. for \(C_{28}H_{26}N_2O_2S\): C, 73.97; H, 5.78; N, 6.16. Found: C, 74.08; H, 5.85; N, 6.09.

Oxidation of the tosylhydrazone with potassium permanganate in aqueous acetone yielded diphenyl-\(p\)-tolylacetic acid [m.p. 195-200\(^\circ\), lit. (120) m.p. 205\(^\circ\)].

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(120) A. Bistrzycki and K. Wehrbein, Ber., 34, 3079 (1901).

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Phenyl-di-\(p\)-tolylacetaldehyde Tosylhydrazone

Phenyl-di-\(p\)-tolylacetonitrile (63.44 g., 0.213 mole), sodium borohydride (17.0 g., 0.45 mole) and boron trifluoride etherate (85.2 g., 0.60 mole) were reacted in diglyme (275 ml.) in the same manner as diphenyl-\(p\)-tolylacetonitrile.

Dimeric 2-phenyl-2,2-di-\(p\)-tolylethylideneamino borane
(27.42 g., 0.044 mole, 41% yield) (119) was isolated (121).

(121) An oil (21.53 g) was isolated from the acid wash after neutralization and extraction with ether which crystallized as a white powder from Skellysolve B and is presumably 2-phenyl-2,2-di-p-tolyethylamine (m.p. 64-65°).

**Anal.** Calcd. for C_{22}H_{23}N: C, 87.66; H, 7.69; N, 4.65.

Found: C, 87.82; H, 7.41; N, 4.76.

The ether wash yielded 18.51 g. of an organoboron compound with infrared absorption at 2350, 2410 and 2480 cm.

The ether was hydrolyzed with diglyme and hydrochloric acid as described above, and treated with tosyl hydrazide. Phenyl-di-p-tolylacetaldehyde tosylhydrazone [16.67 g., 0.028 mole, 32% yield, m.p. 214.2-215.0° (corr.)] was crystallized from ethanol-benzene.

**Anal.** Calcd. for C_{29}H_{28}N_{2}O_{2}S: C, 74.33; H, 6.02; N, 5.98.

Found: C, 74.39; H, 5.86; N, 5.88.

p-Chlorophenylidiphenylacetaldehyde Tosylhydrazone •••
P-Chlorophenylidiphenylacetonitrile (35.86 g., 0.118 mole), sodium borohydride (8.52 g., 0.225 mole) and boron trifluoride etherate (42.6 g., 0.30 mole) were reacted in diglyme (115 ml.) in the same manner as diphenyl-p-tolylacetonitrile. Dimeric 2-p-chlorophenyl-2,2-diphenylethylideneamino borane (23.54 g.) (119) was isolated (122). The borane (1.00 g.)

(122) 2-p-Chlorophenyl-2,2-diphenylethyldiamine [9.78 g., 0.032 mole, 27% yield, m.p. 86.8-87.6° (corr.)]
was also isolated.

**Anal.** Calcd. for C$_{20}$H$_{18}$ClN:

- C, 78.04; H, 5.89; Cl, 11.52; N, 4.55.
- Found: C, 77.92; H, 5.78; Cl, 11.49; N, 4.60.

However no attempt was made to isolate the ether soluble organoboron observed in the previous reductions.

with diglyme (25 ml.) and 20% hydrochloric acid (5 ml.) and reacted with tosyl hydrazide (0.45 g.) to yield (123)

(123) The conversion of the borane to the tosylhydrazone on a 1.0 g. scale was successful four times; however the conversion failed when attempted on 10.12 g. of the borane.

**p-chlorophenyldiphenylacetaldehyde tosylhydrazone [0.42 g., m.p. 206.4-206.8° (corr.)].

**Anal.** (124) Calcd. for C$_{27}$H$_{23}$ClN$_2$O$_2$S:

- C, 68.27; H, 4.88; N, 5.90; Cl, 7.46.
- Found: C, 68.55; H, 4.86; N, 6.00; Cl, 7.35.

(124) Analysis by Schwarzkopf Microanalytical Laboratory, 5619 37th Ave., Woodside 77, New York, New York.

**p-Nitrobenzoyl Chloride** ... **p-Nitrobenzoic acid** (168 g., 1 mole) was refluxed with thionyl chloride (700 g., 455 ml.) until all the solid had dissolved (42 hr.). The excess thionyl chloride was removed by distillation at atmospheric pressure; the residue was poured into a 250 ml. Claisen flask equipped with a solids receiver and distilled under reduced pressure. **p-Nitrobenzoyl Chloride [180.6 g., 0.97**
mole, 97% yield, b.p. 155°/17 mm., m.p. 70-71.5°, lit. (125)

(125) H. Gevekoht, Ann., 221, 323 (1883).

m.p. 75°] was used without further purification.

**p-Nitrobenzophenone** → **p-Nitrobenzoyl chloride** (180.6 g., 0.97 mole) was dissolved in benzene (150 ml.) and added slowly to a stirred mixture of aluminum chloride (146.8 g., 1.1 mole) and benzene (250 ml.). The reaction was stirred at room temperature 3 hr., heated on a steam bath 1 hr., cooled, and poured into 20% hydrochloric acid (2 liters). The product was extracted with benzene; **p-nitrobenzophenone** [216 g., 0.95 mole, 98% yield, m.p. 136-137°, lit. (126)

(126) A. Basler, Ber., 16, 2714 (1883).

m.p. 138°] was recrystallized from benzene-ethanol.

**p-Nitrophenylphenyldichloromethane** → **p-Nitrobenzophenone** (216 g., 0.95 mole) was powdered and mixed with phosphorus pentachloride (210 g., 1.01 mole) and refluxed 1 hr. The phosphorus oxychloride was removed under reduced pressure and the black liquid remaining was dissolved in benzene. The benzene was washed with ice water (2x500 ml.) and dried over magnesium sulfate. The benzene was removed under reduced pressure and **p-nitrophenylphenyldichloromethane**
[232 g., 0.82 mole, 87% yield, m.p. 53-54°, lit. (127)

(127) A. Baeyer and V. Villiger, Ber., 37, 597 (1904).

m.p. 56-57°] was crystallized from Skellysolve B.

**p-Nitrophenyldiphenylchloromethane**

**p-Nitrophenylphenyldichloromethane** (185 g., 0.65 mole) in benzene (400 ml.) was added to aluminum chloride (129 g., 0.97 mole) suspended in benzene (1100 ml.). Benzene (220 ml.) was added after the addition was complete. The reaction mixture was stirred 26 hr. at room temperature and poured into 20% hydrochloric acid (2 l.). The layers were separated and the aqueous portion was extracted with ether (3x1 l.). The organic extracts were combined and concentrated; the solution was heated with acetyl chloride (100 ml.) for 0.5 hr. Dilution with Skellysolve F (500 ml.) and cooling produced no crystallization; the solvent was then removed under reduced pressure to yield a brown solid. After three recrystallizations from Skellysolve B, **p-nitrophenyldiphenylchloromethane** [140 g., 0.45 mole, 69% yield, m.p. 90-92°, lit. (128) m.p. 92-93°] was obtained as

(128) A. Baeyer and V. Villiger, Ber., 37, 606 (1904).

colorless needles.
p-Nitrophenyldiphenylacetonitrile...

p-Nitrophenyldiphenylchloromethane (63.56 g., 0.196 mole) was heated with cuprous cyanide (65 g.) at 130-140° for 1 hr. in the same manner as triphenylchloromethane (page 50). p-Nitrophenyldiphenylacetonitrile [42.70 g., 0.136 mole, 69% yield, m.p. 94.8-95.8° (corr.)] crystallized from ethanol as colorless needles.

Anal. Calcd. for C_{20}H_{14}N_{2}O: C, 76.42; H, 4.49; N, 8.91.
Found: C, 76.27; H, 4.69; N, 8.77.

p-Nitrophenyldiphenylacetaldehyde Tosylhydrazone...

p-Nitrophenyldiphenylacetonitrile (50.08 g., 0.159 mole), sodium borohydride (11.35 g., 0.40 mole) and boron trifluoride etherate (56.9 g., 0.40 mole) were reacted in diglyme (100 ml.) at 0°. The mixture was allowed to stand 1 hr. at 0° and then hydrolyzed with 20% hydrochloric acid (700 ml.). The precipitate, presumably dimeric 2-p-nitrophenyl-2,2-diphenylethylideneamino borane (38.90 g., 0.059 mole, 37% yield) was washed with 20% hydrochloric acid and vacuum-dried (129).

(129) There was also isolated an acid soluble oil which was not positively identified. The infrared spectra of the product isolated after neutralization with sodium hydroxide is consistent with the previously isolated amines and it is probably 2-p-nitrophenyl-2,2-diphenylethylamine.
The hydrolysis of the borane was effected under slightly different conditions than previously described. The borane (1.00 g., 0.00152 mole) was suspended in diglyme (20 ml.). The addition of 20% hydrochloric acid resulted in immediate evolution of gas. The mixture was refluxed 15 min. after solution occurred and then cooled to room temperature. The solution was diluted with water (10 ml.) and extracted with ether (25 ml.). The ether was washed with water (5x25 ml.) and saturated sodium chloride solution (1x25 ml.). The ether was removed under reduced pressure to yield an oil (0.08 g.) (130). The infrared spectrum indicates this oil

(130) The aqueous diglyme solution yielded an oil (1.05 g.) which on neutralization with sodium hydroxide produced an oil whose infrared spectrum is identical with the product believed to be 2-<i>p</i>-nitrophenyl-2,2-diphenylethylamine.

is <i>p</i>-nitrophenyldiphenylacetaldehyde (0.08 g., 0.00025 mole, 8% yield) (131). The oil gives a positive

(131) A duplication of this experiment using 11.37 g. (0.017 mole) borane yielded 0.60 g. (0.0019 mole, 11% yield) of the same oil.

2,4-dinitrophenylhydrazone test. Hydrolysis under the conditions previously described yielded identical results. The unpurified oil (0.07 g., 0.0022 mole) was treated with excess tosyl hydrazide in ethanol to yield <i>p</i>-nitrophenyldiphenylacetaldehyde tosylhydrazone (0.09 g.,
0.0020 mole, 90% yield, m.p. 191-192° (corr.). The isolation of the tosylhydrazone is difficult and was accomplished by slow crystallization from methanol or chromatography over silicic acid-celite (60:40). The tosylhydrazone was eluted by benzene.

**Anal. Calcd. for C\textsubscript{27}H\textsubscript{23}N\textsubscript{3}O\textsubscript{4}S:** C, 66.79; H, 4.77; N, 8.65.

**Found:** C, 66.45; H, 4.53; N, 8.58.

**p-Anisylidiphenylacetic Acid** ... Concentrated sulfuric acid (100 ml.) was added dropwise to a solution of benzilic acid (50 g., 0.219 mole) and anisole (24 g., 0.222 mole) in glacial acetic acid (200 ml.) maintaining the reaction mixture between 25 and 30° with external cooling. The mixture was stirred 6 hr. at room temperature and poured into ice and water (1 l.). The p-anisylidiphenylacetic acid [38.42 g., 0.12 mole, 55% yield, m.p. 201.5-202°, lit. (132,133) m.p. 200-200.5°] that separated was recrystallized from methanol.

**2-p-Anisyl-2,2-diphenylethanol** ... Thionyl chloride (200 g., 130 ml.) was added to p-anisylidiphenylacetic acid (38.42 g., 0.121 mole). The mixture was refluxed 30 min. after the
acid dissolved and evolution of hydrogen chloride ceased. The excess thionyl chloride was removed by distillation (65 ml.); the solution was poured into ice water (250 ml.) and extracted with ether. The ether extract was dried over anhydrous magnesium sulfate, concentrated, and added, under nitrogen, to a slurry of lithium aluminum hydride (8.0 g., 0.21 mole) in ether. The reaction mixture was refluxed 9 hr., and hydrolyzed with 20% hydrochloric acid (100 ml.); the product was extracted in ether. The ether was removed under reduced pressure and 2-p-anisyl-2,2-diphenylethanol [13.56 g., 0.0445 mole, 37% yield, m.p. 98.4-99.0° (corr.)] was fractionally crystallized from petroleum ether (65-110°). A second product (1.90 g., m.p. 180-185°) was not investigated.

**Anal. Calcd. for C_{21}H_{20}O_2**: C, 82.36; H, 6.62.
**Found**: C, 82.62; H, 6.73.

**p-Anisyl diphenylacetaldehyde** ... 2-p-Anisyl-2,2-diphenylethanol (7.0 g., 0.023 mole) in pyridine (70 ml.) was added to the complex from chromium trioxide (7.0 g.) and pyridine (70 ml.). The reaction mixture was stirred and stored overnight, poured into water (250 ml.), and extracted with ether (3x150 ml.). The ether extracts were combined and the ether removed under reduced pressure.

**p-Anisyl diphenylacetaldehyde** [3.18 g., 0.105 mole, 46% yield,
m.p. 73-74.5°, lit. (134) m.p. 75°] was crystallized from

(134) A. Orechow and M. Tiffeneau, Compt. rend.,
171, 475 (1920).

methanol.

\[ \text{p-Anisylidiphenylacetaldehyde Tosylhydrazone} \] \[ \cdots \text{Tosyl}

hydrazide (2.05 g., 0.011 mole) in ethanol (25 ml.) and 20% hydrochloric acid (15 drops) were added to

\[ \text{p-anisylidiphenylacetaldehyde} \] (3.18 g., 0.0105 mole) in ethanol (25 ml.). The solution was refluxed 4.5 hr.; the ethanol was partially removed by distillation and the solution was cooled. \[ \text{p-Anisylidiphenylacetaldehyde}

tosylhydrazone \] [3.96 g., 0.0084 mole, 80% yield, m.p.

153.9-154.9° (corr.)] was collected by filtration.

**Anal. Calcd. for C\text{28}H\text{26}N\text{2}O\text{3}S:** C, 71.46; H, 5.57; N, 5.95.

**Found:** C, 71.30; H, 5.38; N, 6.08.
Thermal Decomposition and Rearrangement of Tosylhydrazones

General Technique

Two general methods for the decomposition and rearrangement of the tosylhydrazones were used (135):

(135) No significant difference resulted in the use of either method.

1. Base (sodium methoxide), tosylhydrazone, and solvent (diethyl Carbitol) were mixed at room temperature and slowly heated to 160°.

2. Base (sodium methoxide or sodium amide) and solvent (diethyl Carbitol) were mixed and heated to a predetermined temperature (maintained at +1° by a Thermocap manufactured by Niagra Electron Laboratories, Andover, New York). The tosylhydrazone was added all at once, as a solid, to the heated mixture.

Reagents

Diethyl Carbitol was purified by long standing over potassium hydroxide followed by successive distillations from potassium hydroxide and calcium hydride at atmospheric pressure, and lithium aluminum hydride under reduced pressure. Gas chromatography indicated a purity of 99.86%. Sodium methoxide (Matheson, Coleman and Bell) was titrated and found to be 94% pure. It was stored under nitrogen and sealed with paraffin wax. Sodium amide (synthesized from
isoprene, sodium and liquid ammonia and having a titrated purity of 100% was kindly furnished by Mr. Bruce Otto and stored under nitrogen in a sealed container.

**Analysis of Rearrangement Products**

The same procedure was followed for the analysis of all rearrangement products. The diethyl Carbitol solution of the decomposed tosylhydrazone (10 ml.) was diluted with water (25 ml.) and the layers were separated. The organic portion was dissolved in ether (25 ml.) and washed with water (5x25 ml.). When sodium amide was the base used, the organic portion was also washed with dilute hydrochloric acid (1x25 ml.). The ether solution was then washed with saturated sodium chloride solution (1x25 ml.), and the ether removed under reduced pressure. The residue was dissolved in a mixture of acetone (60 ml.), water (20 ml.) and acetic acid (2 ml.) and oxidized with potassium permanganate (4:1 molar ratio) at room temperature for 1 hr. (136). The excess permanganate was destroyed with sodium bisulfite and the mixture was filtered; the precipitate was washed with acetone and hot water. The acetone was removed in an air stream on a steam bath and the aqueous residue was extracted with ether. The ether was washed with

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(136) The general procedure was that of C. J. Collins and W. A. Bonner, *J. Am. Chem. Soc.*, 75, 5372 (1953); 75, 5379 (1953).
saturated sodium bicarbonate solution to remove the acidic components. The bicarbonate solution was acidified with hydrochloric acid and extracted with ether. The ether solution of aromatic acids was concentrated, and an ethereal solution of diazomethane (prepared from N-nitroso-N-methylurea) was added until the yellow diazomethane color did not fade. The ether solution was dried over magnesium sulfate, concentrated, and the aromatic esters were analyzed by gas chromatography. The chromatographic column employed was Dow-Corning silicon oil #550, 5%, 15 ft., on Fluoropack (137).

(137) Fluoropack was purchased from Wilkens Instrument and Research, Inc., Walnut Creek, California.

A second esterification procedure was used for a few analyses. The acids were refluxed in excess methanol to which slightly more than 1 molar equivalent of 2,2-dimethoxypropane and a few drops of sulfuric acid had been added for 14-16 hr. Most of the excess solvent was removed, ether was added and the solution was washed with water, saturated sodium bicarbonate solution, and saturated sodium chloride solution. The solution was concentrated and used directly for gas chromatographic analysis. A number of large-scale (5.0 to 50.0 g.) runs showed the esterification to be quantitative.
Gas Chromatography

A model A-90-C Aerograph gas chromatographic instrument equipped with thermal conductivity cell detectors (helium carrier gas) and connected to a 2.5 millivolt full scale deflection Brown recorder was used for the analyses. Peak areas, calculated by multiplying the peak height by the peak width at half-height, were used to determine product composition. Quantitative measurements of the composition of many mixtures of organic compounds can be made by using the peak areas resulting from gas chromatographic analyses (138). No corrections were made for differences in the thermal conductivities of the compounds involved (139).


(139) Studies of a representative mixture containing aromatic, cyclic, and aliphatic hydrocarbons, acetone, acetaldehyde, and methyl and ethyl alcohols indicate that the maximum error resulting from the assumption that all the compounds possess the same thermal conductivity is 3.5% [M. Dimbat, P. E. Porter, and F. H. Stross, Anal. Chem., 28, 290 (1956)]. In the present study analyses made of known mixtures of methyl benzoate and methyl-$o$-toluate and methyl benzoate and methyl-$p$-toluate gave results deviating less than 1% from the known composition.

Decomposition of Triphenylacetaldehyde Tosylhydrazone ... Triphenylacetaldehyde tosylhydrazone (2.00 g., 0.0045 mole) was dissolved in diethyl Carbitol (20 ml.). Sodium
methoxide (0.27 g., 0.005 mole) was added and the stirred mixture was heated to 160°. The mixture turned orange and visible evolution of nitrogen began at 90°. Gas evolution was complete at 150°. The entire heating process required 1 hr. The nitrogen (100 ml., 86% yield) was collected (on the basis of corrections only for temperature and pressure, 116 ml. of nitrogen are expected). The diethyl Carbitol solution was diluted with water (25 ml.) and extracted with ether (24 ml.). The ether extract was washed with water (10x25 ml.) and removed under reduced pressure. Triphenylethylene (1.24 g., 0.0048 mole, 107% yield) containing a small amount of diethyl Carbitol was isolated but could not be crystallized [lit. (140) m.p. 69-70°].


The presence of triphenylethylene was verified in the following manner:

1. Comparison of its infrared and ultraviolet spectra with reported data (141,142).


2. The crude product (1.24 g.) was dissolved in carbon tetrachloride (2.5 ml.), cooled to 0°, and bromine (0.2 ml.) added. The solvent was evaporated and the product
recrystallized from Skellysolve B. Bromotriphenylethylene [1.34 g., 0.004 mole, 89% yield from tosylhydrazone, m.p. 110-112°, lit. (143,144) m.p. 115°] was obtained.


3. Oxidation of the crude product with potassium permanganate as previously described yielded benzoic acid (40% yield) and benzophenone (63% yield).

Decomposition of 2,2,2-triphenyldiazoethane 

2,2,2-Triphenyldiazoethane (1.46 g., 0.00515 mole) was dissolved in benzene (35 ml.) and heated at 60° for 18 hr. Nitrogen (93 ml. 75.5% yield) was evolved (based on corrections for temperature and pressure, 123 ml. nitrogen are expected). The benzene solution was concentrated and gas chromatographed (5 ft. Silicon GE-SF-96, 265°, flow rate 26 ml./min.). Only one product, triphenylethylene, was observed. Complete removal of benzene under reduced pressure yielded an oil (1.24 g.) which was chromatographed over silicic acid (15% Celite). Triphenylethylene (0.97 g., 0.0038 mole, 74% yield) was isolated as an oil which could not be crystallized. Oxidation of the oil (0.97 g., 0.0038 mole) with potassium permanganate in aqueous acetone as previously described yielded benzoic acid (0.39 g., 0.0032 mole, 84% yield).
Reduction of Triarylacetanitriles with Diborane

Reduction of Triphenylacetanitrile

Triphenylacetanitrile (1.09 g., 0.00372 mole) and sodium borohydride (0.38 g., 0.01 mole) were dissolved in diglyme [8 ml., diglyme was purified by storage over calcium hydride followed by distillation (b.p. 66°/15 mm.) from lithium aluminum hydride].

Boron trifluoride etherate [1.90 g., 0.0133 mole, purified by distillation from calcium hydride (b.p. 45°/10 mm.)] in diglyme (5 ml.) was added slowly to the stirred solution under nitrogen. At this point a white precipitate formed. The mixture was allowed to stand 11 hr., hydrolyzed with water (150 ml.) and stirred 1.5 hr. The precipitate (145)

(145) This product is dimeric 2,2,2-triphenylethylideneamino borane. The structure proof is described at the conclusion of this experimental section (page 77).

was filtered and dried (0.60 g., 0.00196 mole, 56% yield). The filtrate was made basic with sodium hydroxide solution and 2,2,2-triphenylethylamine (0.42 g., 0.00153 mole, 41% yield, m.p. 129-130°) was collected by filtration.

Triphenylacetanitrile (1.0 g., 0.00372 mole), sodium borohydride (0.38 g., 0.01 mole) and boron trifluoride etherate (1.90 g., 0.0133 mole) were reacted in diglyme as described above. The reaction product was hydrolyzed by refluxing with conc. hydrochloric acid (40 ml.) and water (10 ml.) for 18 hr. The hot mixture was filtered through
glass wool to remove undissolved material, cooled, and made basic with sodium hydroxide solution.

2,2,2-Triphenylethylamine (0.53 g., 0.00194 mole, 52% yield, m.p. 125-129°) was collected by filtration.

Triphenylacetonitrile (1.0 g., 0.00372 mole), sodium borohydride (0.38 g., 0.01 mole) and boron trifluoride etherate (1.90 g., 0.0133 mole) were reacted in diglyme as described above. The reaction was allowed to stand 2.5 hr. and was hydrolyzed with conc. sulfuric acid (10 ml.). The mixture was stirred 3 hr. and diluted with water (80 ml.). 2,2,2-Triphenylethylideneamino borane (0.40 g., 0.0007 mole, 33% yield) was collected by filtration. The filtrate was made basic with sodium hydroxide solution and 2,2,2-triphenylethylamine (0.63 g., 0.0023 mole, 62% yield m.p. 129-130.5°) was collected by filtration.

Reduction of p-Anisyldiphenylacetonitrile...

p-Anisyldiphenylacetonitrile (52.46 g., 0.175 mole) and sodium borohydride (14.18 g., 0.375 mole) were dissolved in diglyme (175 ml.). Boron trifluoride etherate (70.8 g., 0.50 mole) in diglyme (25 ml.) was added slowly (2.5 hr.) to the stirred solution under nitrogen. The mixture was allowed to stand 17 hr.; it was hydrolyzed with water (50 ml.) and stirred with 20% hydrochloric acid (300 ml.). The precipitate, presumably p-anisyldiphenylethylideneamino
borane, (31.45 g., 0.050 mole, 57% yield) was filtered, and washed with 10% hydrochloric acid (250 ml.) and ether. The acid wash was made basic and extracted with ether; the ether was washed with water (5x250 ml.) and saturated sodium chloride solution (1x250 ml.) and removed under reduced pressure. 2-p-Anisyl-2,2-diphenylethylamine [16.94 g., 0.056 mole, 32% yield, m.p. 88.8-89.8° (corr.)] was crystallized from Skellysolve B.

**Anal. Calcd. for C_{21}H_{21}NO:**  C, 83.13; H, 6.98; N, 4.62.
**Found:**  C, 82.98; H, 6.80; N, 4.66.

A second organoboron compound (14.83 g., oil, weak infrared B-H absorption at 2460 cm.\(^{-1}\)) was isolated from the ether wash, but it was not investigated.

**Structure Proof of Alkylideneamino Boranes**  
1. **Infrared spectra**  
   Each alkylideneamino borane had an absorption band at 1660 cm.\(^{-1}\), attributed to C=N stretching (146), and a doublet at 2400 and 2350 cm.\(^{-1}\), attributed to the boron-hydrogen stretching of a quarternery boron (147).


(147) Private communication from Dr. S. Shore of this laboratory.
Hawthorne (148) found a C=N stretching band at 1660 cm.\(^{-1}\) and a B-H stretching band at 2390 cm.\(^{-1}\) in alkylideneamino tert-butylboranes; in arylideneamino tert-butylboranes he found C=N stretching at 1640 cm.\(^{-1}\) and either a B-H stretching doublet at 2400 and 2350 cm.\(^{-1}\) or a sharp singlet at 2350 cm.\(^{-1}\). He feels the doublet is undoubtedly the result of interactions in the crystalline state since it appears as a single sharp band in methylene chloride solution. Hence, the spectral characteristics observed by Hawthorne compare exactly with those found in this research.

2. Molecular weight (149) ... The molecular weight of

(149) Molecular weights were determined using a vapor pressure osmometer, Model 301 A, purchased from Mechrolab Inc., Mountain View, California.

2,2,2-triphenylethylideneamino borane was determined in benzene to be 535 (150) and in 1,2-dichloroethane to be 566.

(150) This determination was made with 0.002 molar solution and is less than the optimum (0.005 to 0.01 molar) recommended by the manufacturer. Therefore, the accuracy of the reading is only +10%. The other determinations are accurate to +1%.

The calculated molecular weight of the dimer is 566. The molecular weight of 2-\(\rho\)-chlorophenyl-2,2,2-diphenylethylideneamino borane was found in 1,2-dichloroethane to be 639 (calculated dimer, 635).
3. Chemical reactions ... 

a. Hydrogen peroxide (2.5 ml., 30%) and sodium hydroxide (2 ml., 3 N.) were added to 2-\( p \)-chlorophenyl-2,2-diphenylethylideneamino borane (1.00 g.) dissolved in diglyme (25 ml.). The mixture was allowed to stand 1.5 hr. Water and ether were added; the layers were separated and the ether was washed with water and saturated sodium chloride solution. The ether was removed under reduced pressure and the product (0.48 g., m.p. 70-100°) was crystallized from methanol. Recrystallization from benzene-ethanol yielded a white solid (m.p. 98-104°). The infra-red spectrum indicated this solid is an oxime. Qualitative analysis (sodium fusion) showed the presence of nitrogen and chlorine.

b. 2-\( p \)-Chlorophenyl-2,2-diphenylethylideneamino borane (1.00 g.) was heated with conc. sodium hydroxide (25 ml.) for 1 week. No reaction occurred. No reaction occurred with conc. ammonium hydroxide.

c. 2-\( p \)-Chlorophenyl-2,2-diphenylethylideneamino borane (1.00 g.) was dissolved in diglyme (25 ml.) and heated with sodium hydroxide (25 ml. 8 N.) for 1 hr. After work-up, 2-\( p \)-chlorophenyl-2,2-diphenylethylamine (0.71 g., m.p. 86-88°) was isolated.

d. 2-\( p \)-Chlorophenyl-2,2-diphenylethylideneamino borane (1.00 g.) was dissolved in boiling diglyme (25 ml.).
Aluminum chloride was added; the mixture was warmed for 0.5 hr. and allowed to cool. The mixture was diluted with a little water to dissolve all solid material, charcoaled, and extracted with ether. The ether was washed with water and saturated sodium chloride solution and removed under reduced pressure. An oil (0.56 g.) was isolated; its infrared spectrum shows carbonyl and imine absorption, but no boron-hydrogen absorption. The oil formed a 2,4-dinitrophenylhydrazone (m.p. 197-199°) and $p$-chlorophenyldiphenylacetaldehyde tosylhydrazone (page 60).

Refluxing 2-$p$-chlorophenyl-2,2-diphenylethylideneamino borane (1.00 g.) in diglyme (25 ml.) for 3 hr. without adding aluminum chloride yields a similar oil (1.03 g.) whose infrared spectrum differs from that above only in the relative intensity of the carbonyl and imine absorption. This oil also yields the $p$-tosylhydrazone (0.42 g.). Refluxing 2-$p$-chlorophenyl-2,2-diphenylethylideneamino borane (1.00 g.) in diglyme (25 ml.) and 20% hydrochloric acid (5 ml.) 3 hr. yielded an oil (0.69 g.) similar to the others which was converted to the tosylhydrazone (0.46 g.).

Similar results were obtained with diphenyl-$p$-tolylethylideneamino borane (page 57), di-$p$-tolylphenylethylideneamino borane (page 59), and $p$-anisyldiphenylethylideneamino borane.
4. Physical properties ••• The triarylethylideneamino boranes have no distinct melting point. They decompose over a temperature range which seems to have some dependence on the rate of heating. After several recrystallizations from chloroform, triphenylethylideneamino borane decomposed at @ 165-170°, but was stable for 3 minutes in a bath preheated to 205°. Decomposition at 205° occurred with visible gas evolution. Phenyl-di-p-tolylethylideneamino borane had a decomposition point of 201-208°; p-chlorophenyl-diphenylethylideneamino borane decomposed at 227-230°. A brief examination of the solubility of triphenylethylideneamino borane indicated slight solubility in chloroform, 1,2-dichloroethane, hot tetrahydrofuran and hot benzene and insolubility in acetone, cyclohexane, petroleum ether (65-110°), ether, cold tetrahydrofuran, cold benzene, methanol, ethanol, water, hydrochloric acid and sodium hydroxide.
Reduction of Triarylacetonitriles with

Lithium Aluminum Hydride

Intermediates

Diphenyl-o-tolylmethanol ••• o-Bromotoluene (50 g., 0.292 mole) and magnesium (7.1 g., 0.292 mole) were stirred in tetrahydrofuran (125 ml.) under nitrogen. Benzophenone (52.4 g., 0.290 mole) in tetrahydrofuran (250 ml.) was slowly added and the reaction mixture was refluxed overnight. The reaction mixture was poured into 20% hydrochloric acid (100 ml.); the layers were separated and the aqueous portion extracted with ether (2x200 ml.). The organic layers were combined, concentrated, and steam-distilled to yield a white solid which was dissolved in ether and dried over magnesium sulfate. The ether was removed under reduced pressure and diphenyl-o-tolylmethanol [62.9 g., 0.23 mole, 79% yield, m.p. 99°, lit. (151)


m.p. 97-99°] was crystallized from benzene-petroleum ether (65-110°).

Diphenyl-o-tolylchloromethane ••• Diphenyl-o-tolylmethanol (54.56 g., 0.199 mole) was warmed with benzene (50 ml.). Acetyl chloride (50 ml.) was added and the solution refluxed
15 min. Acetyl chloride (50 ml.) was added in 10 ml. portions in 10 min. and the solution was refluxed 1 hr. The solution was cooled, diluted with petroleum ether (30-60°, 500 ml.) and placed in a freezer.

Diphenyl-o-tolylchloromethane [54.91 g., 0.187 mole, 94% yield, m.p. 128-132°, lit. (151) m.p. 135°] was collected by filtration.

**Diphenyl-o-tolylacetonitrile ...**

Diphenyl-o-tolylchloromethane (57.44 g., 0.196 mole) was heated with cuprous cyanide (60 g.) as was triphenylchloromethane (page 50).

Diphenyl-o-tolylacetonitrile [50.03 g., 0.177 mole, 90% yield, m.p. 120.4-120.8° (corr.)](152) was crystallized from methanol.

**Anal.** Calcd. for C_{21}H_{17}N: C, 89.05; H, 6.05; N, 4.94.

    Found: C, 88.99; H, 6.22; N, 5.01.

**p-Bromoanisole ...** Anisole (108 g., 1 mole) was dissolved in chloroform (200 ml.) and cooled to 0° in an ice-bath. Bromine (160 g., 1 mole) was added slowly (2 hr.) to the stirring solution. After 1 hr. of additional stirring,
water (300 ml.) was added and the chloroform layer was separated, washed with saturated sodium bicarbonate (2x200 ml.), and saturated sodium chloride solutions (1x300 ml.), dried over magnesium sulfate, and concentrated under reduced pressure. Distillation yielded 

\[ \text{p-bromoanisole (174.4 g., 0.93 mole, 93\% yield, b.p. 92-94^\circ/9 \text{ mm.}, 77-78^\circ/3 \text{ mm.})} \]

\[ \text{p-Anisyldiphenylchloromethane} \ldots \text{p-Bromoanisole (112 g., 0.60 mole) and magnesium (14.55 g., 0.60 mole) were stirred in ether for 8 hr. under nitrogen. The ether was distilled and replaced by benzene. Benzophenone (107 g., 0.59 mole) in benzene (200 ml.) was added and the mixture refluxed 12 hr. The mixture was hydrolyzed with 20\% hydrochloric acid (400 ml.) and the layers separated. The benzene extract was washed with 20\% hydrochloric acid (2x200 ml.) and saturated sodium chloride solution (2x200 ml.), concentrated and steam-distilled. The oily residue was dissolved in benzene (75 ml.), refluxed with acetyl chloride (180 ml.) for 30 min., diluted with petroleum ether (30-60\^\circ) and cooled in a refrigerator for three weeks.} \]

\[ \text{p-Anisyldiphenylchloromethane [30.50 g., 0.099 mole, 17\% yield, m.p. 115-117^\circ, lit. (153) m.p. 124^\circ] was recrystallized from benzene-petroleum ether (65-110^\circ).} \]

(153) A. Baeyer and V. Villiger, Ber., 36, 2774 (1903).
p-Anisylidiphenylacetonitrile ••• p-Anisylidiphenylchloromethane
(30.5 g., 0.099 mole) was heated with cuprous cyanide (35 g.)
as was triphenylchloromethane (page 50).
p-Anisylidiphenylacetonitrile [29 g., 0.97 mole, 98% yield,
m.p. 116.8-117.5° (corr.), lit. (154) m.p. 117-118°]

(154) J. Lifschitz and G. Girbes, Ber., 61, 1463 (1928).
crystallized from methanol as white, polyhedric crystals.

Anal. Calcd. for C_{21}H_{17}NO:  C, 84.25; H, 5.72; N, 4.68.
    Found:  C, 84.01; H, 5.57; N, 4.86.

Methyl p-bromobenzoate ••• p-Bromobenzoic acid (90 g.,
0.445 mole) was dissolved in hot methanol (1400 ml.).
2,2-Dimethoxypropane (57.5 g., 0.55 mole) and conc. sulfuric
acid (2 ml.) were added and the reaction was refluxed 67 hr.
Most of the solvent (1200 ml.) was removed by distillation
and on cooling a white, crystalline solid precipitated.
Methyl p-bromobenzoate [88 g., 0.41 mole, 92% yield, m.p.
75-76°, lit. (155) m.p. 79-80°] was recrystallized from


petroleum ether (65-100°).
p-Bromophenyldiphenylchloromethane ... Bromobenzene (134 g., 0.85 mole) was stirred with magnesium (20.6 g., 0.85 mole) in tetrahydrofuran (250 ml.) under nitrogen. Methyl p-bromobenzoate (88 g., 0.409 mole) in tetrahydrofuran (200 ml.) was added slowly; the solution was refluxed 18 hr. and hydrolyzed with hydrochloric acid (100 ml.) and water (50 ml.). The aqueous portion was extracted with ether (3x200 ml.). The organic extracts were combined, washed with saturated sodium chloride solution, concentrated, and steam-distilled to produce a yellow oil. This oil would not crystallize; it was dissolved in benzene and refluxed with acetyl chloride (100 ml.) for 3 hr. and diluted with petroleum ether (30-60°). Upon cooling, p-bromophenyldiphenylchloromethane [114 g., 0.32 mole, 78% yield, m.p. 101-106°, lit. (113) m.p. 113-114°] was collected by filtration.

p-Bromophenyldiphenylacetonitrile ...

p-Bromophenyldiphenylchloromethane (114 g., 0.32 mole) was heated with cuprous cyanide (120 g.) in the same manner as triphenylchloromethane (page 50).

p-Bromophenyldiphenylacetonitrile [101 g., 0.29 mole, 90% yield, m.p. 129.4-130.3° (corr.)] crystallized as white needles from ethanol.
Reduction of Triphenylacetonitrile (156) •••

(156) The reduction of triphenylacetonitrile with lithium aluminum hydride in refluxing ether is described on page 50.

Triphenylacetonitrile (6.13 g, 0.0228 mole) was dissolved in ether (60 ml.) and cooled to -70°. Lithium aluminum hydride (1.0 g., 0.026 mole) in ether (20 ml.) was added slowly; the mixture was stirred for 20 min. and allowed to warm to room temperature (1 hr.). The excess hydride was hydrolyzed with a few drops of water and 20% hydrochloric acid (60 ml.). The layers were separated; the aqueous portion was extracted twice with ether and the ether extracts were combined. The ether extract was washed with saturated sodium bicarbonate solution (3x50 ml.) and then concentrated. Fractional crystallization from ethanol yielded triphenylacetonitrile (2.0 g., 0.007 mole, 30% recovery, m.p. 124-125°) and triphenylmethane (1.0 g., 0.004 mole, 17% yield, m.p. 90-91°).

Reduction of Diphenyl-o-tolylacetonitrile •••

Diphenyl-o-tolylacetonitrile (35.48 g., 0.125 mole) in ether was added slowly to a slurry of lithium aluminum
hydride (11 g., 0.29 mole) in ether under nitrogen. The reaction mixture was refluxed 12 hr., cooled, and poured into potassium sodium tartrate (200 g.) in water (500 ml.). The organic layer was decanted and the remainder filtered. The filtrate was extracted with benzene; the organic portions were combined and concentrated under reduced pressure. Diphenyl-o-tolylmethane [29.0 g., 0.108 mole, 87% yield, m.p. 80-81°, lit. (157) m.p. 82-83°] was crystallized from

(157) A. Bistrzycki and J. Gyr, Ber., 37, 1245 (1904).

acetone-water (158).


Reduction of p-Anisylidiphenylacetonitrile ...

p-Anisylidiphenylacetonitrile (28.31 g., 0.94 mole) dissolved in ether (500 ml.) and tetrahydrofuran (50 ml.) was added to a slurry of lithium aluminum hydride (8.0 g., 0.21 mole) in ether (75 ml.) under nitrogen. The reaction mixture was refluxed overnight, cooled, and poured into a solution of potassium fluoride (200 g.) in water (300 ml.). The organic layer was decanted and the remainder was filtered. The filtrate was extracted with benzene; the organic portions upon concentration gave an oil which resisted all attempts at crystallization. The product was dissolved in ether and
washed with 20% hydrochloric acid. After the ether had been removed under reduced pressure, \( p \)-anisylidiphenylmethane [7.41 g., 0.027 mole, 29% yield, m.p. 59-60°, lit. (159)]

(159) A. Bistrzycki and C. Herbst, Ber., 35, 3133 (1902).

m.p. 61°] was crystallized from methanol-chloroform. The acid wash did not yield additional material.

Reduction of \( p \)-Bromophenyldiphenylacetonitrile ...

\( p \)-Bromophenyldiphenylacetonitrile (100 g., 0.288 mole) dissolved in ether (500 ml.) and tetrahydrofuran (200 ml.) was added to a slurry of lithium aluminum hydride (25.8 g., 0.60 mole) in ether under nitrogen. The mixture was refluxed overnight, cooled, and poured into a solution of potassium fluoride (200 g.) in water (500 ml.). The organic layer was decanted and the remainder was filtered. The filtrate was extracted with benzene; the organic portions were combined and the solvent removed under reduced pressure to yield a solid (48.11 g.). The precipitate was digested with benzene; removal of the benzene yielded additional semi-solid (28 g.). After several recrystallizations from acetone-water and from benzene, triphenylmethane [21.86 g., 0.09 mole, 31% yield, m.p. 93-93.4° (corr.), lit. (160) m.p. 92.5°] was isolated. The structure was
verified by the absence of nitrogen and bromine, comparison of its infrared spectrum with authentic triphenylmethane, and analysis:

Calcd. for C\textsubscript{19}H\textsubscript{16}: C, 93.40; H, 6.56.

Found: C, 93.23, 93.66; H, 6.74, 6.73.
AUTOBIOGRAPHY

I, Peter Barry Sargeant, was born in Cedar Rapids, Iowa, January 18, 1936. I received my elementary and secondary education (Wilson High School) in the public schools of Cedar Rapids. I was awarded a Bachelor of Science degree in Chemical Technology by Iowa State University in June, 1958. While completing the requirements for the degree of Doctor of Philosophy at The Ohio State University, I have been a Research Fellow and a National Science Foundation Fellow.