

Unusual Aromatic Nitrations

Hitomi SUZUKI*

Received April 30, 1972

Aromatic compounds undergo three different types of reactions with nitrating agents under ionic conditions; replacement by nitro group of an atom or group from a ring position (ordinary nitration), reaction on substituent groups, and addition reaction followed by various transformations. The present survey is directed towards the latter two types of reactions, which have hitherto not yet been summarized in chemical literature. It includes;

1. Reactions on Substituent Groups.
 - 1.1 Side-chain Nitro-oxylation.
 - 1.2 Side-chain Acetoxylation and Acetamidation.
 - 1.3 Side-chain Nitration.
 - 1.4 Reactions on Lateral Nitrogen or Oxygen Atoms.
2. Reactions on Aromatic Ring.
 - 2.1 Acyloxylation and Alkoxylation.
 - 2.2 Oxynitration.
 - 2.3 Formation of Unsaturated Cyclic Ketones.
 - 2.4 Nitritive Condensations.
 - 2.5 Nitrations with Rearrangement.

Nitration is one of the most basic reactions in organic chemistry and is widely used for the preparation of nitro compounds which are among the most valuable intermediates in organic synthesis. The compounds to be nitrated may be either aliphatic or aromatic, but the reaction has more significance in aromatic chemistry. Aromatic nitration is the process in which the nitro group replaces an atom or group from a ring position of an aromatic compound. The reaction has already been dealt with by a number of reviews and books.¹⁾ In recent years, however, several new reactions have come to light which give the results considerably deviated from the ordinary concept of aromatic nitration. They include varied substitutions on the alkyl side-chain of polyalkylbenzenes, nitritive coupling, oxidation to cyclic ketones, and nuclear acyloxylation. In spite of the mechanistic implications, these unusual reactions have so far been described only as a subtopic. This article is therefore intended to provide a basis for understanding these as yet unsystematized area of aromatic nitrations. Although earlier works are included as far as they seem to be pertinent, the emphasis is not on an exhaustive coverage of the literature but on a survey of the broad spectrum of anomalous nitration.

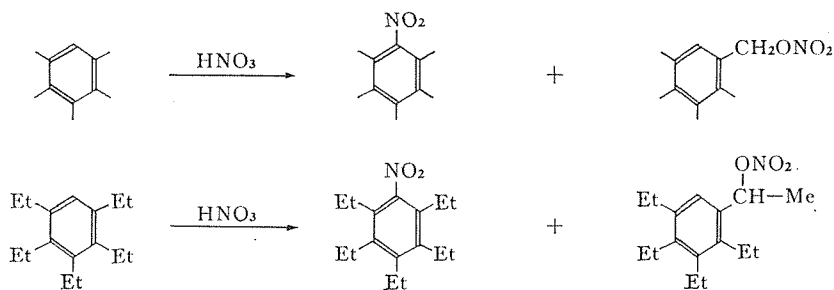
I. REACTIONS ON SUBSTITUENT GROUPS

I.1. Side-chain Nitro-oxylation

i) **Polyalkylbenzenes.** When pentamethylbenzene is nitrated with excess of

* 鈴木仁美: Department of Chemistry, Faculty of Science, Hiroshima University, Higashi-sendamachi, Hiroshima.

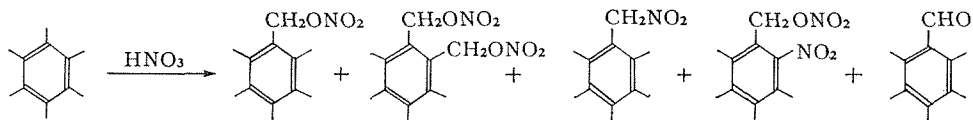
nitric acid below 0°, the product is mainly a mixture of nitropentamethylbenzene and 2,3,4,5-tetramethylbenzyl nitrate.²⁾ Other isomeric nitrates are not formed in any significant amount. 6-Nitro-2,3,4,5-tetramethylbenzyl nitrate, 2,3,4,5-tetramethylbenzaldehyde, 2,3,4,5-tetramethylbenzyl alcohol, and some polymethyldiphenylmethanes are among the minor products. Pentaethylbenzene similarly gives a mixture of nitropentaethylbenzene and α -methyl-2,3,4,5-tetraethylbenzyl nitrate along with some minor products of oxidation.



Preferential side-chain attack occurs at the primary alkyl group *ortho* to the unsubstituted ring position. Thus, 1-methyl-2,3,4,5-tetraethylbenzene gives benzyl nitrate and α -methylbenzyl nitrate nearly in equal amounts, while 3-methyl-1,2,4,5-tetraethylbenzene yields them in an approximately ratio of 1 : 3.

The side-chain nitro-oxylation seems to be limited to the methyl and ethyl groups. 3,6-Diisopropyl-1,2,4-trimethylbenzene undergoes extensive nitrodealkylation, and 3,4-dimethyl-2,5-diisopropylbenzyl nitrate is the only side-chain substituted product identified.²⁾

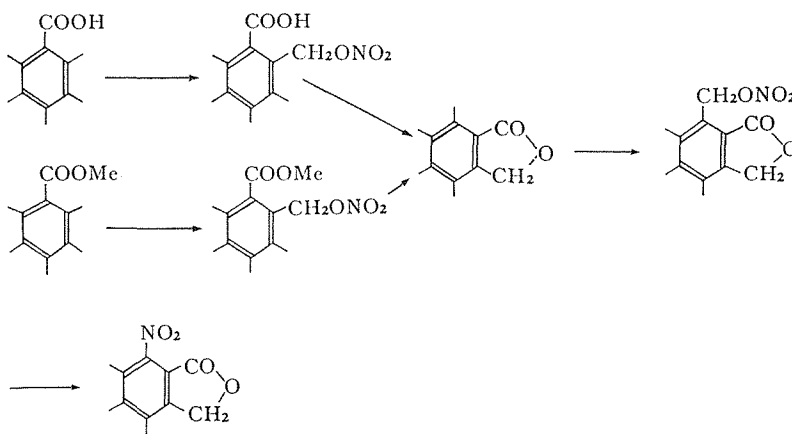
The nitration of pentamethylbenzene and hexamethylbenzene has been reported to give dinitrotetramethylbenzene.³⁾ Reinvestigation of the reaction, however, revealed that the products were not so simple as had been described in literature. A syrupy substance formed in quantity during the nitration of hexamethylbenzene to dinitroreihnene has been found to be a complicated mixture of pentamethylbenzyl nitrate, 5,6-bis(nitro-oxyethyl)-1,2,3,4-tetramethylbenzene, nitropentamethylbenzene, 6-nitro-2,3,4,5-tetramethylbenzyl nitrate, pentamethylphenylnitromethane, bis(pentamethylbenzyl) ether, pentamethylbenzaldehyde, and several other unidentified carbonyl compounds, nitrite esters, and aliphatic nitro compounds.⁴⁾



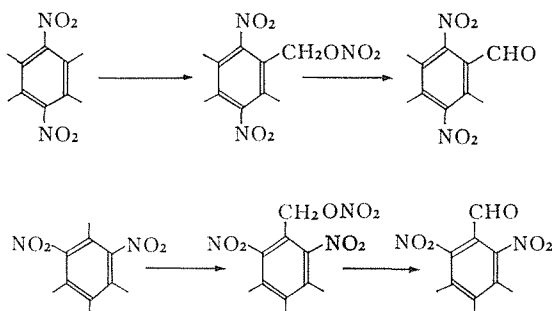
ii) Nitro and Carbonyl Derivatives of Polyalkylbenzenes. Strongly electron-withdrawing substituents such as nitro, carboxyl, and carbomethoxy groups bring about almost exclusive *ortho* substitution. Thus, nitropentamethylbenzene treated with excess of fuming nitric acid gives 6-nitro-2,3,4,5-tetramethylbenzyl nitrate together with small amounts of 5-nitro-2,3,4,6-tetramethylbenzyl nitrate. No 4-nitro-2,3,5,6-tetramethylbenzyl nitrate is detected.⁵⁾

Unusual Aromatic Nitrations

Nitration of pentamethylbenzoic acid, and its methyl ester and amide similarly leads to the formation of 6-nitro-oxymethyl-2,3,4,5-tetramethylbenzoic acid, methyl 6-nitro-oxymethyl-2,3,4,5-tetramethylbenzoate, and 6-nitro-oxymethyl-2,3,4,5-tetramethylbenzamide, respectively, which upon acid hydrolysis are readily converted into 4,5,6,7-tetramethylphthalide. Action of the nitrating agent upon 4,5,6,7-tetramethylphthalide gives 7-nitro-oxymethyl-4,5,6-trimethylphthalide, which is further nitrated to 7-nitro-4,5,6-trimethylphthalide.^{5,6)}



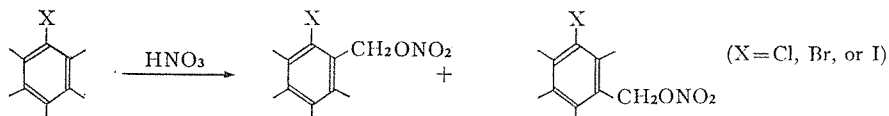
Dinitrodurene is stable towards the action of fuming nitric acid, but on heating with mixed acid at 40–50° it is slowly converted into 3,6-dinitro-2,4,5-trimethylbenzyl nitrate, which is allowed to react further produces 3,6-dinitro-2,4,5-trimethylbenzaldehyde. Dinitroisodurene reacts readily with fuming nitric acid at room temperature, affording 2,6-dinitro-3,4,5-trimethylbenzaldehyde in 76–84% yield. Small amounts of 2,6-dinitro-3,4,5-trimethylbenzoic acid, 2,6-dinitro-3,4,5-trimethylphenylnitromethane, and 2,6-dinitro-3,4,5-trimethylbenzyl alcohol are obtained as by-product. If dinitroisodurene is dissolved into mixed acid and stood at room temperature, 2,6-dinitro-3,4,5-trimethylbenzyl nitrate soon separates from the reaction mixture.⁷⁾



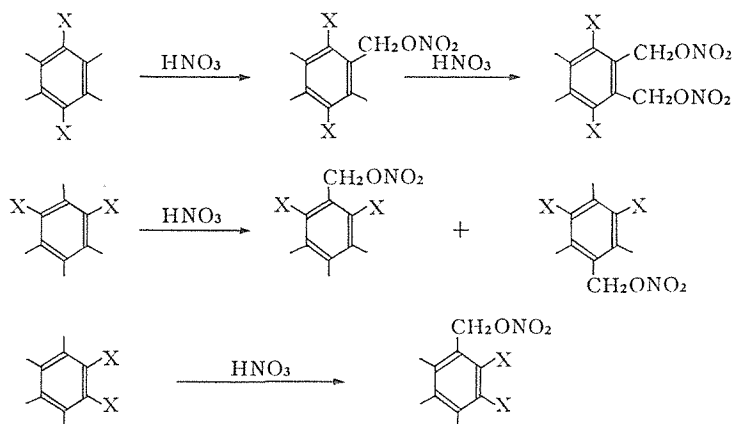
Dinitroprehnitene is unique in its behavior towards the nitrating agent and gives an unsaturated cyclic ketone, which will be described in II.3.

iii) Halogen Derivatives of Polyalkylbenzenes. The action of the nitrating agent upon halopentamethylbenzenes leads to comparable amounts of 5-halo-2,3,4,6-tetramethylbenzyl nitrate and 6-halo-2,3,4,5-tetramethylbenzyl nitrate. 4-Halo-2,3,5,6-

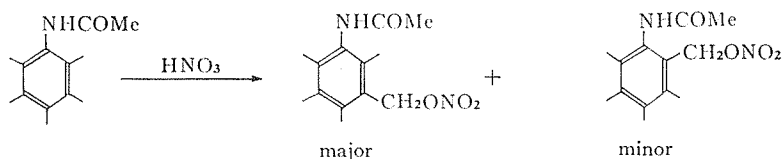
tetramethylbenzyl nitrate is never formed in any significant amounts. The amount of *meta* substitution relative to *ortho* (*m/o*) steadily increased from 42/58 ($X = \text{Cl}$) to 44/56 ($X = \text{Br}$) to 47/53 ($X = \text{I}$) as the atomic number of halogen increases. The reaction of iodopentamethylbenzene is always accompanied by an extensive nitrodeiodination.⁸⁾



The nitration of dihalodurene with fuming nitric acid gives, depending on the reaction conditions, 3,6-dihalo-2,4,5-trimethylbenzyl nitrate or 1,2-bis(nitro-oxymethyl)-3,4,5,6-tetramethylbenzene. Dihaloisodurene yields a mixture of 3,5-dihalo-2,4,6-trimethylbenzyl nitrate and 2,6-dihalo-3,4,5-trimethylbenzyl nitrate, the latter in somewhat greater amount. Dihaloprehnitenes gives 5,6-dihalo-2,3,4-trimethylbenzyl nitrate. The reaction affords a new convenient route to some precursors of various polysubstituted benzylic compounds hitherto not easily obtained by ordinary methods.⁹⁾



iv) Polyalkylphenols and its Ethers, and Polyalkylacetanilides. Pentamethylphenol and its methyl ether gives a cyclohexadienone, together with small amounts of 3-substituted 2,4,5-trimethylbenzyl nitrate. Under similar conditions, pentamethylacetanilide readily undergoes the side-chain nitro-oxylation to give two nitro-oxymethyl-trimethylacetanilides. The location of the nitro-oxymethyl group in the product seems to be most likely *ortho* and *meta*, the latter being predominant.⁵⁾

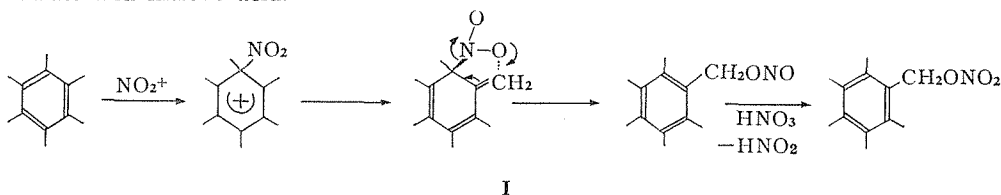


The side-chain nitro-oxylation of polyalkylbenzenes and their derivatives depends closely on the positional relationship of alkyl groups in the nucleus, and preferential formation of *p*-alkylbenzyl nitrate is always observed. Relative reactivity of substituted pentamethylbenzenes $\text{C}_6\text{Me}_5\text{X}$ for side-chain substitution decreases from 1 to 2×10^{-2} to 4×10^{-4} to 3×10^{-6} with the change of substituent groups from Me to H to Br to NO_2

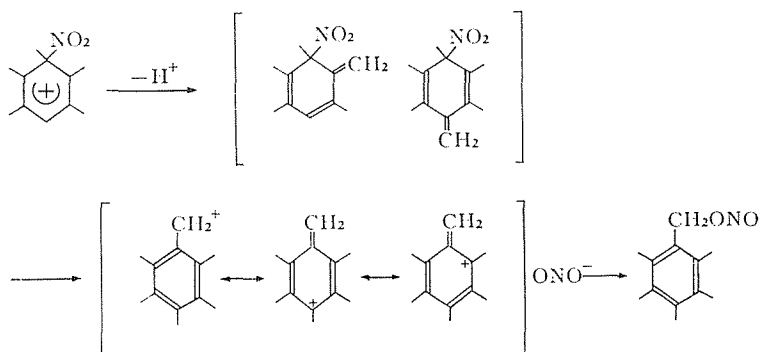
Unusual Aromatic Nitrations

in accordance with the ionic character of the reaction. Added electrolytes have profound influence on the reaction rates, but the ratio of products from side-chain nitro-oxylation and nuclear nitration remains almost unchanged, indicating that both processes share a common intermediate.¹⁰⁾

The substitution on the alkyl side-chain may be explained by a process similar to that postulated for the side-chain chlorination of hexamethylbenzene,¹¹⁾ *i.e.*, a cyclic process involving the initial attack of the nitronium ion at the ring carbon, followed by the hyper-conjugative release of a proton from the neighboring methyl group and the rearrangement of the unstable intermediate (I) to the benzyl nitrite, which is further transformed into the nitrate and nitrous acid.

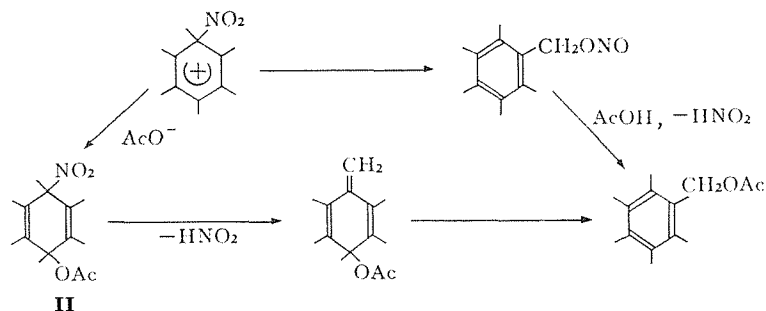


An alternative possibility may involve the ion-pair; a proton is removed hyper-conjugatively from the alkyl side-chain to form a sort of methylene-cyclohexadiene or benzylic intermediate-nitrite ion-pair, which will subsequently be converted into the nitrite.

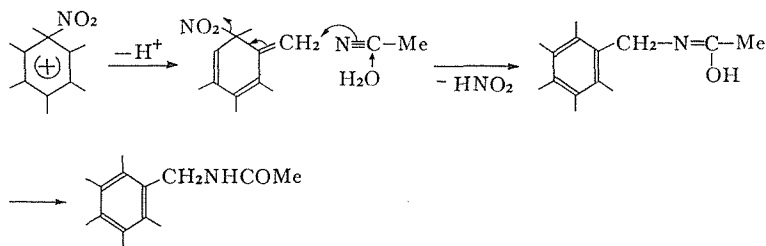


1.2. Side-chain Acetoxylation and Acetamidation

When polymethylbenzenes are nitrated with fuming nitric acid in acetic acid, substantial amounts of polymethylbenzyl acetates are obtained.^{5,12)} They could arise from the acetolysis of the initially formed benzylic esters, as well as from the decomposition of the intermediary addition product(II).



The use of acetonitrile as solvent leads to the formation of a good yield of *N*-acetylbenzylamine. The acetamidation would probably involve the nucleophilic attack of a nitrile nitrogen atom upon the benzylic carbon followed by the isomerization of the resulting imino compound.¹³⁾



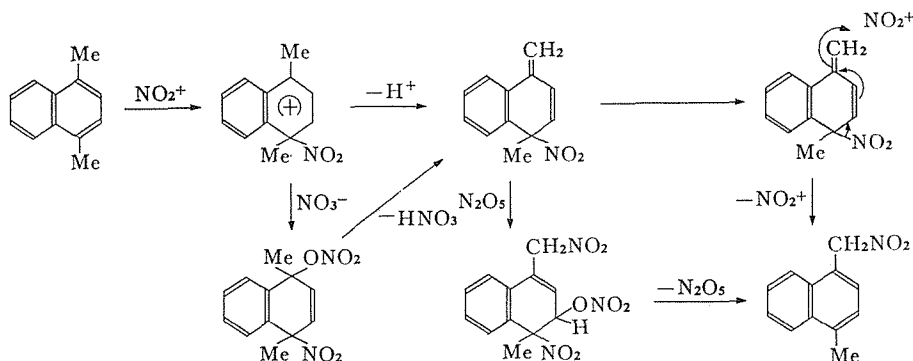
I.3. Side-chain Nitration

Side-chain nitration of polyalkylbenzenes was first observed by Willstätter and Kubli,¹⁴⁾ who treated several polymethylbenzenes with benzoyl nitrate in carbon tetrachloride and obtained, besides the expected ring nitration product, some phenylnitromethane derivatives. The action of fuming nitric acid or acetyl nitrate upon hexamethylbenzene also gives some pentamethylphenylnitromethane.^{4,12)}

When 1,4-dimethylnaphthalene is treated with nitric acid in nitromethane at -10° , and the mixture is quenched after a day, the product is 1-methyl-4-nitromethylnaphthalene.¹⁵⁾ Among various polymethylnaphthalenes so far investigated, anomaly seems to be encountered only with these systems in which both 1 and 4 positions are occupied by methyl groups. Thus, 1,2,4-trimethylnaphthalene readily undergoes side-chain nitration at less hindered methyl group to give 3,4-dimethyl-1-nitromethylnaphthalene as the principal product. 1,2,3,4-Tetramethylnaphthalene similarly gives 2,3,4-trimethyl-1-nitromethyl naphthalene. In contrast, 1,2,3-trimethylnaphthalene is merely nitrated at the ring position to give 1,2,3-trimethyl-4-nitronaphthalene in high yield.¹⁶⁾

Side-chain nitration also occurs in the nitration of heterocyclic compounds. When treated with acetyl nitrate, 2,3-dimethylbenzo[*b*]thiophen undergoes nitration in the 2-methyl group.¹⁷⁾

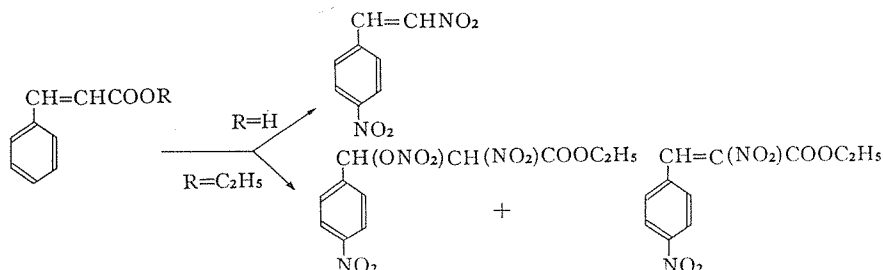
Probable reaction sequences which account for side-chain nitration are shown below:



The action of absolute nitric acid upon cinnamic acid and some of its derivatives often results in the replacement of carboxyl group by a nitro group, giving a good yield

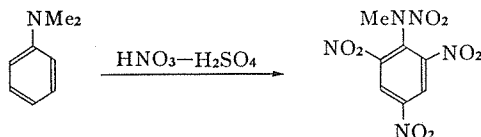
Unusual Aromatic Nitrations

of β -nitrostyrene.¹⁸⁾ In some cases, the products formed by the addition of nitric acid to the unsaturated side-chain are isolated. These can rather be classed to aliphatic nitrations and will not be described further.



I.4. Reactions on Lateral Nitrogen or Oxygen Atoms

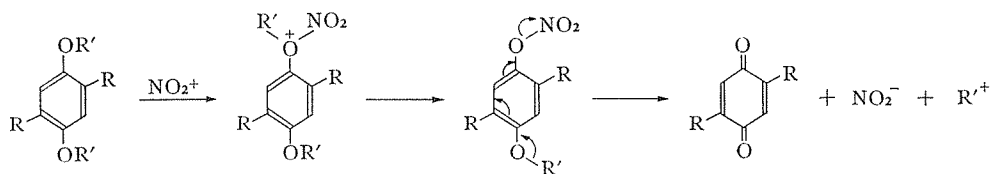
When *N,N*-dimethylaniline is treated with mixed acid at 40–55°, one of the methyl groups in dimethylamino function is replaced by a nitro group. On the nitration routes are encountered various intermediates, which include 2,4-dinitro-*N*-methylaniline, and its *N*-nitroso and *N*-nitro derivatives, 2,4-dinitro-*N,N*-dimethylaniline, 2,4,6-trinitro-*N*-methylaniline and its *N*-nitroso derivatives.¹⁹⁾ The essential reagent for dealkylation of aromatic tertiary amine is nitrous acid and only one alkyl group being eliminated. Although the *N*-nitrosoamine is often isolated, the easiest isolable product is the secondary amine.



Similar results are observed when *p*-dimethylaminobenzoic acid is nitrated at 60–70°. ²⁰⁾

The nitration of anisole often leads to the formation of a mixture of nitroanisoles and nitrophenols in proportions which depend upon experimental conditions.²¹⁾ The reaction has been assumed to involve the attack of nitronium ion at oxygen atom to which alkyl group is attached to form an oxonium ion, which loses an alkyl carbonium ion after the usual heterolytic pattern of the onium ion decomposition.²²⁾ The phenyl nitrate thus formed usually undergoes a further decomposition to yield quinone, quinol, quinomethide, or decendent of these.

Dealkylation and subsequent oxidation by nitric acid is typical of 1,4-dialkoxybenzenes having certain electron-donating substituents in the 2 and 5-positions.²³⁾ The process may be explained as follows:



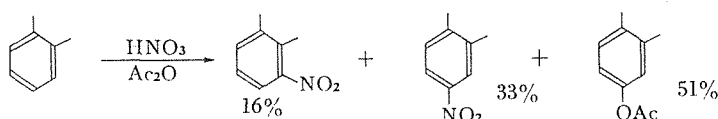
The behavior of diphenyl ethers on nitration is in many ways similar. Thus, when 4'-methyl-4-chloro-2-nitrobiphenyl is dissolved in cold fuming nitric acid, the main product is 4-chloro-2,6-dinitrophenol.²⁴⁾



II. REACTIONS ON AROMATIC RING

II.1. Acyloxylation and Alkoxylation

A reaction which bears somewhat different feature is the nuclear acyloxylation observed during the nitration of some polymethylbenzenes with acetyl nitrate. When *o*-xylene is nitrated with nitric acid in acetic anhydride, the products are 4-acetoxy-*o*-xylene besides the expected 3- and 4-nitro-*o*-xylenes.



Hemimellitene and pseudocumene behave similarly (Table I). The reaction was first suggested to involve the attack of protonated acetyl nitrate (AcONO_2H^+),²⁵⁾ but a strong evidence in support of addition-elimination route has recently been presented. Two adducts isolated from the reaction mixture, III and IV, give the 4-acetoxy-*o*-xylene in contact with aqueous acetic acid.²⁶⁾

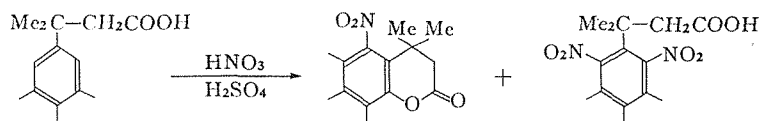


Upon treatment with fuming nitric acid and sulfuric acid at 10°, β -(3,4,5-trimethylphenyl) isovaleric acid or its methyl ester yields a cyclic compound, 4,4,6,7,8-pentamethyl-5-nitrohydrocoumarin, along with the expected dinitro derivative.²⁷⁾ The reaction may involve the attack of the protonated acyl nitrate, but the situation is not clear as yet.

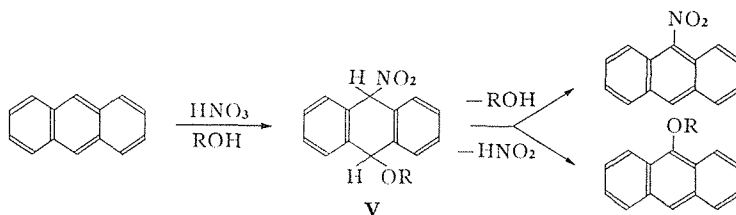
Table 1. Nitration and Acetoxylation of Trimethylbenzenes

Compound	Nitro-compounds (%)			Acetoxy-compounds (%)		
	3	4	5	3	4	5
Hemimellitene (1,2,3-Trimethylbenzene)	—	46.4	7.7	—	10.6	35.3
Pseudocumene (1,2,4-Trimethylbenzene)	10.0	—	49.5	10.3	—	25.6

Unusual Aromatic Nitrations

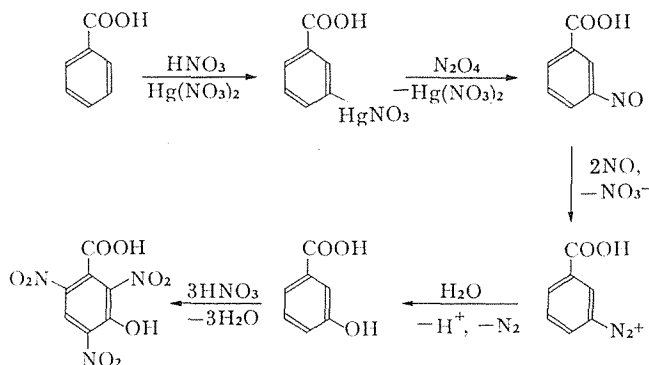


Polycyclic aromatic hydrocarbons readily undergo addition reaction with electrophile. Thus, when treated with nitric acid in the presence of an appropriate nucleophile, ROH, anthracene forms an isolable adduct V which on heating loses either nitrous acid or ROH to give two products of substitution.²⁸⁾



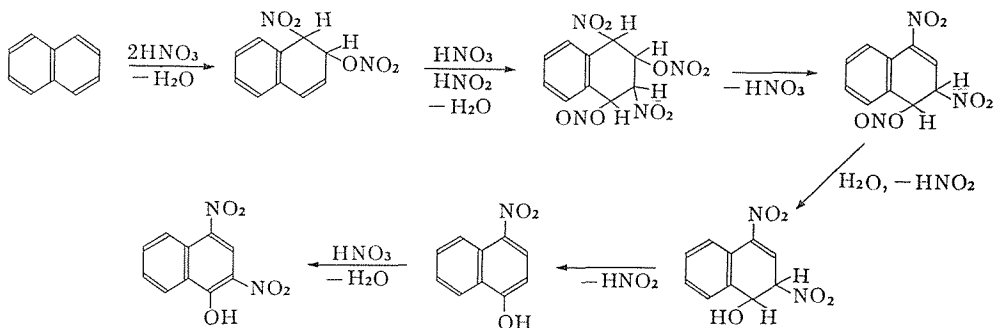
II.2. Oxyinitration

When *o*-xylene is nitrated with concentrated nitric acid or mixed acid and the aqueous ammonia washings of the crude product is treated with dilute acid, there is obtained a small amount of 4,6-dinitro-2,3-dimethylphenol.²⁹⁾ 3-Nitro-4-methyl-6-iodoanisole similarly yields 6-hydroxy-4-methyl-2,3,5-trinitroanisole in addition to the normal nitration products.³⁰⁾ The formation of phenolic substances is facilitated when some metal ion catalyst is added to the system. Thus, when benzene or its derivatives are nitrated in the presence of mercuric nitrate, polynitrohydroxy derivatives are obtained in good yield.³¹⁾ The reaction is supposed to involve initial mercuration, followed by the displacement of the mercury by a nitroso group, and the reduction of the nitroso group to a diazonium ion. This decomposes to a phenol which is then nitrated. A similar course is followed in the nitric acid oxidation of *o*-nitrotoluene to picric acid.³²⁾



Nitration of naphthalene forms small amounts of 2,4-dinitro-1-naphthol, and the amount of this by-product is increased by carrying out the reaction in the presence of nitrite

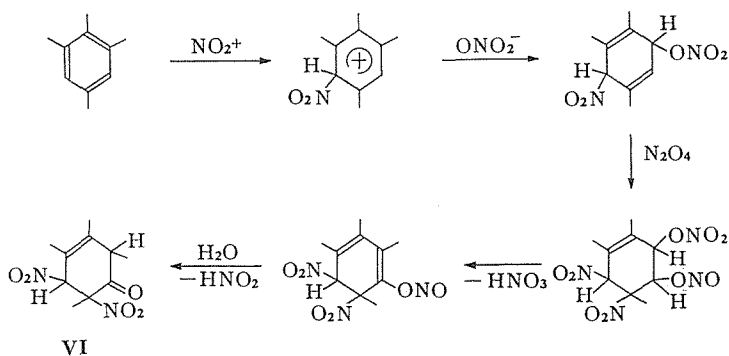
ions. The addition-elimination sequence is suggested to be involved in the reaction.³³⁾



The action of nitric acid upon 9-bromoanthracene affords nitroanthranol and 9-bromo-10-nitroanthracene, the former being predominant.^{3,4)}

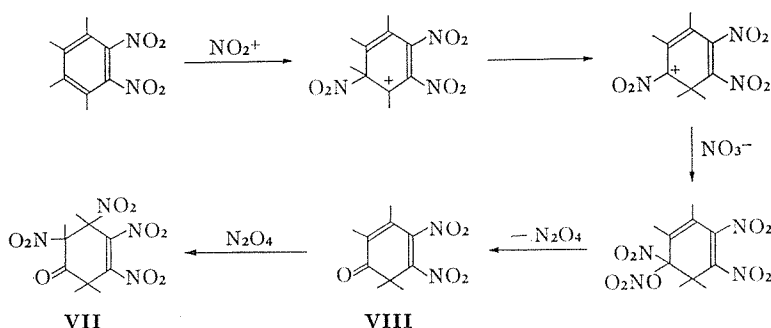
II.3. Formation of Unsaturated Cyclic Ketones

i) **Cyclohexenones and Cyclohexadienones.** When isodurene is treated with excess of fuming nitric acid in dichloromethane below 0°, small amount of unsaturated cyclic dinitroketone VI is obtained in addition to normal ring substitution products. Ethylmesitylene similarly gives 3-ethyl-2,4,6-trimethyl-5,6-dinitrocyclohex-3-enone in low yield. Although these unusual products seem to be formed from many polyalkylbenzenes, most are non-crystallizable syrups which darken when kept.³⁵⁾ The ketones are probably formed by an addition-elimination sequence shown below:

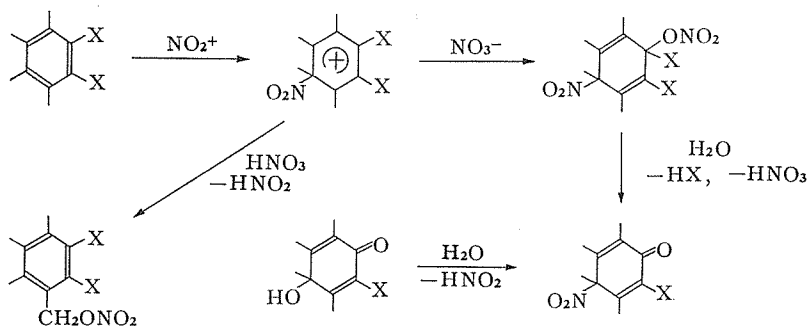


The formation of cyclic ketones seems to be quite sensitive to the type of substitution on the aromatic ring. Whereas the treatment of fully substituted derivatives of durene and isodurene with fuming nitric acid leads to either displacement of one of the substituent groups by a nitro group, or substitution on the alkyl side-chain to yield benzyl nitrate, dinitroprehnitene in contact with cold fuming nitric acid gives 2,3,4,5-tetranitro-2,3,6,6-tetramethylcyclohex-4-enone (VII) in high yield. The ketone VII is thermally unstable and on heating it readily liberated nitrogen dioxide to give 4,5-dinitro-2,3,6,6-tetramethylcyclohexa-2,4-dienone (VIII).³⁶⁾ A probable mechanism is shown below:

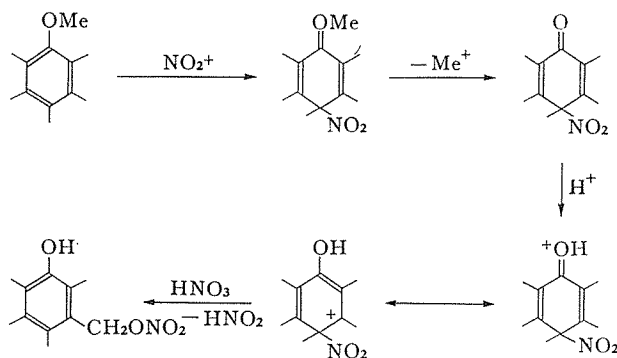
Unusual Aromatic Nitrations



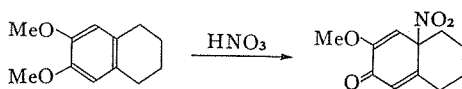
The action of the nitrating agent upon dihaloprehnitenes formed, as well as the expected 5,6-dihalo-2,3,4-trimethylbenzyl nitrates, appreciable amounts of 4-nitro-6-halo-2,3,4,5-tetramethylcyclohexa-2,5-dienones, which are presumably formed by the sequence depicted below:³⁷⁾



Nitration of phenols and phenolic ethers results in the formation of cyclohexadienones. Both pentamethylphenol and pentamethylanisole react actively with nitric acid to give an oily substance of almost identical composition. The product is 4-nitro-2,3,4,5,6-pentamethylcyclohexa-2,5-dienone, accompanied by small amounts of 5-hydroxy-2,3,4,6-tetramethylbenzyl nitrate. The methoxyl cleavage and *meta*-nitro-oxylation observed in the nitration of pentamethylanisole may be explained as follows:⁵⁾



6,7-Dimethoxytetralin gives a similar product.³⁸⁾



ii) **Quinones and Quinols.** Formation of quinones during the nitration of phenols and phenolic ethers is quite common and some of typical examples are listed in Table 2. The oxidation to quinones would involve the electrophilic attack by nitronium ion at the site *para* to an oxygen atom, followed by removal of cationic species from the oxygen and hydrolysis of the resulting cyclic ketone IX to the quinone X.

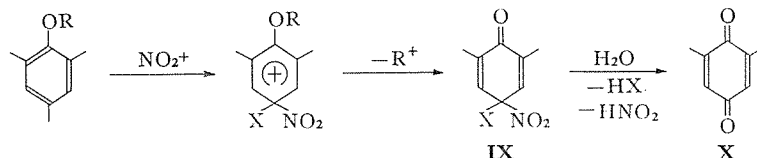
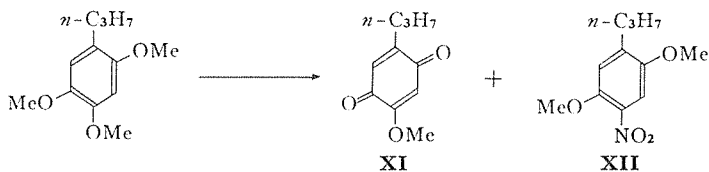


Table 2. Nitration of Phenols and Phenolic Ethers

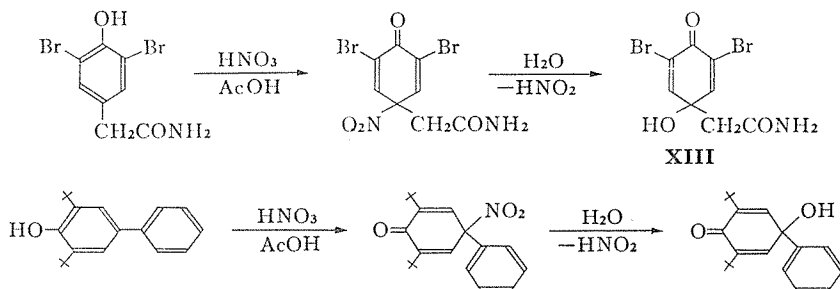
Compound	Product	Condition	References
		fum-HNO ₃	40
		HNO ₃ -AcOH	41
		HNO ₃	42
		HNO ₃ -AcOH	43
		HNO ₃ -Ac ₂ O	44

An interesting reaction is observed when 1-*n*-propyl-2,4,5-trimethoxybenzene is subjected to the nitration; with fuming nitric acid at -18° , it gives the quinone XI as the major product, while with 45% nitric acid in acetic acid at 50° , XII is predominant in the product mixture, methoxy group being displaced by nitro group.^{39,45)} No mechanistic study of the reaction has been reported yet.



Unusual Aromatic Nitrations

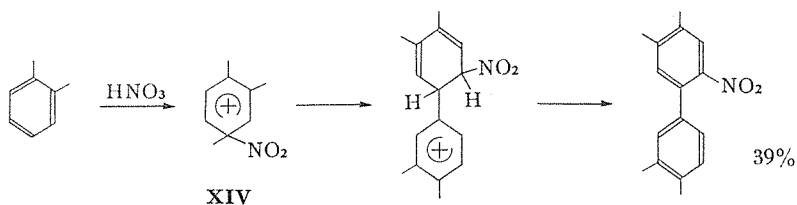
In some cases quinols are obtained during the nitration. 3,5-Dibromo-4-hydroxyphenylacetamide is nitrated with nitric acid in acetic acid to give the *p*-quinol XIII.⁴⁶⁾ 4-Hydroxy-3,5-di-*t*-butylbiphenyl behaves similarly.⁴⁷⁾ The nitro group at 4-position of these systems is subject to a facile hydrolysis.



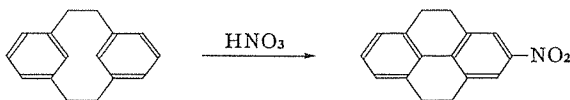
II.4. Nitritive Condensations

i) **Coupling.** Nitration of alkyl homologs of benzene is often accompanied by coupling to nitrobiphenyls if the nitric acid is added to the hydrocarbon. The reaction was observed as early as in 1911,⁴⁸⁾ but its synthetic value has received no attention until recently. The reaction is sensitive to the structure of the hydrocarbon. Thus, *o*-xylene, *o*-ethyltoluene, pseudocumene, and hemimellitene give appreciable amounts of coupling, while toluene, *m*- and *p*-xylene, mesitylene, and prehnitene formed little or no coupling product.⁴⁹⁾ When mixture of *o*-xylene or hemimellitene with more basic methylbenzenes are similarly treated, cross-coupled products are obtained in acceptable yield.⁵⁰⁾ In these, the predominant path is coupling followed by nitration.

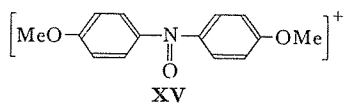
The nitritive coupling is suggested to proceed through the intermediate common with the nitration, *i.e.*, the nitroarenonium ion XIV:



When [2,2] metacyclophane is nitrated with concentrated nitric acid in acetic acid, 2-nitro-4,5,9,10-tetrahydropyrene is obtained in 83% yield.⁵¹⁾

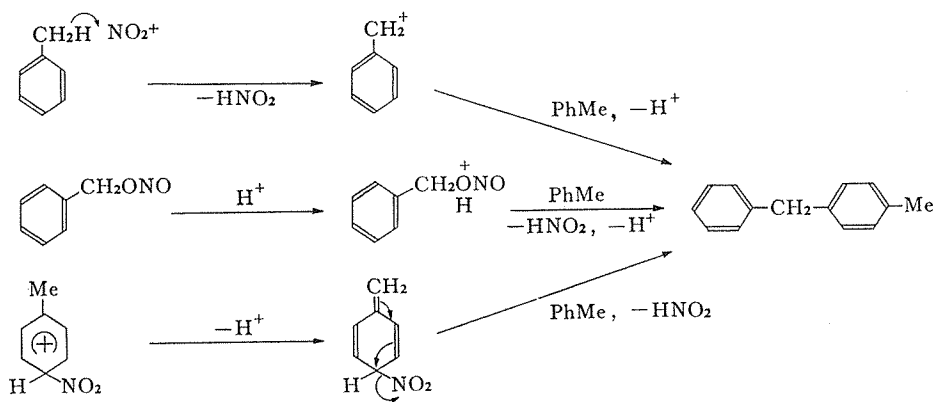


During the nitration of anisole in acetic acid, there is formed a deep purple-colored substance, identified as the dianisylloxidoammonium ion XV. The proportions in which this cation is produced are quite large, and are frequently in the range 5–15%.¹⁹⁾



ii) **Formation of Diarylmethanes.** The action of nitrating agent upon polyalkylbenzenes at low temperatures often forms small amounts of polyalkyldiphenylmethanes.⁴⁹⁾ Durene treated with mixed acid in nitromethane gives 2,2',3,4',5,6,6'-heptamethyldiphenylmethane in 5–12% yield, in addition to the expected mono and dinitrodurene.¹³⁾ Pentamethylbenzene gives 2,2',3,3',4,4',5,5',6-nonamethyldiphenylmethane and 2,2',3,3',-4,4',5,5'-octamethyl-6-nitro-oxymethyldiphenylmethane in low yield.²⁾

Several assumed mechanistic schemes are illustrated below:



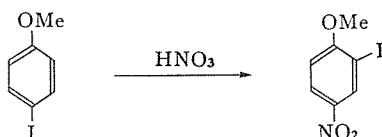
II.5. Nitrations with Rearrangement

Nitration of halophenols and haloanisoles often leads to the migration of halogen atom. The reaction was named after Reverdin, who discovered that the reaction of cold fuming nitric acid with *p*-iodoanisole gave 2-iodo-4-nitroanisole.⁵²⁾ Several examples are listed in Table 3.

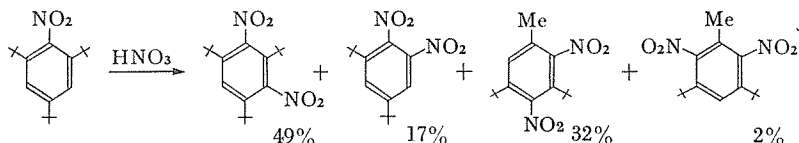
Table 3. Nitration of Halophenols and Haloanisoles

Compound	Product	Condition	References
		HNO ₃	53
		HNO ₃	30
		HNO ₃ -AcOH	54
(X=Cl, Br)			

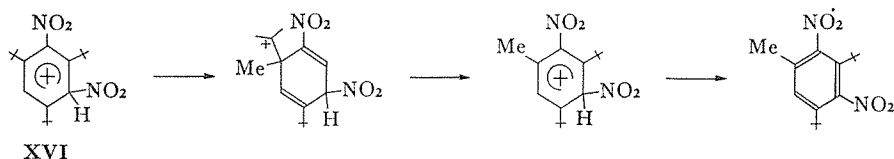
Unusual Aromatic Nitrations



When 2,4,6-tri-*t*-butylnitrobenzene is nitrated with 90% nitric acid at 0°, migration of methyl group from the side-chain to the nucleus occurs, giving four substitution products.⁵⁵⁾



Replacement of a *t*-butyl group by methyl is explained by a process involving a rearrangement of the intermediate cyclohexadienyl cation XVI followed by oxidative cleavage of the isopropyl moiety.



REFERENCES

- (1) For recent monographs; P. B. D. de la Mare and J. H. Ridd, *Aromatic Substitution, Nitration and Halogenation* (Butterworths, London, 1959); R. O. C. Norman and R. Taylor, *Electrophilic Substitution in Benzenoid Compounds* (Elsevier, London, 1965); J. G. Hoggett, R. B. Moodie, J. R. Penton, and K. Schofield, *Nitration and Aromatic Reactivity* (University Press, Cambridge, 1971).
- (2) H. Suzuki and K. Nakamura, *Bull. Chem. Soc. Japan*, **43**, 473 (1970).
- (3) L. I. Smith and S. A. Harris, *J. Amer. Chem. Soc.*, **57**, 1289 (1935); K. Galle, *Ber.*, **16**, 1744 (1883).
- (4) H. Suzuki, *Bull. Chem. Soc. Japan*, **43**, 879 (1970); H. Suzuki, *Nippon Kagaku Zasshi*, **91**, 179 (1970).
- (5) H. Suzuki and K. Nakamura, *Bull. Chem. Soc. Japan*, **44**, 227 (1971).
- (6) S. Isaev, L. A. Ostashevskaya, A. A. Morozov, L. M. Bestchetonova, and V. A. Koptyug, *Zhur. Org. Khim.*, **7**, 2321 (1971).
- (7) H. Suzuki and K. Nakamura, *Chem. Commun.*, **1972**, 340; H. Suzuki and K. Nakamura, *Bull. Chem. Soc. Japan*, **45**, 2534 (1972); H. Suzuki and K. Nakamura, *Synthesis*, **1972**, in press.
- (8) H. Suzuki, *Bull. Chem. Soc. Japan*, **43**, 481 (1970).
- (9) H. Suzuki, K. Nakamura, and M. Takeshima, *ibid.*, **44**, 2248 (1971).
- (10) K. Nakamura, *ibid.*, **44**, 133 (1971).
- (11) E. Baciocchi, A. Ciana, G. Illuminati, and C. Pasini, *J. Amer. Chem. Soc.*, **87**, 3953 (1965).
- (12) R. Astolfi, E. Baciocchi, and G. Illuminati, *Chimica e Industria*, **53**, 1153 (1971).
- (13) S. B. Hanna, E. Hunziker, T. Saito, and H. Zollinger, *Helv. Chim. Acta*, **52**, 97 (1969); E. Hunziker, J. R. Penton, and H. Zollinger, *ibid.*, **54**, 2043 (1971).
- (14) R. Willstätter and H. Kubli, *Ber.*, **42**, 4151 (1909).
- (15) R. Robinson and H. W. Thompson, *J. Chem. Soc.*, **1932**, 2015.
- (16) H. Suzuki and K. Nakamura, *Bull. Chem. Soc. Japan*, **44**, 303 (1971).
- (17) F. G. Bordwell and T. W. Cutshall, *J. Org. Chem.*, **29**, 2020 (1964).
- (18) P. Pfeiffer, *Ber.*, **47**, 1755 (1914); van der Lee, *Rec. Trav. Chim.*, **45**, 674 (1926).

- (19) J. Glazer, E. D. Hughes, C. K. Ingold, A. T. James, G. T. Jones, and E. Roberts, *J. Chem. Soc.*, **1950**, 2657.
- (20) F. Reverdin, *Ber.*, **40**, 2442 (1907).
- (21) R. M. Schramm and F. H. Westheimer, *J. Amer. Chem. Soc.*, **70**, 1782 (1948).
- (22) C. A. Bunton, E. D. Hughes, C. K. Ingold, D. I. H. Jacobs, M. H. Jones, G. J. Minkoff, and K. I. Reed, *J. Chem. Soc.*, **1950**, 2628.
- (23) G. Schill, *Ann.*, **691**, 79 (1966).
- (24) D. L. Fox and E. E. Turner, *J. Chem. Soc.*, **1930**, 1115.
- (25) A. Fischer, J. Packer, J. Vaughan, and G. J. Wright, *Proc. Chem. Soc.*, **1961**, 369; A. Fischer, J. Vaughan, and G. J. Wright, *J. Chem. Soc., B*, **1967**, 368.
- (26) D. J. Blackstock, A. Fischer, K. E. Richards, J. Vaughan, and G. J. Wright, *Chem. Commun.*, **1970**, 641.
- (27) L. I. Smith and W. W. Prichard, *J. Amer. Chem. Soc.*, **62**, 780 (1940); L. I. Smith and L. J. Spillane, *ibid.*, **65**, 282 (1943).
- (28) O. Dimroth, *Ber.*, **34**, 219 (1901); J. Meisenheimer and E. Connerade, *Ann.*, **133**, 330 (1904); E. de B. Barnett, J. W. Cook, and M. A. Mathews, *J. Chem. Soc.*, **123**, 1994 (1923).
- (29) E. Noelting and B. Pick, *Ber.*, **21**, 3158 (1888).
- (30) G. M. Robinson, *J. Chem. Soc.*, **109**, 1078 (1916).
- (31) R. Wolfenstein and O. Boters, *Ber.*, **46**, 586 (1913); R. Wolfenstein and W. Paar, *ibid.*, **46**, 589 (1913); F. H. Westheimer, E. Segel, and R. Schramm, *J. Amer. Chem. Soc.*, **69**, 773 (1947); M. Carmack, M. M. Baizer, G. R. Handrick, L. W. Kissinger, and E. H. Specht, *ibid.*, **69**, 785 (1947).
- (32) C. Hakanson and M. Nilson, *Acta Chem. Scand.*, **21**, 1978 (1967).
- (33) T. L. Davis, *J. Amer. Chem. Soc.*, **44**, 1588 (1922); W. Enz and F. Pfister, *Helv. Chim. Acta*, **13**, 194 (1930); H. E. Fierz-David and R. Sponagel, *ibid.*, **26**, 98 (1943).
- (34) E. de B. Barnett and J. W. Cook, *J. Chem. Soc.*, **125**, 1084 (1922).
- (35) H. Suzuki, M. Sawaki, and R. Sakimoto, *Chem. Commun.*, **1971**, 1509; H. Suzuki, M. Sawaki, and R. Sakimoto, *Bull. Chem. Soc. Japan*, **45**, 1515 (1972); H. Suzuki, M. Sawaki, and R. Sakimoto, *ibid.*, **45**, 1834 (1972).
- (36) H. Suzuki and K. Nakamura, *Chem. Commun.*, **1972**, 340; H. Suzuki and K. Nakamura, *Bull. Chem. Soc. Japan*, **45**, 2534 (1972).
- (37) H. Suzuki and K. Nakamura, *ibid.*, **45**, 1270 (1972).
- (38) H. J. Lewis and R. Robinson, *J. Chem. Soc.*, **1934**, 1253.
- (39) H. Thomas, *Ber.*, **36**, 854, 1715 (1903).
- (40) H. H. Hodgson and J. Nixon, *J. Chem. Soc.*, **1930**, 1085.
- (41) I. Sobolev, *J. Org. Chem.*, **26**, 5080 (1961).
- (42) L. I. Smith and F. J. Dobrovolny, *J. Amer. Chem. Soc.*, **48**, 1693 (1926).
- (43) M. Kohn and L. W. Guttman, *Monatsh.*, **45**, 573 (1924).
- (44) W. F. Gum, M. R. W. Levy, and M. M. Joullie, *J. Chem. Soc.*, **1965**, 2282.
- (45) A. Töhl and H. Tripke, *Ber.*, **28**, 2459 (1895).
- (46) G. M. Sharma and P. R. Burkholder, *Tetrahedron Lett.*, **42**, 4147 (1967).
- (47) E. Müller, A. Schick, and K. Scheffler, *Chem. Ber.*, **92**, 474 (1959).
- (48) A. W. Crossley and C. H. Hampshire, *J. Chem. Soc.*, **99**, 721 (1911).
- (49) I. Puskas and E. K. Fields, *J. Org. Chem.*, **31**, 4205 (1966).
- (50) I. Puskas and E. K. Fields, *ibid.*, **32**, 589 (1967).
- (51) N. L. Allinger, B. J. Gorden, S. E. Hu, and R. A. Ford, *ibid.*, **32**, 2272 (1967).
- (52) F. Reverdin, *Ber.*, **29**, 997 (1896).
- (53) A. B. Sen, *Proc. Natl. Acad. Sci. India*, **9**, 89 (1939); *Chem. Abstr.*, **35**, 1038 (1941).
- (54) P. W. Robertson and H. V. A. Briscoe, *J. Chem. Soc.*, **101**, 1964 (1912).
- (55) P. C. Myhre and M. Beug, *J. Amer. Chem. Soc.*, **88**, 1569 (1966); P. C. Myhre, M. Beug, K. S. Brown, and B. Östman, *ibid.*, **93**, 3452 (1971).