temperature. "Quantitative" conversion of the acetophenone to α-phenethyl acetate was obtained.

**Procedure II. Preparation of Isopropyl Acetate.** (This procedure was used when reaction D was the predominant reaction using procedure I.) Acetyl chloride (0.78 ml, 11.0 mmoles) in 4 ml of benzene was added dropwise at room temperature to a solution of 0.62 ml (8.5 mmoles) of acetone and 3.6 ml (16.6 mmoles[11]) of triphenyltin hydride in 4 ml of benzene over a period of 33 hr. "Quantitative" conversion of the acetone to isopropyl acetate was obtained.

**Procedure III. Preparation of Isopropyl Benzoate.** (This procedure was used when reactions B and C were predominant using procedure I.) Triphenyltin hydride (1.8 ml, 8.3 mmoles[11]) in 2 ml of benzene was added dropwise to a refluxing (91° bath temperature) solution of 0.31 ml (4.3 mmoles) of acetone and 0.75 ml (6.5 mmoles[11]) of benzoyl chloride in 2 ml of benzene over a period of 14 min. The reaction mixture was then refluxed for an additional 14 min; 90% conversion of the acetone to isopropyl benzoate was obtained.

**Acknowledgments.** We are grateful to M and T Chemicals for a gift of triphenyltin chloride and to the National Science Foundation for funds for the purchase of a Varian A-60 nmr spectrometer.

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# The Structure of the Cyclopropylmethyl Carbonium Ion

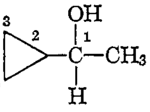
**Herman G. Richey, Jr.,[1] and Jane M. Richey**

*Contribution from the Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802. Received June 4, 1966*

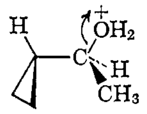
**Abstract:** The stereochemical consequence of formation and reaction of the cyclopropylmethyl carbonium ion was investigated by comparing the rate of acid-catalyzed racemization of optically active cyclopropylmethylcarbinol (**1**) with the rate of replacement of the hydroxyl group. It was observed that $k_{rac} \sim k_{ex}$. The implications of this finding for the structure of the cyclopropylmethyl carbonium ion are discussed.

A variety of experiments indicate that the cyclopropyl group is remarkably more effective than other alkyl groups in stabilizing carbonium ions.[2,3] In fact, stabilization by cyclopropyl is even greater than by phenyl. This stabilization must be due, of course, to extensive delocalization of positive charge into the cyclopropyl rings, and a number of representations have been proposed for this delocalization.[2]

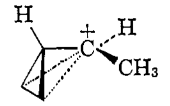
This study of the stereochemistry of product formation from the carbonium ion generated from optically active cyclopropylmethylcarbinol (**1**) in aqueous acid provides evidence relating to the geometric requirement for maximum conjugation in cyclopropyl carbonium ions. Attention is focused particularly on the dihedral angle around the cyclopropyl–C$^+$ bond. The reaction chosen was the replacement of $H_2O$ by $H_2O^{18}$. The stereochemistry of this substitution can be inferred from comparison of the rate of this exchange ($k_{ex}$) with the rate of racemization ($k_{rac}$).



**1**

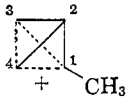


**2**



**3**

If, for example, the ion had the "crown" geometry[3,4] depicted in **3** (the dotted lines are intended to clarify the geometry, not to indicate the nature of the bonding), optically active products might be expected since **3** itself is active. Substitution with predominant retention of configuration would be reasonable; probably departure of water from the protonated alcohol (**2**) would lead to **3** (rather than to the enantiomer of **3**) and addition of water would give back **2**. Of the structures that have been proposed to represent the delocalization of charge in cyclopropyl carbonium ions, the tricyclobutonium ion structure (**4**),[5,6] which postulates direct bonding of C-1 to C-3 and C-4, would be expected to have the crown geometry. A distorted crown geometry would be predicted for the bicyclobutonium ion structure (**5**), which involves direct bonding of C-1 to C-4.[6,7]



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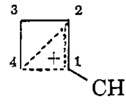
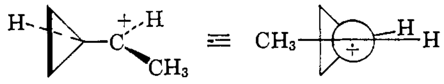
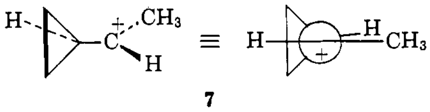


**5**

Alternatively, if the ion had a "bisected" geometry[3] (**6** or **7**), inactive products would be expected since **6**



**6**



**7**

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[1] Alfred P. Sloan Foundation Research Fellow.

[2] Reviewed by H. G. Richey, Jr., in a chapter prepared for "Carbonium Ions," G. A. Olah and P. von R. Schleyer, Ed., to be published by John Wiley and Sons, Inc., New York, N. Y.

[3] N. C. Deno in "Progress in Physical Organic Chemistry," Vol. 2, S. G. Cohen, A. Streitwieser, Jr., and R. W. Taft, Ed., Interscience Publishers, Inc., New York, N. Y., 1964.

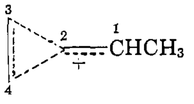
[4] Though the following discussion assumes that the cyclopropyl groups of cyclopropyl carbonium ions are not greatly distorted, the problem of distinguishing between crown and bisected geometries would exist even if cyclopropyl rings were greatly altered.

[5] J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 3542 (1951); C. G. Bergstrom and S. Siegel, *ibid.*, 74, 145 (1952). This structure has already been eliminated as a possible description since C-1, C-3, and C-4 are not always equilibrated completely in reactions thought to proceed through unsubstituted cyclopropyl carbonium ions (see ref 6).

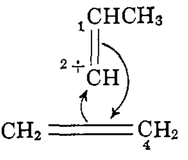
[6] R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver, and J. D. Roberts, *ibid.*, **81**, 4390 (1959).

[7] M. E. H. Howden and J. D. Roberts, *Tetrahedron*, **19** [2], 403 (1963). Ion **5** is assumed to be in rapid equilibrium with closely related isomers in which C-1, C-3, and C-4 have interchanged positions.

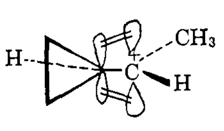
and 7 have planes of symmetry. The bisected geometry might be expected for the proposed symmetrical homoallylic structure[8] (**8**) or for the similar $\pi$ complex structure (**9**).[9] The bisected geometry also is predicted by considering the delocalization of charge to be due to overlap of an orbital of high p character in the plane of the cyclopropyl ring with the p orbital of the trigonal carbon as shown in **10**.[3,10] Descriptions of bonding in cyclopropane agree in proposing that the orbitals at each carbon used to form the ring bonds have a high degree of p character.[11]



**8**



**9**



**10**

## Results

The hydrogen phthalate ester (**11**) of alcohol **1** was resolved by recrystallization of its brucine salt. The brucine salt was reconverted to an active hydrogen phthalate which in turn was reduced with lithium aluminum hydride to active **1**, $[\alpha]^{25}\text{D}$ +21.7° (neat).

Pseudo-first-order rate constants were determined in 0.94 $M$ solutions of **1** in 0.0696 $M$ aqueous perchloric acid. The rate constant for racemization at 24.94° was $4.64 \times 10^{-5}\ \text{sec}^{-1}$ (mean deviation for four rates = $0.02 \times 10^{-5}\ \text{sec}^{-1}$). Identical conditions were used for the exchange runs except that about 8% of the water was $H_2O^{18}$; the exchange was followed by isolation by glpc of **1** from quenched aliquots and determination of $O^{18}$ content by mass spectrometry. A rate constant for exchange of $4.46 \times 10^{-5}\ \text{sec}^{-1}$ (mean deviation for four rates = $0.11 \times 10^{-5}\ \text{sec}^{-1}$) was determined using data obtained from two runs by independent use of two sets of O-containing peaks.

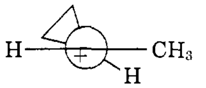
## Discussion

The rate of exchange of the hydroxyl group of **1** was about $10^2$ faster than the rate[12] of a similar exchange of phenylmethylcarbinol, indicating a considerable rate enhancement due to the cyclopropyl group.[14] Therefore the exchange must have involved formation of a carbonium ion rather than a bimolecular displacement by water on protonated **1**. Exchange did not proceed through formation of an olefin followed by rehydration since samples of **1** recovered after many half-lives from similar reactions carried out in $D_2O$ contained no detectable excess deuterium bonded to carbon.

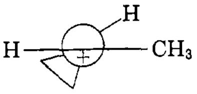
The small difference between $k_{\text{rac}}$ and $k_{\text{ex}}$ may be within the limits of error. The comparison of these rate constants is affected not only by experimental errors in the determinations of $k_{\text{rac}}$ and $k_{\text{ex}}$, but also, though probably not significantly, by small kinetic and equilibrium isotope effects on $k_{\text{ex}}$ that are ignored in this work.[15] The larger difference between $k_{\text{rac}}$ and $k_{\text{ex}}$ ($k_{\text{rac}} > k_{\text{ex}}$) observed with phenylmethylcarbinol[13,16] was attributed to reaction of the carbonium ion before the departing water molecule had time to equilibrate completely with the solvent water molecules; if carbonium ion lifetime is short, the leaving water molecule has a greater probability of reacting with the carbonium ion than has a water molecule in the bulk of the solvent. The difference between $k_{\text{rac}}$ and $k_{\text{ex}}$ for **1** could be rationalized similarly, the smaller magnitude of the difference being due to the greater stability and hence longer lifetime of the carbonium ion.

We conclude that formation of racemic product was the stereochemical consequence of formation and reaction of the carbonium ion from optically active **1**. Other studies of products formed from the cyclopropylmethyl carbonium ion have had similar results. Goering and Rubenstein reported recently that hydrolysis of the *p*-nitrobenzoate of optically active **1** leads to completely racemic **1**.[17] Vogel and Roberts observed that diazotization of optically active cyclopropylmethylamine and hydrolysis of optically active N-methyl-4-(cyclopropylmethylcarbinyloxy)pyridine both lead to formation of **1** that is nearly racemic but exhibits the small excess of inversion typical of unimolecular nucleophilic displacements.[18]

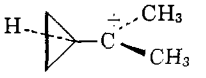
The observation that $k_{\text{rac}} \sim k_{\text{ex}}$ can be explained most readily by assuming that the ion has a bisected geometry (**6** or **7**). A crown geometry, however, is difficult to reconcile with the experimental results. Variations of the crown geometry, such as structures in which C-1 is nonplanar or tilted structures such as **12**, also should lead to optically active **1**. Some more complicated variants of the bisected geometry, for example, a rapid equilibration between tilted forms such as **12** and **13**, also would be consistent with the experimental observations. Other recent studies[2] have suggested that the bisected geometry is preferred, not only for cyclopropyl carbonium ions, but also for neutral compounds in which cyclopropyl groups are attached to $sp^2$ carbons.



**12**



**13**



**14**

The observation that $k_{\text{rac}} \sim k_{\text{ex}}$ also could be explained either by formation of an optically active ion that racemized before reacting with water or by formation of an ion that had no greatly preferred dihedral

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(8) S. Winstein and E. M. Kosower, *J. Am. Chem. Soc.*, **81**, 4399 (1959); M. Simonetta and S. Winstein, *ibid.*, **76**, 18 (1954).

(9) M. J. S. Dewar and A. P. Marchland, *Ann. Rev. Phys. Chem.*, **16**, 321 (1965).

(10) C. U. Pittman, Jr., and G. A Olah, *J. Am. Chem. Soc.*, **87**, 5123 (1965).

(11) C. A. Coulson and W. E. Moffitt, *Phil. Mag.*, 40, 1 (1949); A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).

(12) Estimated from data in ref 13.

(13) E. Grunwald, A. Heller, and F. S. Klein, *J. Chem. Soc.*, 2604 (1957).

(14) The rate also was about $10^2$ times greater than the rate of similar exchanges involving *t*-butyl alcohol [R. H. Boyd, R. W. Taft, Jr., A. P. Wolf, and D. R. Christman, *J. Am. Chem. Soc.*, **82**, 4729 (1960); I. Dostrovsky and F. S. Klein, *J. Chem. Soc.*, 791 (1955)]. Data for other exchanges of alcohols have been summarized [D. Samuel and B. L. Silver in "Advances in Physical Organic Chemistry," Vol. 3, V. Gold, Ed., Academic Press, London, 1965].

(15) Medium effects [for example, see E. R. Thornton, *J. Am. Chem. Soc.*, **84**, 2474 (1962)] should be particularly small since only about 8% of the solvent was $H_2O^{18}$. A brief discussion of the isotope effects expected for a reaction of this kind is contained in H. L. Goering and R. R. Josephson, *ibid.*, **84**, 2779 (1962).

(16) Such differences have been observed in other studies [H. L. Goering and R. E. Dilgren, *J. Am. Chem. Soc.*, **82**, 5744 (1960); C. A. Bunton and R. B. Henderson, *Tetrahedron Letters*, 1829 (1963)].

(17) H. L. Goering and K. E. Rubenstein, Abstracts, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966.

(18) M. Vogel and J. D. Roberts, *J. Am. Chem. Soc.*, **88**, 2262 (1966).

angle around the cyclopropyl–C$^+$ bond. However, because of the results of Pittman and Olah[10] these possibilities seem unlikely. They proposed a bisected structure (**14**) for the cyclopropyldimethyl carbonium ion to explain the observation of a discrete nmr absorption for each methyl group. There was no apparent coalescence of the methyl absorptions at −35°, so rotation around the cyclopropyl–C$^+$ bond had a half-time considerably greater than $10^{-2}$ sec even at that low temperature. The cyclopropylmethyl carbonium ion should have even stronger conjugation between the cyclopropyl group and C$^+$ than does the cyclopropyldimethyl carbonium ion and an even higher barrier to rotation. Therefore, rotation should not occur in the cyclopropylmethyl carbonium ion in the short time before it is attacked by water.

The rates of exchange and racemization of **1** are more than $10^3$ greater than the combined rates of all processes that lead to disappearance of **1**. This illustrates dramatically that the reactions of cyclopropyl carbonium ions in which C-1 is not primary often lead predominantly to unrearranged products.

## Experimental Section

A 15 ft × 0.25 in. column packed with 35% (w/w) dioctyl phthalate on 60–80 mesh Gas-Chrom P (Applied Science Laboratories) was used at 100° and a flow rate of 90 ml/min for glpc separations in an Aerograph A-90P (Wilkens Instrument and Research) gas chromatograph. A Nuclide Analysis Associates 12-90-Gl mass spectrometer was used for mass spectral analyses with an ionizing voltage of 70 v, a trap current of 50 $\mu$a, and a Faraday cup detector. A Franz Schmidt and Haensch (10910) polarimeter was used. Elemental analyses were done by Midwest Microlab. Melting points were taken in capillary tubes.

**Hydrogen Phthalate Ester of Cyclopropylmethylcarbinol (1).** A mixture of cyclopropylmethylcarbinol (39.8 g, 0.463 mole), phthalic anhydride (95 g, 0.64 mole), and pyridine (101 g, 1.28 moles) was heated on a steam bath for 5 hr. The solution was diluted with 250 ml of benzene, washed with two 300-ml portions of 10% sulfuric acid, washed repeatedly with water, and dried over sodium sulfate. Removal of the solvent at reduced pressure left 96 g (0.410 mole, 89%) of product, mp 68–69°. Two recrystallizations from ether–pentane gave solid of mp 70–71°.

*Anal.* Calcd for $C_{13}H_{14}O_4$: C, 66.66; H, 6.02. Found: C, 66.94; H, 6.34.

**Resolution of Hydrogen Phthalate Ester of Cyclopropylmethylcarbinol (11).** Brucine (367 g, 0.931 mole) and racemic **11** (218 g, 0.931 mole) were refluxed in 10 l. of acetone. The solution was filtered to remove a small amount of undissolved solid, and then solvent was distilled off until only 4.5 l. of solution remained, at which time considerable precipitate had appeared. The solution was allowed to cool slowly to room temperature and then placed in an icebox overnight. Filtration provided 381 g of the brucine salt of **11**. Since the brucine salt was soluble in acetone only with difficulty, it was convenient in recrystallizing this material to use an excess of acetone, as above, to effect solution, and then, after filtering off any traces of undissolved material, to concentrate the solution to the desired volume. The solutions were allowed to cool slowly and then left in an icebox overnight. Three such recrystallizations from acetone (using 3, 2.5, and 1.0 l., respectively, as the final solvent volumes) gave 143 g of brucine salt of **11**, mp 176–177.5°, $[\alpha]^{25}\text{D}$ −5.2° (*c* 5.0, 95% ethanol), that did not alter significantly in rotation or melting point on further recrystallization.

*Anal.* Calcd for $C_{36}H_{40}O_8N_2$: C, 68.77; H, 6.41; N, 4.46. Found: C, 68.49; H, 6.50; N, 4.39.

The brucine salt (141 g, 0.224 mole) was shaken with 1.2 l. of ether and 1.0 l. of 5% sulfuric acid. The layers were separated, and the ether layer was washed with five 400-ml portions of water and dried over Drierite. The solvent was removed at reduced pressure leaving 47 g (0.202 mole) of optically active **11**, mp 63–65°, $[\alpha]^{25}\text{D}$ +48.6° (*c* 2.3, 95% ethanol). The infrared spectrum ($CHCl_3$) of the optically active ester was identical with that of the racemic ester. Four recrystallizations from ether–pentane gave a solid with mp 66.5–66°.

*Anal.* Calcd for $C_{13}H_{14}O_4$: C, 66.65; H, 6.02. Found: C, 66.97; H, 6.12.

Efforts to obtain in pure form the diastereoisomeric brucine salt were unsuccessful. In fact, (−)-**11** with the largest rotation was obtained by taking the solid contained in the mother liquors that remained after the initial precipitation of brucine salt and, without prior recrystallization, converting it directly to phthalate ester using the procedure described above.

**Conversion of (+)-Hydrogen Phthalate Ester of Cyclopropylmethylcarbinol to (+)-Cyclopropylmethylcarbinol.** A solution of (+)-**11** (44.7 g, 0.191 mole) in 250 ml of ether was added over 1 hr to a stirred solution of 14.9 g (0.393 mole) of lithium aluminum hydride in 200 ml of ether that was cooled in an ice bath. After addition was completed, the ice bath was removed and the solution allowed to stir for 2 additional hr. Then 100 ml of water was added slowly with stirring. As much as possible of the ether solution was decanted. Then 200 ml of ether was added to the residue in the flask, stirred with the contents, and also decanted. This process was repeated with three more 200-ml portions of ether. The combined ether extracts were washed with water and dried over Drierite. The solution was filtered and distilled. A fraction of 10.75 g was collected at 118–124° (733 mm). Careful redistillation of this fraction gave 9.65 g (0.112 mole, 59%) at 120–122° (733 mm), $[\alpha]^{25}\text{D}$ +20.7° (neat). The infrared and nmr spectra of the resolved alcohol were identical with those of the inactive alcohol.

**Polarimetric Rate Constants.** A solution was prepared by weighing about 2.0 g of a stock solution of aqueous perchloric acid into a 10 ml volumetric flask and adding about 6 ml of distilled water. The solution was allowed to equilibrate in a constant temperature bath and then 900 $\mu$l of optically active **1** was added, and the flask was filled to the mark with distilled water. Such solutions were 0.0696 *M* in acid and 0.94 *M* in alcohol. The solution was transferred to a 11.9-cm jacketed polarimeter tube with permanently sealed windows and a center opening for filling. Water from the constant temperature bath was circulated rapidly through the jacket. The bath temperature was 24.94 ± 0.02°. The initial rotations were about 1.02°, and the polarimeter could be read to 0.01°. Readings were taken rapidly and 3–6 readings were averaged to obtain each point. As racemization proceeded, rotations became more difficult to read due to faint turbidity in the solutions caused by formation of traces of insoluble material. For this reason, rates were followed for only about two half-lives. Excellent pseudo-first-order rate plots were obtained. Each rate constant was determined from about 25 points using a least-squares computer program.

**Exchange Rate Constants.** Solutions were prepared as for the polarimetric experiments except on one-half the scale. The same perchloric acid[19] stock solution was used but water containing excess $O^{18}$ (Isomet Corp., 11.75% $O^{18}$, 0.016% $O^{17}$, normalized to normal abundance of deuterium) was used in place of distilled water. The volumetric flask was maintained in the constant temperature bath, and aliquots of about 0.5 ml were withdrawn at intervals. The samples used for determinations of infinity values were withdrawn after about 48 hr. Immediately after removal from the bath, an aliquot was added to a test tube containing 300 mg of potassium carbonate and the mixture was agitated. Ether (0.5 ml) was added and the tube shaken further. The ether was removed with a syringe and dried over Drierite. About 300 $\mu$l of the ether solution was injected into the gas chromatograph. The cyclopropylmethylcarbinol peak was trapped in a collection tube that was inserted into the outlet of the gas chromatograph. The tube was fitted at either end with vacuum stopcocks and had a joint for attachment to a vacuum line.

Control experiments demonstrated that the chromatographic procedure did not alter the isotopic content of **1**. The analysis of a sample labeled with about 6% $O^{18}$ was the same within experimental error after the sample had been submitted again to the chromatographic procedure. The rotation of a sample of optically active **1** did not change on chromatography, further evidence that no exchange occurred during the chromatographic procedure.

Experiments using similar solutions prepared with unlabeled water demonstrated that the peak that was collected and then analyzed contained only **1**. The mass spectra (particularly the relative heights of the 73 and 71 peaks or of the 47 and 45 peaks)

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[19] The perchlorate anion does not exchange with $H_2O^{18}$ under these conditions [T. C. Hoering, F. T. Ishimori, and H. O. McDonald, *J. Am. Chem. Soc.*, 80, 3876 (1958); A. E. Brodsky, *J. Chim. Phys.*, 55, 40 (1958)].

of pure **1** and of a sample of **1** collected after 39 hr were the same within experimental error. Similarly, nmr and infrared spectra of material from this peak, isolated even after 32 days in the acid solutions, were identical with those of pure **1**. On standing in aqueous acid, **1** was converted ultimately to a complex mixture of compounds, some of which separated from the aqueous solution. The concentration of **1** remaining could be estimated using its characteristic nmr absorptions (particularly the complex absorptions of the cyclopropyl hydrogens). In several experiments it was noted that the rate of disappearance of **1** had a half-time of greater than 1 month.

The sample to be analyzed was transferred to the mass spectrometer. The height of the 73 relative to the 71 peak and of the 47 relative to the 45 peak was determined carefully with a slow sweep. For every sample, to eliminate small errors due to drifting with time, a given peak ($n$) was swept 4–12 times, the accompanying peak ($n + 2$) swept a corresponding number of times, and the original peak again swept the same number of times. All values were averaged to obtain the relative heights of the peaks. Ratios determined on the same day were generally reproducible to 0.0005 in the range (0 to 0.1) in which the ratios fell.

The pseudo-first-order rate constants for exchange then were calculated from the usual first-order rate expression for an exchange process.[20] The concentrations of $O^{18}$-labeled **1** to put into this expression were taken from values of $(\text{height}_n)/(\text{height}_n + \text{height}_{n+2})$ for the labeled samples from which were subtracted the (small) value of this term obtained for unlabeled **1**.[21] For each run (two runs with 6 and 8 significant points, respectively), separate rate constants were determined with a least-squares computer program using the data from the two sets of mass spectral peaks.

A similar experiment used $D_2O$ instead of $H_2O^{18}$ as the solvent. After 22 hr, the solution (10 ml) was poured into 10 ml of ether. The ether solution was washed with four 5-ml portions of 0.01 *M* aqueous perchloric acid and with 5 ml of a concentrated potassium carbonate solution, dried over Drierite, and concentrated. The **1** isolated by chromatography gave 72:71 and 46:45 ratios the same within experimental error as those given by pure **1** and exhibited an infrared spectrum identical with that of pure **1**.

**Acknowledgment.** We are grateful for support of this research by the National Science Foundation and the Alfred P. Sloan Foundation. We are pleased to acknowledge the assistance of the National Science Foundation in providing funds to aid in the purchase of the Varian A-60 nmr spectrometer and the Nuclide Analysis Associates 12-90-Gl mass spectrometer used in this research. We thank Professors F. W. Lampe and N. C. Deno for helpful discussions, R. A. Plepys and Dr. G. G. Hess for the mass spectral analyses, and Dr. K. W. Michael for assistance with the polarimetric rates.

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(20) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1961, p 192.

(21) More elaborate corrections [see C. G. Swain, G.-I. Tsuchihashi, and L. J. Taylor, *Anal. Chem.*, **35**, 1415 (1963)] would not have significantly altered the results.

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# Organic Ions in the Gas Phase. XVIII. Mass Spectra of Nitroarenes

**Seymour Meyerson,[1a] Imre Puskas,[1b] and Ellis K. Fields[1b]**

*Contribution from the Research and Development Department, American Oil Company, Whiting, Indiana, and Research Department, Amoco Chemicals Corporation, Whiting, Indiana.* *Received April 30, 1966*

**Abstract:** The mass spectra of unlabeled and deuterated isomeric nitrotoluenes, of the isomeric nitrobiphenyls, and of a dimethoxy-2-nitrophenol help define the roles of steric and mesomeric effects in decomposition of nitroarenes under electron impact. Intramolecular oxidation–reductions and isomerization to aryl nitrites, prominent in these systems, parallel and can thus serve as precedents for interpretation of thermal and photochemical reactions.

An exploratory study of aromatic nitration[2] furnished an opportunity and incentive to study the mass spectra of a group of nitroarenes. The most prominent features of nitroarene spectra are well known.[3–12] Nitrobenzene and many derivatives show evidence for primary loss of O, NO, and $NO_2$,[13] and for formation of $NO^+$. Derivatives with an *ortho* substituent containing α hydrogens—$CH_3$, $NH_2$, or OH—show primary loss of OH rather than O; such loss of OH is often followed by loss of CO. Mechanistic details of this reaction sequence, as well as of competing processes, have been the subject of study and speculation.

The pronounced effects of *ortho* substitution on the mass spectra of nitroarenes are presumably related to the wide range of poorly understood reactions displayed by *ortho*-substituted nitroarenes in more conventional chemical[14] and photochemical[15] systems. Within the

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(1) (a) American Oil Co.; (b) Amoco Chemicals Corp.

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