[Contribution from the Richardson Chemistry Laboratories, Tulane University]

TRITYLATION OF AROMATIC COMPOUNDS

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Received October 12, 1954

A. WITH TRIPHENYLCHLOROMETHANE

Triphenylchloromethane has been employed, to a limited extent, as a reagent for the introduction of the triphenylmethyl group into aromatic compounds. When the benzene ring is substituted with the groups —OH (1–7) and —NR_2 (8) the reaction leads to a good yield of *para*-tritylated product.

To this group may be added —NH_2, —NHR, —OR, and —$NHCOCH_3$. Ethers (anisole and phenetole) were cleaved by the reagent and the *p*-hydroxytetraphenylmethane was obtained in each case. Cleavage to *p*-aminotetraphenylmethane was not observed with acetanilide; the product isolated was *p*-acetaminotetraphenylmethane. A similar result was reported by Hickinbottom (8) for N-methylacetanilide.

A reaction was not observed when the substituent was nitro, carboxyl, chloro, bromo, iodo, and alkyl. With thiophenol only the sulfide was obtained; when the reaction was carried out at a higher temperature, triphenylmethane was formed but none of the *para*-tritylated product was isolated.

It has been claimed by van Alphen (3) that lateral substitution occurs with *o*-cresol. Parson and Porter (6) agreed with this view whereas Iddles and coworkers (9) and Boyd and Hardy (5) presented evidence to show it was in error. The matter has been further discussed recently by Baker (26). In the present work alkylbenzenes were found to be unreactive with trityl chloride; neither lateral nor nuclear substitution occurred.

Triphenylmethane has been reported as a product in some of the reactions (3, 5, 8, 10). It was observed by the present authors that when tritane was formed it was always accompanied by an uncrystallizable, gummy substance of, as yet, unknown composition. Sometimes, as with dimethylaniline, the *p*-trityl derivative was obtained also from the reaction mixture.

There is some reason to believe that at the relatively high temperatures employed, a free radical reaction is involved in the formation of the triphenylmethane. For example, when trityl chloride is heated alone it is converted, in part, to 9-phenylfluorene and triphenylmethane (11). It is difficult to explain the products obtained (or the triphenylmethane, resinous-like material, and hydrogen chloride of the present work) except by a reaction involving the homolytic cleavage of the carbon-chlorine bond. Furthermore, when the triphenylmethyl free radical is treated with hydrogen chloride, in the absence of light, it is changed to tritane and trityl chloride (12). In view of these circumstances

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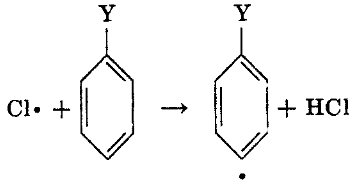
it seems reasonable to consider the present reaction leading to triphenylmethane formation as proceeding as follows:

(A) $$(C_6H_5)_3CCl \rightarrow (C_6H_5)_3C\cdot + Cl\cdot$$

(B)

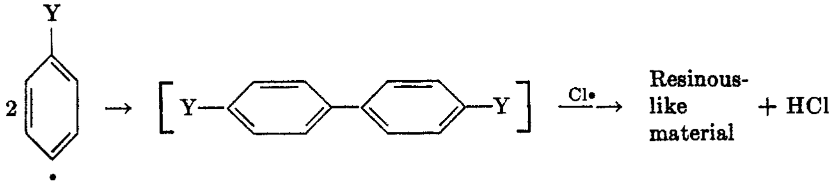


Y = A strong *ortho*- and *para*-directing group

(C) $$2(C_6H_5)_3C\cdot + HCl \rightarrow (C_6H_5)_3CH + (C_6H_5)_3CCl$$

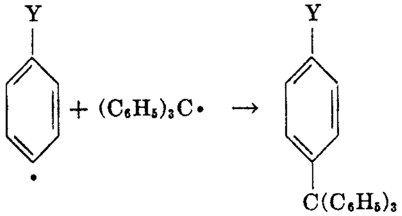
Evidence is not available to account for the disappearance of the starting substituted benzene compound. No simple compound such as  was ever found in any of the reaction mixtures. One could speculate that a reaction of this type occurred:

(D)



The diphenyl derivative, shown as the intermediate, was never isolated; if it formed, the reaction must have continued in a direction leading to the resinous product.

Since the *para*-tritylated product is sometimes obtained with the tritane its formation may occur by the combination of the phenyl free radical of Step B with the triphenylmethyl free radical of Step A:



It is not likely that the *para*-tritylated compound serves as an intermediate in the triphenylmethane formation since it was not possible to cleave it with dry hydrogen chloride.

Triphenylmethane formation was prevented by keeping the temperature as low as possible and, in a practical way, not more than 10° above the point at which the evolution of hydrogen chloride was first noted.

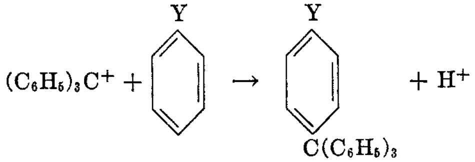
In attempting to explain how the *para*-tritylation reaction occurred, van

Alphen (3, 10) thought that with phenols and *o*-toluidine an addition reaction first took place at the oxygen or nitrogen atoms followed by the elimination of hydrogen chloride; the ether or N-substituted amine formed then underwent a rearrangement reaction to produce the *para*-tritylated product. Van Alphen's view was based mainly on the observation that when phenol was treated with trityl chloride in pyridine, the hydrogen chloride was held by the pyridine and rearrangement did not occur; only the ether was obtained.

Recent kinetic data by Hart and Cassis (13) indicates that, with phenol, the ether is not an intermediate. Instead the trityl chloride appears to dissociate in the presence of the phenol to a triphenyl carbonium ion:

$$(C_6H_5)_3CCl \rightleftharpoons (C_6H_5)_3C^+ + Cl^-$$

The *para*-tritylated product then results from the attack of the carbonium ion at the *para* position, thus



Evidence in support of the latter idea and opposed to the former may be listed as follows:

1. Jones and Seymour (14) failed in their efforts to obtain an onium salt from trityl chloride and trimethylamine. It seems unlikely, for steric reasons, that an amine such as dimethylaniline would form such a salt in the tritylation reaction.

2. Hickinbottom (8) concluded that the tritylation of N-methylacetanilide involved a direct attack of a trityl ion at the *para* position.

3. In a related reaction (5), triphenylcarbinol used alone with phenol gave the *para* product. In this case any ether formed would have to undergo rearrangement in the absence of a strong acid. In this connection it was not possible in this investigation to convert tritylphenyl ether to the *para*-tritylated product by the action of heat alone up to 200°. The same statement can be made for N-tritylaniline.

4. In the present work it was not possible to isolate N-triphenylmethylaniline from the action of trityl chloride on aniline; only the *para*-tritylated product was obtained. Operating at temperatures thought favorable for the formation of the N-substituted product did not lead to its isolation.

5. Kinetic data of Hart and Cassis previously cited.

6. The reaction proceeds most readily in the presence of reagents which would be expected to promote the dissociation of the trityl chloride:

$$(C_6H_5)_3CCl \rightleftharpoons (C_6H_5)_3C^+ + Cl^-$$

In this laboratory it was found that alkylbenzenes are inert to trityl chloride. This is attributed not so much to a lack of ring activation, as to the failure of the reagent to assist in the dissociation of the chloride. It has been shown in the following section (Part B) that under more favorable conditions, *i.e.*, triphenylcarbinol in an acetic acid-hydrochloric acid mixture, toluene will substitute the trityl group in the *para* position.

Table I lists pertinent information for the various compounds used.

EXPERIMENTAL

General procedure. Triphenylchloromethane and the compound to be tritylated were mixed in an approximately 1:1 molar ratio with the aromatic compound in a very slight excess. A solvent was not employed. A two-necked flask, fitted with a thermometer, condenser, and drying tube was used. All known compounds prepared were checked by employing the mixture melting point technique with authentic samples.

Structural proof of *p*-acetaminotetraphenylmethane was obtained by (a) acetylation of *p*-aminotetraphenylmethane and (b) hydrolysis of the compound to *p*-aminotetraphenylmethane.

Acetylation of p-aminotetraphenylmethane. A mixture of 2.0 g. of *p*-tritylaniline, 20 ml. of glacial acetic acid, and 10 ml. of acetic anhydride was refluxed for 7 hours. The mixture was cooled to room temperature and poured into a beaker containing 75 ml. of cold water. The taffy-like material which formed gradually solidified and was recrystallized from tolluene; m.p. 233–234°. A mixture of this compound and the one obtained from the tritylation of acetanilide showed no depression in the melting point.

Hydrolysis of p-acetaminotetraphenylmethane. One gram of *p*-acetaminotetraphenylmethane, from either of the two sources previously described, was mixed with 5.0 ml. of concentrated hydrochloric acid and 15 ml. of glacial acetic acid. The mixture was refluxed for six hours then transferred to a beaker containing about 50 g. of ice and water. The solid obtained was recrystallized from toluene; m.p. 256–257°. A mixture of this compound and an authentic sample of *p*-aminotetraphenylmethane showed no depression in the melting point.

SUMMARY

1. The tritylation of benzene substituted with the groups OH, OR, NH_2, NHR, NR_2, and $NHCOCH_3$ with trityl chloride gave compounds with the trityl group substituted exclusively in the *para* position. Ethers were cleaved so that the product obtained was *p*-hydroxytetraphenylmethane. The acetyl group was not removed from acetanilide.

2. The following compounds were inert to the reagent: nitrobenzene, benzoic acid, chloro-, bromo-, and iodo-benzenes. With alkylbenzenes neither lateral nor nuclear substitution occurred.

3. Thiophenol gave only the sulfide.

4. Triphenylmethane formation was explained on the basis of a free radical mechanism. The formation of this undesirable product was prevented by a proper control of reaction temperatures.

5. Evidence was offered to show that the *para*-tritylation reaction involved an attack on the *para* position by a triphenyl carbonium ion.

B. WITH TRIPHENYLCARBINOL

Many tetraphenylmethane compounds have been prepared by the method first described by Baeyer and Villiger (18). The process involves the treatment

TABLE I

TRIPHENYLCHLOROMETHANE

Compound	Temperature	Reaction time	M.P.[a], °C.		Ref.	Yield, %	Product	Crystallized from
			Found	Lit.				
Thiophenol	40–45	8 hours	105.0–105.5	105	(2)	90	Triphenylmethylphenyl sulfide	Ethanol
Thiophenol	80 or higher	6 hours	93.0–93.5	92–93	(8)	83	Triphenylmethane	Benzene
α-Naphthol	80–90	4 hours	204–205	204–204.5	(15)	93	4-Triphenylmethyl-1-naphthol	Ethanol
β-Naphthol	125–135	4 hours	227–228	228	(15)	80	1-Triphenylmethyl-2-naphthol	Ethanol
Anisole	reflux	23 hours	284–285	284	(1)	82	*p*-Hydroxytetraphenylmethane	Acetic acid
Phenetole	110–120	6 hours	284–285	284	(1)	95	*p*-Hydroxytetraphenylmethane	Acetic acid
Aniline	reflux	2 hours	256–257	256	(16)	96	*p*-Aminotetraphenylmethane	Toluene
N-Methylaniline	110–115	1 hour	211–212	211–212	(8)	83	*p*-Methylaminotetraphenylmethane	Ethanol
N-Ethylaniline	120–130	3 hours	172–173	172–173	(17)	72	*p*-Ethylaminotetraphenylmethane	Ligroin
Acetanilide	125–135	8 hours	233–234	—	—	93	*p*-Acetoaminotetraphenylmethane	Toluene
Acetanilide	140 or higher	8 hours	93.0–93.5	92–93	(8)	81	Triphenylmethane	Benzene
Alkylbenzenes[b]	reflux	44 hours	—	—	—	—	No reaction	—
Halobenzenes[c]	reflux	3 days	—	—	—	—	No reaction	—
Benzoic acid	90–100	16 hours	—	—	—	—	No reaction	—
Nitrobenzene	reflux	44 hours	—	—	—	—	No reaction	—

[a] Uncorrected. [b] Toluene, ethylbenzene, cumene, and *tert*-butylbenzene; toluene was not tritylated in the presence of zinc chloride. [c] Chloro-, bromo-, and iodo-benzenes.

of an aromatic compound with triphenylcarbinol in a sulfuric acid-acetic acid solution.

para-Tritylated products have been reported for phenol, the cresols, the naphthols, and anisole as well as for a number of structurally related compounds (4, 5, 7, 9, 15, 19). A modification of the method was suggested by Gomberg and Kamm (20) who substituted hydrochloric acid for the sulfuric acid. Compounds prepared by the modified method include the toluidines, methylaniline, dimethylaniline, and phenol (8, 10, 15–17, 21).

In the present work the emphasis was on the use of hydrochloric acid.

para-Methoxytetraphenylmethane was obtained by the hydrochloric acid method; phenetole, by the same procedure, was cleaved to *p*-hydroxytetraphenylmethane. Hardy (15) reported the isolation of *p*-ethoxytetraphenylmethane from the Baeyer and Villiger process.

Acetanilide, in sulfuric acid, gave the *para*-tritylated derivative whereas in hydrochloric acid the acetyl group was removed to give *p*-aminotetraphenylmethane.

Thiophenol, in sulfuric acid, has been reported (22) to form only a sulfide. The same result was obtained with hydrochloric acid. When benzene was monosubstituted with any of the following groups or atoms the tritylation reaction did not occur, using either sulfuric acid or hydrochloric acid: chloro, bromo, iodo, nitro, and carboxyl. Negative results were obtained also with benzene and naphthalene.

A result of special interest was the conversion of toluene, in hydrochloric acid, to *p*-methyltetraphenylmethane. This compound was unobtainable by the sulfuric acid process. Work is continuing, in this laboratory, with other aromatic hydrocarbons.

It has been reported (4, 5, 15) that in the presence of sulfuric acid, triphenylmethane is sometimes a product of the reaction and, in some cases, it is the only product obtained. In the present work it has been noted that when triphenylmethane forms, the reaction is due apparently to the action of sulfuric acid on triphenylcarbinol. When the two reagents are heated together, a good yield of triphenylmethane is obtained. An explanation for this reaction cannot be offered at the present time. Significantly, triphenylmethane formation was not observed when hydrochloric acid was used as the catalyst.

Table II lists certain significant information about the compounds prepared by the two methods. In general, the hydrochloric acid method was found to be better since it gave a cleaner product without triphenylmethane as a by-product. Resinous materials along with triphenylmethane were commonly obtained when sulfuric acid was used.

The large trityl group finds the *para* position more accessible than the *ortho* since the reaction invariably leads to a *para*-tritylated derivative if the *para* position is available for reaction. When the *para* position is blocked, *ortho* substitution may occur. At least one example of an *ortho*-tritylated compound has been reported. Iddles and co-workers (7) obtained 2-hydroxy-3-methyl-5-bromotetraphenylmethane by the Baeyer and Villiger method from 4-bromo-2-methylphenol.

TABLE II
TRIPHENYLCARBINOL

Compound	Reaction time	Temperature	M.P.[a], °C.		Ref.	Yield, %	Product	Crystallized from
			Found	Lit.				
Phenol[b]	8 hours	Reflux	284–285	284	(18)	92	*p*-Hydroxytetraphenylmethane	Acetic acid
Thiophenol	1 hour	Reflux	105.0–105.5	105	(2)	87	Triphenylmethylphenyl sulfide	Ethanol
α-Naphthol[b]	4 days	Reflux	204–205	204.0–204.5	(15)	91	4-Triphenylmethyl-1-naphthol	Ethanol
β-Naphthol[b]	4 days	Reflux	227–228	228	(15)	73	1-Triphenylmethyl-2-naphthol	Ethanol
o-Cresol[b]	70 hours	Reflux	182–183	182–183	(9)	89	4-Hydroxy-3-methyltetraphenylmethane	Ethanol
m-Cresol[b]	97 hours	Reflux	213–214	213–214	(5)	63	4-Hydroxy-2-methyltetraphenylmethane	Acetic acid
Anisole[b]	16 hours	Reflux	194–195	194	(18)	89	*p*-Methoxytetraphenylmethane	Acetic acid
Phenetole[b]	14 hours	Reflux	284–285	284	(18)	85	*p*-Hydroxytetraphenylmethane	Acetic acid
Aniline[c]	6 hours	Reflux	256–257	256	(21)	85	*p*-Aminotetraphenylmethane	Toluene
Dimethylaniline[c]	5 hours	85 or higher	93.0–93.5	92–93	(8)	81	Triphenylmethane	Benzene
Dimethylaniline[c]	4 hours	75–80	210–211	210	(21)	91	*p*-Dimethylaminotetraphenylmethane	Acetone
Dimethylaniline[d]	14 hours	Reflux	210–211	210	(21)	90	*p*-Dimethylaminotetraphenylmethane	Acetone
Acetanilide[c]	4 days	75–80	233–234	—		38	*p*-Acetaminotetraphenylmethane	Toluene
Acetanilide[c]	18 hours	85 or higher	93.0–93.5	92–93	(8)	86	Triphenylmethane	Benzene
Acetanilide[b]	14 hours	Reflux	256–257	256	(21)	95	*p*-Aminotetraphenylmethane	Toluene
Benzene[c]	22 hours	67 or higher	93.0–93.5	92–93	(8)	80	Triphenylmethane	Benzene
Benzene[d]	16 hours	Reflux	93.0–93.5	92–93	(8)	85	Triphenylmethane	Benzene
Benzene[b,e]	2 days	Reflux	—	—		—	No reaction	—
Toluene[c]	52 hours	75 or higher	93.0–93.5	92–93	(8)	70	Triphenylmethane	Ethanol
Toluene[b]	4 days	Reflux	163.0–163.5	163	(25)	36	*p*-Methyltetraphenylmethane	Chloroform-ethanol
Naphthalene[b]	4 days	Reflux	—	—	—	—	No reaction	—
Halobenzenes[f,b]	4 days	Reflux	—	—	—	—	No reaction	—
Benzoic acid[b]	4 days	Reflux	—	—	—	—	No reaction	—
Nitrobenzene[b]	4 days	Reflux	—	—	—	—	No reaction	—

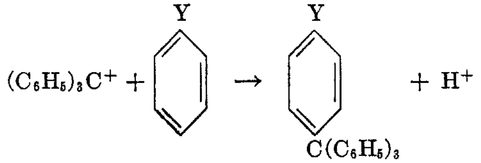
[a] Uncorrected. Catalyst: [b] HCl; [c] H_2SO_4; [d] HBr; [e] H_3PO_4; [f] Chloro-, bromo-, and iodo-benzenes.

It has been suggested (4–7, 9, 10, 15, 23) that the tritylation reaction occurs by the initial formation of an ether or N-tritylated compound followed by a rearrangement of the trityl group to the *para* position. In this investigation it was observed that triphenylmethylphenyl ether in a sulfuric acid-acetic acid mixture or hydrochloric acid-acetic acid mixture was converted to *p*-hydroxytetraphenylmethane. The same kind of result was obtained with N-triphenylmethylaniline. An exceptional case was found with triphenylmethylphenyl sulfide which cleaved to thiophenol.

It appears likely that the reaction does not require an intermediate of the type claimed; instead a direct attack of a triphenyl carbonium ion on the *para* position is indicated:

(A) $$(C_6H_5)_3COH + H^+ \rightleftharpoons (C_6H_5)_3C^+ + H_2O$$

(B)



Where Y is a strong *ortho-* and *para*-directing group.

Evidence in support of the reaction proceeding in this way may be listed as follows:

1. An examination of the Fisher-Taylor-Hirschfelder models indicates that with a group as bulky as the triphenylmethyl group the formation of an onium compound is not favored. Although this steric factor is not observable with phenol it is quite noticeable with compounds such as N,N′-dimethylaniline or acetanilide.

2. The medium employed is one expected to promote the formation of the triphenyl carbonium ion.

3. Iddles and co-workers (7) were unable to rearrange *p*-bromo-*o*-cresyltriphenylmethyl ether to 2-hydroxy-3-methyl-5-bromotetraphenylmethane in sulfuric acid-acetic acid solution; yet they did succeed in obtaining the tetraphenylmethane derivative by treating 4-bromo-2-methylphenol with triphenylcarbinol according to the Baeyer-Villiger method.

4. An initial onium-type compound is not possible with toluene yet it was found possible to *para*-tritylate it. In a related reaction it has recently been reported (24) that alkylbenzenes are attacked at a ring position by diphenylcarbinol in a sulfuric acid-acetic acid solution.

EXPERIMENTAL

General procedure. Triphenylcarbinol, the acid and the compound to be tritylated were mixed in an approximately 1:1:1 molar ratio with the aromatic compound in very slight excess. For reactions using a 0.1 mole of the carbinol, about 20 ml. of glacial acetic acid were employed. In the reactions employing sulfuric acid a flask fitted with a reflux condenser was used. When hydrochloric acid was used, a trap containing dilute sodium hydroxide was connected to the top of the condenser. Products were isolated by pouring the reaction mixture into water.

All known compounds prepared were checked by employing the mixture melting point technique with authentic samples.

Triphenylcarbinol in acetic acid-sulfuric acid solution. A mixture of 2.6 g. of triphenylcarbinol, 5 ml. of conc'd sulfuric acid, and 30 ml. of glacial acetic acid was refluxed for 15 hours. The red-brown solution was poured into about 50 g. of an ice and water mixture. The solid obtained was recrystallized from ethanol; m.p. 93–94°. A mixture melting point determination with an authentic sample of triphenylmethane showed no depression in the melting point. Yield, 90% (2.2 g.)

Rearrangement of N-triphenylmethylaniline. One gram of N-triphenylmethylaniline and 4 ml. of conc'd hydrochloric acid (or 2.0 ml. of conc'd sulfuric acid) were mixed with 15 ml. of glacial acetic acid. The solution was heated to reflux for 14 hours, then cooled and poured into an ice and water mixture. The solid obtained was recrystallized from toluene; m.p. 256–257°. A mixture of the product and *p*-aminotetraphenylmethane showed no depression in the melting point. Yield 80% (from sulfuric acid; 50%).

Rearrangement of triphenylmethylphenyl ether. One gram of triphenylmethylphenyl ether was added to 15 ml. of glacial acetic acid containing 5 ml. of conc'd hydrochloric acid (or 2 ml. of conc'd sulfuric acid). This mixture was refluxed for 16 hours. Crystals separated when the mixture was cooled; they were filtered and recrystallized from glacial acetic acid; m.p. 284–285°. A mixture melting point determination with *p*-hydroxytetraphenylmethane gave no depression in the melting point. Yield: 80% (in sulfuric acid: 67%).

Attempted rearrangement of triphenylmethylphenyl sulfide. One gram of triphenylmethylphenyl sulfide was mixed with 15 ml. of glacial acetic acid and 4 ml. of conc'd hydrochloric acid. The mixture was refluxed for 18 hours, cooled, and poured into a small quantity of cold water. A solid, which formed slowly, was filtered and recrystallized from ligroin; m.p. 163–164°. A mixture melting point with authentic sample of triphenylcarbinol showed no depression in the melting point.

The presence of thiophenol in the aqueous filtrate was indicated by its characteristic odor.

SUMMARY

1. A comparison was made of the use of hydrochloric acid and sulfuric acid in the tritylation of aromatic compounds with triphenylcarbinol. Hydrochloric acid was shown to give a cleaner reaction without the formation of triphenylmethane and the resinous product observed in the presence of sulfuric acid.

2. Toluene, with hydrochloric acid but not sulfuric acid as the catalyst, was changed to *p*-methyltetraphenylmethane.

3. Triphenylcarbinol was converted to triphenylmethane when it was heated in an acetic acid-sulfuric acid mixture.

4. Thiophenol could not be tritylated in the *para* position; only the sulfide was obtained.

5. When reaction occurred only substitution in the *para* position was noted.

6. Triphenylmethylphenyl ether and N-triphenylmethylaniline underwent rearrangement to *p*-hydroxytetraphenylmethane and *p*-aminotetraphenylmethane, respectively, when heated with either hydrochloric acid or sulfuric acid.

7. Evidence was presented to show that the *para*-tritylation reaction occurred by the attack of a triphenyl carbonium ion on the benzene ring.

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REFERENCES

(1) BAEYER, *Ber.*, **42**, 2624 (1909).
(2) VON MEYER, *J. prakt. Chem.*, **82**, 521 (1911).

(3) van Alphen, *Rec. trav. chim.*, **46,** 287 (1927).
(4) Schorigin, *Ber.*, **60,** 2373 (1927).
(5) Boyd and Hardy, *J. Chem. Soc.*, 630 (1928).
(6) Parson and Porter, *J. Am. Chem. Soc.*, **54,** 363 (1932).
(7) Iddles, Miller, and Powers, *J. Am. Chem. Soc.*, **62,** 71 (1940).
(8) Hickinbottom, *J. Chem. Soc.*, 1700 (1934).
(9) Iddles, French, and Mellon, *J. Am. Chem. Soc.*, **61,** 3192 (1939).
(10) van Alphen, *Rec. trav. chim.*, **46,** 501 (1927).
(11) Hurd and Mold, *J. Org. Chem.*, **13,** 339 (1948).
(12) Waters, *The Chemistry of Free Radicals*, Oxford University Press, London, 1948, p. 35–61.
(13) Hart and Cassis, *J. Am. Chem. Soc.*, **76,** 1634 (1954).
(14) Jones and Seymour, *J. Am. Chem. Soc.*, **50,** 1150 (1928).
(15) Hardy, *J. Chem. Soc.*, 1000 (1929).
(16) Ullmann and Munzhuber, *Chem. Zentr*, **I,** 585 (1903).
(17) Clapp, *J. Am. Chem. Soc.*, **61,** 523 (1939).
(18) Baeyer and Villiger, *Ber.*, **35,** 1189 (1902).
(19) von Zincke and Wugk, *Ann.*, **363,** 284 (1908).
(20) Gomberg and Kamm, *J. Am. Chem. Soc.*, **39,** 2009 (1917).
(21) Izmail'skii and Surkov, *J. Gen. Chem.* (U.S.S.R.), **13,** 848 (1943).
(22) Finzi and Bellavita, *Gazz. chim. ital.*, **62,** 699 (1932).
(23) Iddles and Minckler, *J. Am. Chem. Soc.*, **62,** 2757 (1940).
(24) Kundiger and Ovist, *J. Am. Chem. Soc.*, **76,** 2501 (1954).
(25) Gomberg and Cone, *Ber.*, **39,** 1461 (1906).
(26) Baker, *Hyperconjugation*, Oxford Press, 1952, pp. 56–57.