Partial Rate Factors for the Nitration of Cyclopropylbenzene Derivatives. Influence of Geometry on the Stability of 3- and 4-Cyclopropylbenzenonium Ions[1]

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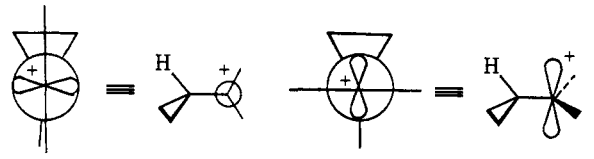
Abstract: Relative rates and isomer distributions for the nitration of cyclopropylbenzene and several derivatives with acetyl nitrate in methylene chloride at −25° have been determined. The results for cyclopropylbenzene, 2,6-dimethylcyclopropylbenzene, *syn*- and *anti*-(*cis*-2,3-dimethylcyclopropyl)benzene, spiro(cyclopropane-1,1′-indan) and 3′,3′-dihydrospiro(cyclopropane-1,1′(2*H*′)-naphthalene) and related compounds indicate that 3_f(cyclopropyl) ranges from 2 to 5 for both the perpendicular and bisected conformations and that 4_f(cyclopropyl) is small, probably no more than 10, for the perpendicular conformation, but about 1800 for the bisected conformation. The relationship between these results and the relative reactivities inferred from calculations based on the CNDO model is discussed.

Electrophilic aromatic substitution reactions[3] and the electrophilic reactions of side-chain derivatives of benzene[4] have long served as testing ground for theories concerning the relationship between molecular structure and reactivity. Reactions of this kind have been used by Brown, Hahn, Martin, and Shechter and their associates to study the influence of the cyclopropyl group on the stability of electron-deficient molecules.[5-8] To illustrate, an investigation of the solvolysis of 2-chloro-2-(3- and 2-chloro-2-(4-cyclopropylphenyl)propane established that the 4-cyclopropyl group stabilized the incipient carbonium ion importantly and that the stabilization was diminished significantly by methyl groups in the 3 and 5 positions.[5,6] These results meshed beautifully with other emerging



observations and theories which implied that the maximum stabilization was achieved when the cyclopropane substituent was in the bisected conformation rather than in the perpendicular conformation.[9] Hahn, Corbin, and Shechter also estimated the partial rate factors, $3_f \simeq 2$ and $4_f \simeq 950$, for the nitration of cyclopropylbenzene.[6] Hahn and his students and we, in conjunction with an investigation of the electron spin resonance spectra of 4-nitrocyclopropylbenzene anion radicals,[10] have independently extended the investigation of the nitration reaction to other aromatic compounds to assess the influence of perpendicular and bisected cyclopropyl groups.

Results

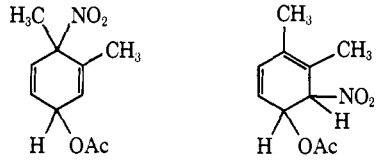
Features of the Nitration Reaction. We attempted to use the highly selective noncatalytic bromination reaction, $\rho^+ = -12.1$, to define the relative reactivity of the cyclopropylbenzenes. Unfortunately, spiro(cyclopropane-1,1′-indan) isomerized in acetic acid in the presence of bromine and hydrogen bromide. The product, 1-ethylindene, was isolated and identified by its nmr spectrum. Under the mild experimental conditions of the bromination reaction, this olefin brominated to yield a complex mixture of products.[11]

The successful nitration of cyclopropylbenzene by several investigators prompted us to explore the use of this reaction.[6,11] In particular, Hahn, Corbin, and Shechter reported that nitric acid in acetic anhydride yielded 95% 2- and 4-nitrocyclopropylbenzene.[6] Preliminary experiments revealed that the nitration of spiro(cyclopropane-1,1′-indan) at 25° produced substantial amounts of 1-ethylindene. However, the nitration of spiro(cyclopropane-1,1′-indan) in acetic anhydride at −25° proceeded at a reasonable rate without the formation of a detectable amount of the indene. This result encouraged us to adopt this reaction to define the influence of perpendicular and bisected cyclopropane substituents on reactivity.

The concurrent formation of aryl acetates in the nitration of 1,2-dimethylbenzene in acetic anhydride is a troublesome side reaction. Fischer, Vaughan, and Wright and their associates investigated this reaction.[12]

(1) This research was supported by the National Science Foundation.
(2) Fellow of the New York State Board of Regents, 1968–1969; Fellow of the Petroleum Research Fund, 1969–1970.
(3) (a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter 6; (b) P. B. D. de la Mare and J. H. Ridd, "Aromatic Substitution," Butterworths Scientific Publications, London, 1959; (c) R. O. C. Norman and R. Taylor, "Electrophilic Substitution in Benzenoid Compounds," Elsevier, Amsterdam, 1965.
(4) (a) H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, 80, 4979 (1958); (b) L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, **1**, 35 (1963).
(5) H. C. Brown and J. C. Cleveland, *J. Amer. Chem. Soc.*, 88, 2051 (1966).
(6) R. C. Hahn, T. F. Corbin, and H. Shechter, *ibid.*, **90**, 3404 (1968).
(7) (a) R. C. Hahn, P. H. Howard, S. Kong, G. A. Lorenzo, and N. L. Miller, *ibid.*, **91**, 3558 (1969); (b) R. C. Hahn, *et al.*, unpublished results concerning the nitration of spiro(cyclopropane-1,1′-indan) and 3′,4′-dihydrospiro(cyclopropane-1,1′(2*H*′)-naphthalene). We thank Professor Hahn for advising us of his work prior to publication.
(8) (a) T. Sharpe and J. C. Martin, *ibid.*, 88, 1815 (1966); (b) J. C. Martin and B. C. Ree, *ibid.*, **91**, 5882 (1969).
(9) For a complete summary of the literature see G. W. van Dine and P. von R. Schleyer, *ibid.*, 88, 2321 (1966), and P. von R. Schleyer and V. Buss, *ibid.*, **91**, 5880 (1969).
(10) P. E. Young, Ph.D. Thesis, University of Chicago Library, 1971.
(11) Presumably less reactive cyclopropanes, such as cyclopropylbenzene, cleave under similar conditions: R. Ya. Levina and P. A. Gembitskii, *J. Chem. Chem. USSR*, **31**, 3242 (1961); Yu. S. Shabarov, S. N. Burenko, and R. Ya. Levina, *Zh. Org. Khim.*, **4**, 66 (1968). The related acetylation of cyclopropylbenzene and the accompanying ring cleavage reaction have been investigated: H. Hart, R. H. Schlosberg, and R. K. Murray, Jr., *J. Org. Chem.*, **33**, 3800 (1968).
(12) (a) A. Fischer, J. Packer, J. Vaughan, and G. J. Wright, *J. Chem. Soc.*, 369 (1961); (b) A. Fischer, A. J. Read, and J. Vaughan,

They initially argued that protonated acetyl nitrate was an ambident electrophilic reagent capable of both nitration and acetyloxylation. The similarity between nitration in acetic anhydride and other organic media, such as nitromethane, is striking. In the latter solvent, the nitronium ion has been identified as the reactive electrophile.[13] Accordingly, an addition–elimination mechanism was suggested by de la Mare and Ridd.[13] The recent isolation of intermediate adducts by the New Zealand group offers cogent evidence for the addition–elimination pathway.[12c,12d,13b]



We found that dilution of the nitric acid–acetic anhydride reaction mixture with methylene chloride substantially reduced the amount of aryl acetate. When 1,2-dimethylbenzene (0.005 mol) was allowed to react with nitric acid (0.001 mol) in acetic anhydride (0.213 mol) at −20°, vpc analysis revealed about 80% acetate and 20% nitrate. However, when this hydrocarbon (0.005 mol) was allowed to react with nitric acid (0.0011 mol) and acetic anhydride (0.0022 mol) in methylene chloride (40 ml) at −20°, vpc analysis revealed only 2% acetate and 98% nitrate. To establish that selective destruction of the acetate did not occur during the isolation of the products prior to vpc analysis, we also investigated the nmr spectra of untreated reaction solutions. Absorptions due to vinyl protons were monitored in reaction mixtures containing spiro(cyclopropane-1,1′-indan) and 1,2- and 1,3-dimethylbenzene. Based on internal standards, the nmr study revealed that acetate adduct formation never exceeded 10% of the reaction products in 1,2-dimethylbenzene. Similar analysis of the nitration products of spiro(cyclopropane-1,1′-indan) indicated that acetate formation was much less significant. The nmr spectra of reaction solutions of 1,3-dimethylbenzene showed no absorption by vinyl hydrogen atoms. Thus, the side reaction is only a minor reaction pathway in the dilute methylene chloride solutions.

Schofield and his group[13b,14] report that the rates of nitration of some very reactive hydrocarbons may be, under certain conditions, encounter controlled. However, their study also established that the reaction of mesitylene in acetic anhydride at 25° was not encounter controlled.[14c] Under the conditions of our experiments, mesitylene nitrates about sixfold more rapidly than 1,3-dimethylbenzene and more than twofold more rapidly than the most reactive cyclopropylbenzene examined. Consequently, the relative rates measured in this study reflect differences in chemical reactivity rather than differences in diffusion rates.

Schofield also proposed that compounds such as phenol and anthanthrene which exhibit reactivity greater than that of mesitylene undergo nitration *via* nitrosation.[14c] This conclusion was supported by the observation that even trace amounts of nitrous acid in nitric acid yielded enormous rate enhancements. Experiments designed to detect the involvement of nitrous acid under the conditions of our work all gave negative results. For example, the addition of urea had no significant effect on either the rate or isomer distribution for the nitration of either 1,2-dimethylbenzene or mesitylene. We conclude therefore that nitration *via* prior nitrosation is insignificant under these conditions and that the relative rates reflect the influence of structure on the stability of the incipient benzenonium ions.

The hydrocarbons used in the rate measurements were purified by fractionation or by preparative vpc. The nitrobenzene derivatives which were not available from commercial sources and which were necessary for chromatographic analyses were prepared by the nitration of the corresponding hydrocarbons. The 2 and 4 isomers of the monosubstituted compounds, cyclopropylbenzene, *syn*- and *anti*-(*cis*-2,3-dimethylcyclopropyl)benzene, and (1-methylcyclopropyl)benzene were readily separated and isolated by vpc and identified by their mass and nmr spectra. The 4 isomer had the longer retention time when chromatographed on Carbowax 20M and the nmr spectra of these compounds contained an AB(AA′BB′) pattern in the aromatic proton region.[15] In contrast, the 2 isomer obtained as the second major product exhibited a distinctly shorter retention time and a more complex aryl proton spectrum. The 3-nitro derivatives of toluene, cumene, and cyclopropylbenzene were available. However, the 3-nitro derivatives of the other monosubstituted compounds were not available for the analytical work.

The nitro derivatives of the disubstituted benzenes were also obtained, for the most part, by nitration of the hydrocarbons. Again the mass and nmr spectra enabled a confident assignment of structure. The known nitroindans were characterized by their physical and spectroscopic properties. The appearance of one and two methyl frequencies in the nmr spectra of 3- and 4-nitro-2,6-dimethylcyclopropylbenzene, respectively, established the structure of these compounds. The isomeric nitrospiro(cyclopropane-1,1′-indans) were recently prepared and characterized by Hahn and his students who generously provided us with information concerning their physical and spectroscopic properties.[6,7] Three nitro derivatives, one in rather small amount, were obtained in the nitration of 1,1-dimethylindan. The nmr spectra of the two major products were similar to the spectra of 5- and 6-nitrospiro(cyclopropane-1,1′-indan). To verify the assignment of structure we prepared 5-nitro-1,1-dimethylindan by an unambiguous route as described in the Experimental Section. The other major product was assigned the structure of 6-nitro-1,1-dimethylindan on the basis of the expectation that this isomer should be produced in important amounts and on the basis of the nmr spectrum.[15] The third isomer produced in small amount in the nitration of 1,1-dimethylindan is 4-nitro-1,1-di-

ibid., 3691 (1964); (c) D. J. Blackstock, A. Fischer, K. E. Richards, J. Vaughan, and G. J. Wright, *J. Chem. Soc. D*, 641 (1970); (d) D. J. Blackstone, J. R. Cretney, A. Fischer, M. P. Hartshorn, J. E. Richards, J. Vaughan, and G. J. Wright, *Tetrahedron Lett.*, 2793 (1970).

(13) (a) J. H. Ridd, "Studies of Chemical Structure and Reactivity," J. H. Ridd, Ed., Methuen, London, 1966, Chapter 7; (b) J. H. Ridd, *Accounts Chem. Res.*, 4, 248 (1971).

(14) (a) R. G. Coombes, R. B. Moodie, and K. Schofield, *J. Chem. Soc. B*, 800 (1968); (b) J. G. Hoggett, R. B. Moodie, and K. Schofield, *ibid.*, 1 (1969); (c) J. G. Hoggett, R. B. Moodie, and K. Schofield, *J. Chem. Soc. D*, 605 (1969).

(15) The spectroscopic properties of many compounds in this series have been discussed by Hahn and his associates, ref 7.

methylindan. This assignment is based on the expectation that substitution should be more rapid at the less-hindered 4 position. Finally, 3′,4′-dihydrospiro(cyclopropane-1,1′(2*H*′)-naphthalene) was nitrated to yield the 6-nitro and the 8-nitro derivatives as the major products. These compounds were identified by comparison of their spectroscopic properties with authentic materials.[16] The 5- and 7-nitro derivatives were not isolated.

Rates, Isomer Distributions. The nitration of the aromatic hydrocarbons was carried out with preformed acetyl nitrate in methylene chloride at −25°. The products of competitive nitration reactions were analyzed by vpc using known mixtures of pure isomers as chromatographic standards. The results of replicate analyses are summarized in Table I.

Table I. Relative Rates of Nitration of Hydrocarbons by Acetyl Nitrate in Methylene Chloride at −25°

Compound	Rel rate, $k/k_{C_6H_6}$
Benzene	1.0
Toluene	89.3
Isopropylbenzene	58.7
Cyclopropylbenzene	912
syn-(*cis*-2,3-Dimethylcyclopropyl)benzene	161
(1-Methylcyclopropyl)benzene	373
anti-(*cis*-2,3-Dimethylcyclopropyl)benzene	3290
1,2-Dimethylbenzene	509
1,3-Dimethylbenzene	1250
1,3-Dimethyl-2-cyclopropylbenzene	2380
Indan	428
1,1-Dimethylindan	417
Spiro(cyclopropane-1,1′-indan)	1690
3′,4′-Dihydrospiro(cyclopropane-1,1′(2*H*′)-naphthalene)	2150
Mesitylene	7410

The isomer distributions were determined for nitration under the conditions of the competition reactions. Known mixtures of the isomeric compounds were used as chromatographic standards in the determination of the concentrations of all the principal products. In addition, the concentrations of 3-nitrotoluene, 3-nitrocumene, and 3-nitrocyclopropylbenzene were determined in this way. The small amount (0.9%) of 5-nitro-1,3-dimethylbenzene was established by the comparison of the chromatograms of known mixtures with the 4 isomer in 100-fold excess. Values for the 3-nitro isomers of (1-methylcyclopropyl)benzene, and *syn*- and *anti*-(*cis*-2,3-dimethylcyclopropyl)benzene were not measured with confidence.

Analysis of the nitration products of the spiro compounds revealed that the 5-nitro:7-nitro isomer ratio for spiro(cyclopropane-1,1′-indan) was 93:7 and that the 6-nitro:8-nitro isomer ratio was 50:50 for 3′,4′-dihydrospiro(cyclopropane-1,1′(2*H*′)-naphthalene). These ratios are very similar to the results of Hahn and his associates for the nitration reaction in acetic anhydride at −45 and 25°.[7b,17] Accordingly, we adopted Hahn's results for the less abundant products at low temperature to obtain the complete isomer distribution for the reaction in methylene chloride at −25°. The results are summarized in Table II.

(16) (a) G. L. Closs and H. B. Klinger, unpublished results; (b) H. B. Klinger, Ph.D. Thesis, The University of Chicago Library, 1967.

(17) For the indan, the product distribution was 0.0% 4-, 83% 5-, 4% 6-, and 13% 7-nitro compound at −45° compared to 0.5% 4-, 86% 5-, 5.5% 6-, and 8% 7-nitro compound at 25°.[7b] For the tetralin, the distribution was 0.5% 5-, 47.5% 6-, 2.5% 7-, and 49.5% 8-nitro compound at −50° compared to 1% 5-, 54% 6-, 4% 7-, and 41% 8-nitro compound at 25°.[7b]

Table II. Isomer Distribution for the Nitration of Hydrocarbons by Acetyl Nitrate in Methylene Chloride at −25°

Compound	Isomer distribution, % 2	3	4	5	6	7	8
Toluene	63.4	2.1	34.5				
Isopropylbenzene	24.2	3.7	71.9				
Cyclopropylbenzene	82.5	0.2	17.3				
syn-(*cis*-2,3-Dimethylcyclopropyl)benzene	56.9	(0.8)[a]	43.1				
(1-Methylcyclopropyl)benzene	70.6	(0.8)[a]	29.4				
anti-(*cis*-2,3-Dimethylcyclopropyl)benzene	87.7	(0.9)[a]	12.3				
1,2-Dimethylbenzene		31.8	68.2				
1,3-Dimethylbenzene	13.5		86.5	0.9			
1,3-Dimethyl-2-cyclopropylbenzene			93.4	6.6			
Indan			12.2	87.8			
1,1-Dimethylindan			4.3	48.9	46.8		
Spiro(cyclopropane-1,1′-indan)[b]			0.0	90.1	3.1	6.8	
3′,4′-Dihydrospiro(cyclopropane-1,1′(2*H*′)-naphthalene)[b]				0.5	48.6	2.2	48.6

[a] Estimated value. [b] The results for nitration in acetic anhydride are presented in ref 17.

Table III. Total Energy Calculated for Cyclopropane Derivatives by the CNDO Method

Compound	Energy, kcal mol^{-1}
Perpendicular cyclopropylcarbinyl cation	−20,873.35
Bisected cyclopropylcarbinyl cation	−20,899.40
Methylcyclopropane	−21,712.79
Perpendicular isobutyl cation	−21,850.95
Bisected isobutyl cation	−21,859.63
Perpendicular 1-methylcyclopropylcarbinyl cation	−26,329.99
Bisected 1-methylcyclopropylcarbinyl cation	−26,349.54
1,1-Dimethylcyclopropane	−27,158.53
Perpendicular *anti*-(*cis*-2,3-dimethylcyclopropyl)-carbinyl cation	−31,777.53
Perpendicular *syn*-(*cis*-2,3-dimethylcyclopropyl)-carbinyl cation	−31,779.80
Bisected *syn*-(*cis*-2,3-dimethylcyclopropyl)-carbinyl cation	−31,804.10
Bisected *anti*-(*cis*-2,3-dimethylcyclopropyl)-carbinyl cation	−31,808.60
syn-(*cis*-2,3-Dimethylcyclopropyl)methane	−32,610.55
anti-(*cis*-2,3-Dimethylcyclopropyl)methane	−32,611.49
Perpendicular cyclopropylbenzene	−44,855.83
Bisected cyclopropylbenzene	−44,866.47
Perpendicular cyclopropylbenzene cation[a]	−45,146.16
Bisected cyclopropylbenzene cation[a]	−45,162.41
Perpendicular cumene	−41,819.05
Bisected cumene	−45,827.16
Perpendicular cumyl cation[b]	−46,107.92
Bisected cumyl cation[b]	−46,123.81

[a] 4-Cyclopropylbenzenonium ion. [b] 4-Isopropylbenzenonium ion.

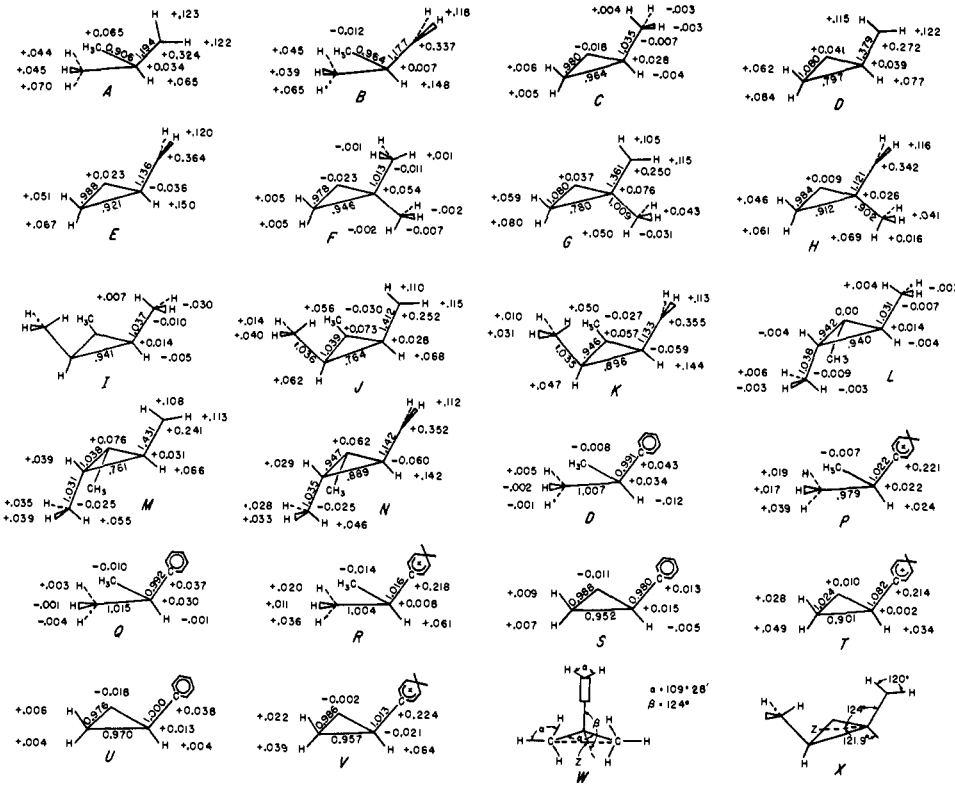


Figure 1. Charge distributions and bond indices calculated by the CNDO/2 method. The bond indices are presented in the conventional way. The hydrogen atom charges are presented with only the sign preceding the decimal point. The carbon atom charges are presented with the sign and a zero preceding the decimal point. A and B, bisected and perpendicular isobutyl ions. C, 1-methylcyclopropane. D and E, bisected and perpendicular cyclopropylcarbinyl ions. F, 1,1-dimethylcyclopropane. G and H, bisected and perpendicular 1-methylcyclopropylcarbinyl ions. I, *syn-cis*-1,2,3-trimethylcyclopropane. J and K, bisected and perpendicular *syn-cis*-2,3-dimethylcyclopropylcarbinyl ions. L, *anti-cis*-1,2,3-trimethylcyclopropane. M and N, bisected and perpendicular *anti-cis*-2,3-dimethylcyclopropylcarbinyl ions. O and P, bisected cumene and the related benzenonium ion. Q and R, perpendicular cumene and the related benzenonium ion. S and T, bisected phenylcyclopropane and the related benzenonium ion. U and V, perpendicular phenylcyclopropane and the related benzenonium ion. W, geometry used for the benzenonium ion derived from cumene and typical of the geometry used for the phenylcyclopropanes and the isobutyl ions. The isopropyl unit has one mirror plane through C_4 of the aromatic ring, C_1 of the cyclopropane ring, and the point Z which is the midpoint of the C_2–C_3 distance and a second mirror plane through C_2C_3Z. X, illustrates the geometry used for the cyclopropane derivatives and the staggered orientation of the hydrogen atoms of the methyl group with respect to the hydrogen atom of the cyclopropane ring shown. We departed from this geometry only for 1,1-dimethylcyclopropane. In this instance one methyl group was located as shown in X. The hydrogen atoms of the second methyl group were staggered with respect to those of the first.

CNDO Analysis. The energy content, charge distributions, and bond indices for representative molecules have been calculated by a modified CNDO method.[18] The molecular structures used for these calculations are based on the structure (microwave) of methylcyclopropane. The conformations chosen for the methyl groups of cumene and the cumyl and isobutyl cations are not necessarily those of lowest energy. These conformations were selected because two hydrogen atoms of each methyl group were located in positions analogous to the γ hydrogen atoms of the cyclopropane ring in the other molecules for which the calculations were carried out. Energies, charge distributions, and bond indices obtained in this study are summarized in Table III and Figure 1. There is remarkable agreement between the results obtained in this laboratory and the results reported by Wiberg for the isobutyl and unsubstituted cyclopropylcarbinyl cations.[19]

(18) R. T. C. Brownlee and R. W. Taft modified the CNDO/2 method to minimize the variation in the charge distribution: *J. Amer. Chem. Soc.*, **92**, 7077 (1970).

(19) K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968).

Discussion

Statistically correct rates of nitration for the positions (2,3,4...) of the cyclopropylbenzene derivatives relative to one position in benzene are summarized in Table IV.

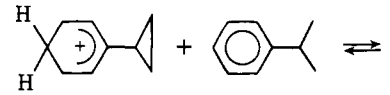
4_f for Methylated Cyclopropyl Groups. The 4_f values for the cyclopropyl group and the three methylated cyclopropyl groups indicate that these substituents have a greater activating effect than either the methyl or the isopropyl group. These results are, of course, compatible with the customary view that the cyclopropane ring is an unusually effective electron donor compared to other alkyl groups.

The results of the CNDO/2 analysis summarized in the equation are not in good accord with this view. The anticipated endothermic reaction is predicted when cyclopropane and cumene are constrained to the perpendicular conformation (case b) or when cyclopropane is constrained to the bisected conformation and cumene is constrained to the perpendicular conformation (case c). It is, however, unlikely that cumene prefers the perpendicular conformation. A detailed analysis of the steric energy requirements for the conformers of iso-

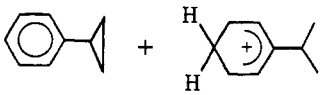
Table IV. Partial Rate Factors for the Nitration of Cyclopropylbenzenes and Related Compounds in Methylene Chloride at −25°

Compound	Partial rate factors						
	2_f	3_f	4_f	5_f	6_f	7_f	8_f
Toluene	170	5.6	185				
Isopropylbenzene	43	6.5	253				
Cyclopropylbenzene	2,260	5.5	947				
syn-(*cis*-2,3-Dimethylcyclopropyl)benzene	275		416				
(1-Methylcyclopropyl)benzene	790		658				
anti-(*cis*-2,3-Dimethylcyclopropyl)benzene	8,660		2430				
1,2-Dimethylbenzene		486	1040				
1,3-Dimethylbenzene	1,010		3240	71			
1,3-Dimethyl-2-cyclopropylbenzene			6680	944			
Indan			157	1130			
1,1-Dimethylindan			108	1220	1170		
Spiro(cyclopropane-1,1′-indan)				9140	314	690	
3′,4′-Dihydrospiro(cyclopropane-1,1′-(2*H*′)-naphthalene)				65	6270	284	6270
Mesitylene	14,800						

propylbenzene indicates that this molecule, as cyclopropylbenzene,[20] exists predominantly in the bisected



(a)	B	B	
(b)	P	P	
(c)	B	P	

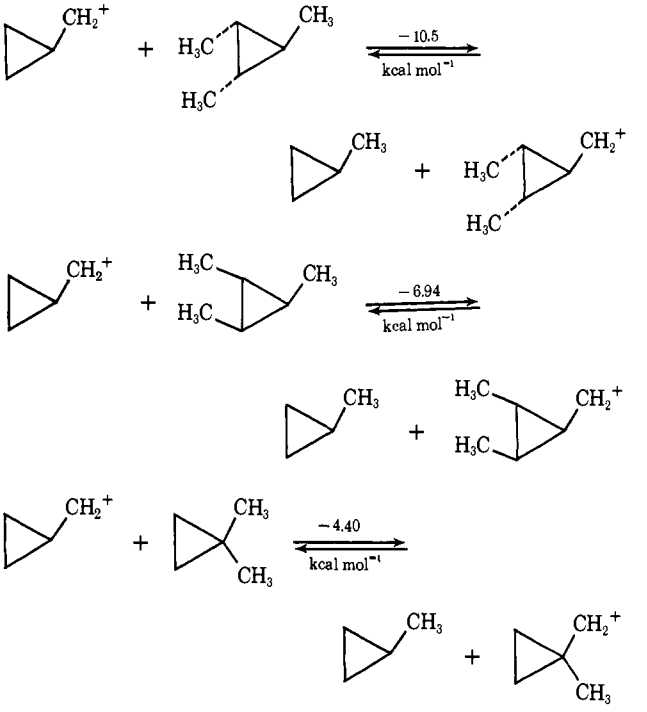


B	B	−0.7
P	P	+1.5
B	P	+7.1

Energy change, kcal mol^{-1}

conformation.[21] Indeed, the perpendicular conformation of this molecule is apparently an energy maximum between two more stable conformations.[21] Several explanations may be advanced to account for the discrepancy between theory and experiment.[22] However, the success realized in Wiberg's application of CNDO/2 theory to cyclopropylcarbinyl compounds[19] and in our preliminary work prompted us to carry out calculations on other cyclopropylcarbinyl derivatives to guide the interpretation of the partial rate factors rather than to investigate the origin of the discrepancy for the benzenonium ions.

Methyl groups in the cyclopropane ring have an important influence on the reaction rate. In particular, 4_f for *syn*-(*cis*-2,3-dimethylcyclopropyl)benzene is somewhat smaller than the value for cyclopropylbenzene, whereas 4_f for the related anti isomer is greater than the value for cyclopropylbenzene. The influence of remote methyl groups on the reactivity of the cyclopropylbenzene contrasts sharply with recent observations of Baas and Wepster.[21] They found that the 4_f values for the isopropyl (68) and 3-pentyl (64) groups were virtually identical for nitration with acetyl nitrate in nitromethane at 25°.[23] Several lines of evidence suggest that destabilizing steric interactions combine with stabilizing charge delocalization effects to dictate 4_f for the methylated cyclopropyl substituents. First, both *syn-cis*- and *anti-cis*-2,3-dimethyl substituents decrease the energy requirements for the solvolysis of cyclopropylcarbinyl derivatives.[9,24] The rate differences for the solvolysis of the 3,5-dinitrobenzoates in aqueous acetone at 100° are impressive (*anti-cis*-2,3-dimethyl-, 110; *syn-cis*-2,3-dimethyl-, 80; cyclopropylcarbinyl, 1.0).[9] Under the same conditions 1-methylcyclopropylcarbinyl 3,5-dinitrobenzoate is fivefold more reactive than the parent compound.[9] Theory suggests electronic factors dictate these results. The reactivity pattern predicted by the CNDO/2 approach for the molecules in the preferred bisected conformation is nicely in accord with experiment. Prior experimental work and the CNDO approach therefore infer that additional methyl groups enhance delocalization of positive charge to the cyclopropane ring and yield an enhanced rate for this reason.



(20) G. L. Closs and H. B. Klinger, *J. Amer. Chem. Soc.*, 87, 3265 (1965).

(21) J. M. A. Baas and B. M. Wepster, unpublished results; J. M. A. Baas, Thesis, Technische Hogeschool, Delft, 1970.

(22) The unexpected energy relationship may result from an unfortunate choice of a critical distance or angle. No attempts were made to minimize the energy content by adjustment of the structural parameters.

(23) The 4_f values for the methyl (64) and *tert*-butyl groups (65) are also nearly equal.

(24) H. Hart and J. M. Sandri, *J. Amer. Chem. Soc.*, 81, 320 (1959); H. Hart and P. A. Law, *ibid.*, 84, 2462 (1962).

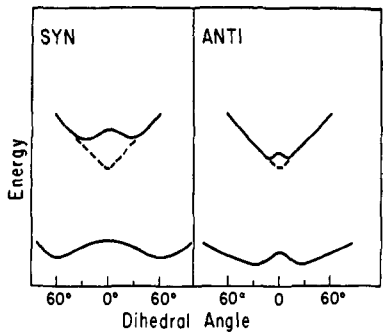
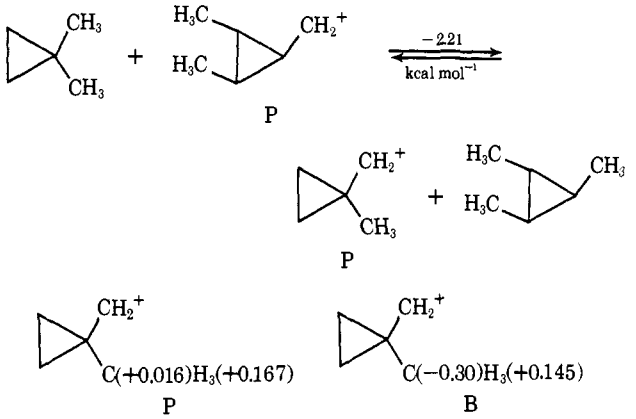


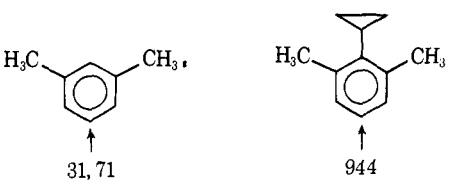
Figure 2. A sketch of the relationship between the energy content of the *syn*- and *anti*-(*cis*-2,3-dimethylcyclopropyl)benzenes (lower curves), the energy content of the related *p*-benzenonium ions (upper curves), and the angle between the plane of the benzenoid nuclei and the C_1–H bond of the cyclopropane ring.

In contrast, remote methyl groups exert a different influence on the reactivity of the cyclopropylbenzenes. Steric interactions are apparently responsible for the altered influence of these groups in the nitration reaction. Nonbonded interactions between, for example, the methyl groups of *syn*-(*cis*-2,3-dimethylcyclopropyl)-benzene and the ortho hydrogen atoms increase the energy content of the bisected conformation. Similar steric interactions are important in (1-methylcyclopropyl)benzene. For these compounds, therefore, steric effects increase the energy content of the bisected conformation. Evidence favoring this view has been presented by Closs and Klinger and by Baas and Wepster.[20,21] Thus, the nitration data for the methylated cyclopropyl substituents reflect conflicting steric and electronic factors that lead to double minima in the energy content of the hydrocarbons and the transition states as the dihedral angle is altered, Figure 2. Because electronic factors become more important in the electron-deficient transition state the minima are displaced toward the bisected conformation in the transition state. This interpretation is illustrated, Figure 2, for the *syn*- and *anti*-(*cis*-2,3-dimethyl) derivatives. The stabilizing electronic interactions of the methyl groups in these molecules are similar but the steric interactions differ considerably leading to a displacement of the minima for the syn compound toward the perpendicular conformation with a resultant increase in the energy requirements for the reaction relative to the less-strained *anti*-(*cis*-2,3-dimethyl) compound.[25]

The small 4_f value for the nitration of (1-methylcyclopropyl)benzene is also the consequence of the serious steric interactions which increase the energy requirements for the reaction. The *syn*-(*cis*-2,3-dimethyl) derivative is nitrated somewhat more slowly than the 1-methyl compound. This modest difference in reactivity may also be related to variable steric effects in the ground and transition states. There is an additional feature, however. The CNDO analysis predicts that the 1-methylcyclopropyl carbonium ion is more stable than the corresponding *cis*-2,3-dimethylcyclopropyl carbonium ion when both occupy the perpendicular conformation. The large charge associated with the methyl group in the perpendicular conformation infers that carbon–carbon hyperconjugation is responsible for the greater stability of the 1-methyl derivative.



4_f for the Perpendicular Conformation. Several approaches may be used to estimate 4_f for the unsubstituted cyclopropyl group in the perpendicular conformation. The experimental value for 5_f for 1,3-dimethylbenzene, 71, is based on the analysis of a small concentration of the 5-nitro derivative in the presence of a large excess of the 4-nitro compound. The value is accordingly somewhat uncertain. The additivity postulate indicates that 5_f for 1,3-dimethylbenzene is 31, $(3_f^{CH_3})^2$. The two values, 71 and 31, are in reasonable agreement when the problems involved in the analytical work and the limitations of the additivity approach are considered.[26] Comparison of the values with the observed 4_f, 944, for 2,6-dimethylcyclopropylbenzene in which the cyclopropane ring is forced toward the perpendicular conformation[27] suggests 4_f for the



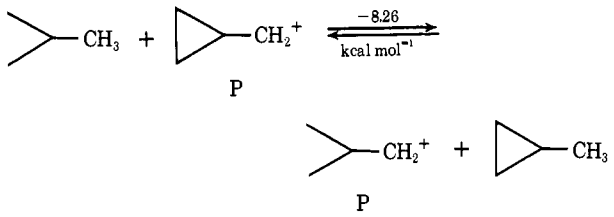
cyclopropane unit in this conformation is between 30 and 13. Steric interactions do not completely inhibit the resonance delocalization of the charge to the cyclopropane fragment in the dialkylbenzene.[8,9,27] Thus, these results establish only an upper limit for 4_f for the perpendicular conformation. Accordingly, it would not be surprising to find that 4_f for this conformation of the cyclopropyl group is somewhat smaller in a molecule with larger 2,6-dialkyl substituents in accord with the observations and suggestions of Schleyer and Martin and their associates.[8,9] Indeed, it is interesting to note that the CNDO/2 analysis predicts this result.

4_f for the Bisected Conformation. The structure of spiro(cyclopropane-1,1′-indan) restricts the cyclopropane ring to the bisected conformation. The 5_f values

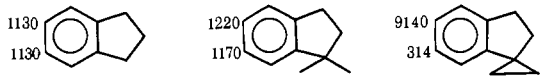
(25) Similar interpretations have been used previously, for example in the analysis of the substitution reactions of biphenyl: L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, **1**, 108 (1963); L. M. Stock and H. C. Brown, *J. Amer. Chem. Soc.*, 84, 1242 (1962).

(26) For the nitration reaction at −25°, the observed reactivities for the 2 and 4 positions of 1,3-dimethylbenzene are only 0.033 and 0.050 that predicted by the additivity postulate. However, the predictions for less reactive positions are much more satisfactory. Reactivity at the unhindered 4 positions of 1,2-dimethylbenzene is 0.5 that predicted by the postulate. These results and prior experience suggest that conclusions based on the additivity postulate will be accurate within a factor of 2 when the partial rate factors are less than 1000.

(27) The coupling constant of the benzylic hydrogen atom of the corresponding 4-nitro-2,6-dimethylcyclopropylbenzene anion radical suggests the average dihedral angle is 32°: L. M. Stock and P. E. Young, unpublished results.

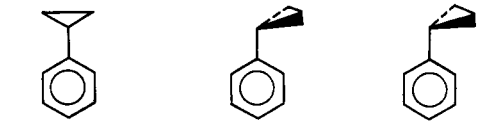


for indan, 1,1-dimethylindan, and the spiro compound reveal that the cyclopropyl group in the bisected conformation is about eightfold more effective as an



electron donor group than the hydrogen atoms or the methyl groups of the reference compounds. Based on these results, the 4_f value for cyclopropylbenzene in the bisected conformation is approximately 1800.

The partial rate factors for the perpendicular and bisected conformers of cyclopropylbenzene are very different. For nitration at −25°, the cyclopropyl



perpendicular		bisected
13-30	950	1800

group is at least 60-fold more effective as an electron donor in the bisected conformation than in the perpendicular conformation. The results for the simple alkylbenzenes suggest that ρ^+ is about −8.0 for nitration under the conditions of these experiments yielding $\sigma^+_{p\text{-}c\text{-}C_3H_7}$ as −0.1 and −0.4 for the perpendicular and bisected conformations, respectively.[28] The value −0.1 for the perpendicular conformation represents a lower limit. The numerical value is almost certainly too small (too negative) because, as already noted, the 2,6-dimethyl groups do not completely inhibit conjugation between the benzene and cyclopropane rings.

3_f for the Bisected and Perpendicular Conformations. Analysis of the reaction products for the nitration of cyclopropylbenzene indicates that only 0.2 ± 0.1% 3-nitrocyclopropylbenzene is formed. The partial rate factor based on this somewhat uncertain result is 5.5. Other estimates for 3_f for the perpendicular and bisected conformations of cyclopropylbenzene may be made on the basis of the additivity postulate. The 3_f value for 2,6-dimethylcyclopropylbenzene is 6680 compared to 3240 for the related 4 position in 1,3-dimethylbenzene. These results suggest that 3_f for the perpendicular conformation is 2.1. The 6_f values for indan, 1,1-dimethylindan, and spiro(cyclopropane-1,1-indan) provide an estimate for 3_f for the bisected conformation. This estimate presumes that the reactivity of the 6 position reflects the additive contribution of the *p*-methylene group which remains constant and the different meta groups. The cyclopropyl group decreases the nitration rate by a factor of 2.8 in the spiroindan and by a factor of 3.5 in the spirotetralin. The results for toluene and cumene suggest that the partial rate factors for the *m*- and *p*-methylene groups in indan are about 5 and 225, respectively. Thus, the 3_f values for the bisected conformation of cyclopropane are estimated to be 1.4 and 1.8 on the basis of the results for the two spiro compounds. These analyses suggest that $\sigma^+_{m\text{-}C_3H_5}$ for both conformations is small, −0.03 ± 0.02, and somewhat less negative than the constants for other alkyl groups.

In conclusion, our assessments of 3_f and 4_f for the conformers of cyclopropylbenzene lead to the conclusion that 3_f is small between 1 and 5 in both conformations whereas 4_f is small, perhaps no more than 10, in the perpendicular conformation but large, as expected, in the bisected conformation. The behavior of the cyclopropyl group in positions where resonance delocalization of electron deficiency is impossible is intermediate between the electron-withdrawing phenyl group, $\sigma^+_{m\text{-}C_6H_5} = 0.1$, and the electron-donating methyl substituent, $\sigma^+_{m\text{-}CH_3} = -0.07$.[29] The results for the cyclopropyl group are nicely in accord with the view that the changing influences of carbon groups originate for the most part in the different bond moments between carbon atoms of different hybridization.[30] The importance of the delocalization of charge to the cyclopropane ring is clearly indicated by the 100-fold increase in reactivity of the bisected para substituent compound to the perpendicular *p*-cyclopropyl group. The reactivity pattern of the *p*-cyclopropyl group observed experimentally, and suggested theoretically, is well accommodated by the concept of electron delocalization *via* hyperconjugation of strained para rich carbon–carbon bonds.[31]

Experimental Section

Materials. Benzene, toluene, cumene, the dimethylbenzenes, and indan were obtained commercially. Cyclopropylbenzene, 2,6-dimethylcyclopropylbenzene, 1,1-dimethylindan, and spiro(cyclopropane-1,1′-indan) were prepared as described subsequently. *syn*- and *anti*-(*cis*-2,3-dimethylcyclopropyl)benzene, (1-methylcyclopropyl)benzene, and 3′,4′-dihydrospiro(cyclopropane-1,1′-(2*H*)-naphthalene) were generously provided by G. L. Closs. All the hydrocarbons were purified by suitable methods to yield compounds shown to be greater than 99% pure by vpc. Anhydrous nitric acid was prepared by distillation *in vacuo* from sulfuric acid.[32] The pure acid was stored at −25° without deterioration as established by the nitron method.[33] The nitro compounds were obtained from commercial sources or by the nitration of the hydrocarbons as described subsequently. These compounds were also shown to be pure by vpc.

Spiro(cyclopropane-1,1′-indan). Indene (59 g, 0.5 mol) was added in about 30 min to a stirred mixture of sodium hydride (1.19 mol, suspended in an equal weight of mineral oil) in monoglyme which had been distilled from sodium. Heat and the addition rate were controlled to maintain gentle reflux. After the addition was complete, the tan mixture was stirred while gently refluxed for 3.5 hr. 1,2-Dibromoethane (94 g, 0.5 mol) was then added dropwise over 2 hr. The resulting pink solution was stirred overnight under nitrogen. The cool suspension was poured into water (600 ml) and extracted

(28) Because steric and electronic interactions are each important, the reactions of cyclopropylbenzene and its derivatives, as those of biphenyl and its derivatives,[25] will not obey a linear free-energy relationship. Presumably, more negative σ^+ values would be realized in reactions that are more selective than the nitration reactions.

(29) Martin and Ree have recently compared the σ_I constants for the vinyl, cyclopropyl, and ethyl groups.[8b] The constant for the cyclopropyl group is about 0.02 and also intermediate between the values for the vinyl and ethyl substituents.

(30) (a) A. D. Walsh, *J. Chem. Soc.*, 398 (1948); (b) M. J. S. Dewar, "Hyperconjugation," The Ronald Press, New York, N. Y., 1962; (c) F. W. Baker, R. C. Parish, and L. M. Stock, *J. Amer. Chem. Soc.*, 89, 5677 (1967).

(31) F. R. Jensen and B. E. Smart, *J. Amer. Chem. Soc.*, **91**, 5686 (1969).

(32) E. D. Hughes, C. K. Ingold, and R. J. Reed, *J. Chem. Soc.*, 2400 (1950).

(33) W. C. Cope and J. Barab, *J. Amer. Chem. Soc.*, **39**, 504 (1917).

with pentane. The pentane layer was washed with water and then dried over magnesium sulfate. Distillation of the solution yielded spiro(cyclopropane-1,1′-indene) (23.5 g, 33%, bp 94–96° (8.7 mm); lit.[16] 90–92° (8.5 mm)). The unsaturated material was reduced by the method of Closs and Klinger.[16] Spiro(cyclopropane-1,1′-indan) (bp 70.5–71.5° (4 mm); lit.[16] 95–97° (10 mm)) was obtained in 82% yield. The compound was further purified by vpc on Carbowax 20M followed by bulb-to-bulb distillation.

1,1-Dimethylindan. 2-Methyl-4-phenylbutan-2-ol was obtained by the reaction of 2-phenylethylmagnesium bromide (prepared in the usual way from 2-phenylethyl bromide) with acetone. The desired product, 2-methyl-4-phenylbutan-2-ol (101 g, 60%, bp 116–123° (12 mm); lit.[34] 121° (13 mm)) was isolated in the customary way. The alcohol was cyclized by the method of Closs and Klinger.[16] 1,1-Dimethylindan (bp 84.8–85.0° (22 mm); lit.[16] 191° (760 mm)) was purified by distillation in a spinning band column. The product was obtained in 70% yield.

Cyclopropylbenzene. This compound was prepared *via* 5-phenyl-Δ^2-pyrazoline by the method of Closs and Schober.[35] The necessary 5-phenyl-Δ^2-pyrazoline was obtained from cinnamaldehyde and hydrazine hydrate. This compound was converted to phenylcyclopropane (bp 23–25° (0.15 mm); lit.[35] 42–45° (0.2 mm)) in 36% yield.

2,6-Dimethylcyclopropylbenzene. 2,6-Dimethylstyrene (4.0 g, 0.03 mol), zinc dust (2.0 g), and a crystal of iodine were suspended in dry monoglyme (20 ml) containing diiodomethane (0.2 g). The mixture was then stirred and heated to reflux. Diiodomethane (8.6 g, 0.033 mol in total) in monoglyme (10 ml) was then added in 1 hr. The reaction mixture was filtered with the aid of Supercel. The residue was washed with monoglyme (100 ml). The filtrates were combined prior to the addition of hydrochloric acid (5%, 80 ml). The yellow solution that resulted was washed with pentane (five extractions appeared desirable). The pentane solution was then washed successively with 5% aqueous sodium bicarbonate solution and saturated aqueous sodium chloride prior to drying the solution with magnesium sulfate. The pentane was then removed *in vacuo*. The nmr spectrum of the residue revealed that unreacted styrene remained. The residue was recycled twice with fresh diiodomethane (10 g) and zinc (2 g) for 12 and 29 hr, respectively. The product (0.8 g, 20%) was collected by vpc on Carbowax 20M. The nmr spectrum, 0.1–1.0 (4 H, m), 1.17–1.16 (1 H, m), 2.22 (6 H, s), 6.70 (3 H, s), characterized the product; mass spectrum, calcd (for $C_{11}H_{14}^+$), 146.1095; found, 146.1093.

5-Nitrospiro(cyclopropane-1,1′-indan). Successful preparative nitration of the phenylcyclopropanes requires that the conditions be selected to minimize the side reactions of ring cleavage and of phenyl acetate formation. The latter problem is most serious with the ortho-disubstituted compounds. In these cases, dilution of the reaction mixture with methylene chloride is beneficial. The following procedure based on the experience gained in this work and on the results of Closs and Klinger[16] proved generally useful.

Nitric acid (0.9 ml, ρ = 1.52 g ml^{-1}) was slowly added to acetic anhydride (3 ml) at −35°. The mixture was stirred for 30 min. Methylene chloride (20 ml) was then added and the solution was cooled to −70°. Spiro(cyclopropane-1,1′-indan) (0.91 g, 6.31 mol) in methylene chloride (15 ml) was then added dropwise with the temperature maintained below −65°. After the addition of the hydrocarbon, the solution was stirred for 30 min. Sodium bicarbonate (1.0 g) was added to the cold reaction mixture and the solution was allowed to warm to ambient temperature. Water (4 ml) was then added and the mixture was stirred for 1 hr. The layers were then separated. The aqueous phase was extracted with ether (25 ml, three portions) which was combined with the original organic layer. This solution was washed with 5% aqueous sodium bicarbonate (10 ml, five portions) and with saturated sodium chloride (10 ml, five portions) prior to drying the solution over magnesium sulfate. The product was isolated by preparative vpc after the removal of the volatile solvents. 5-Nitrospiro(cyclopropane-1,1′-indan) (mp 82.5–83.5°) was purified by vacuum sublimation.[36] The nmr spectrum, 1.02 (4 H, s), 2.20 (2 H, t, J = 7.5 Hz), 6.5–6.8 (1 H, m), 7.8–8.1 (2 H, m), characterized the compound; mass spectrum, calcd (for $C_{11}H_{11}NO_2$), 189.0790; found, 189.0782.

Anal. Calcd for $C_{11}H_{11}NO_2$: C, 69.82; H, 5.86; N, 7.51. Found: C, 70.09; H, 6.08; N, 7.51.

5-Nitro-1,1-dimethylindan. This nitrodimethylindan was prepared by the reduction of 5-nitro-3,3-dimethylindan-1-one. The ketone was obtained through the sequence devised by Koelsch and LeClaire.[37] Following their procedure, benzene was alkylated with mesityl oxide to obtain 4-methyl-4-phenylpentan-2-one in 77% yield. This compound was converted to 3-phenylisovaleric acid by reaction with chlorine in basic solution in 50% yield. Treatment of the acid with phosphorus pentachloride followed by aluminum chloride provided 3,3-dimethylindan-1-one which was nitrated with fuming nitric acid to give 5-nitro-3,3-dimethylindan-1-one (mp 130–131.5°; lit.[35] 133–134°) in 40% yield.

The ketone (2.84 g, 18 mmol) was converted to the semicarbazone (mp 236–239°, 2.11 g, 9 mmol) in the usual way. The pure carbazone was added to a solution of potassium hydroxide (0.7 g) in ethylene glycol (60 ml). The solution was rapidly heated to 195°. This temperature was maintained for 33 min after the carbazone was added to the solution. The product is not stable under the reaction conditions; accordingly the yield achieved depends importantly on the reaction time. The hot reaction mixture was quenched in cold water (300 ml). The product was extracted into carbon tetrachloride. The solution was dried over magnesium sulfate prior to the removal of the solvent *in vacuo* to yield a yellow oil. The oil was dissolved in petroleum ether (bp 30–60°) and 5-nitro-1,1-dimethylindan (mp 50–51.5°) precipitated from the solution at −25°. The product was identified by: nmr 1.21 (6 H, s), 1.95 (2 H, t, J = 7 Hz), 2.91 (2 H, t, J = 7 Hz), 7.13 (1 H, d, J = 9 Hz), 7.86–8.10 (2 H, m); mass spectrum, calcd (for $C_{11}H_{13}NO_2^+$), 191.0946; found, 191.0960.

Nitro-1,1-dimethylindan. The nitration of 1,1-dimethylindan with nitric acid and acetic anhydride in methylene chloride was carried out at 25°. Three compounds were obtained by preparative vpc on Carbowax 20M. 5-Nitro-1,1-dimethylindan was obtained in 20% yield. This compound was identified by comparison of its retention time and mass and nmr spectra with the authentic material.

6-Nitro-1,1-dimethylindan was obtained in about 20% yield by preparative vpc. The structure of this yellow liquid was assigned on the basis of: nmr 1.27 (6 H, s), 1.93 (2 H, t, J = 7 Hz), 2.88 (2 H, t, J = 7 Hz), 6.95–7.20 (1 H, m), 7.63–7.90 (2 H, m); mass spectrum, calcd (for $C_{11}H_{13}NO_2^+$), 191.0946; found, 191.0933.

A third nitro compound, presumably 4-nitro-1,1-dimethylindan, was produced in very small quantity.

Nitrocyclopropylbenzene. The nitration of cyclopropylbenzene with nitric acid and acetic anhydride in methylene chloride at 25° produced a 2:1 mixture of 2-nitro- and 4-nitrocyclopropylbenzene in 64% yield. The pure isomers subsequently used as chromatographic standards were obtained by preparative vpc.

Nitro-2,6-dimethylcyclopropylbenzene. The nitration of 2,6-dimethylcyclopropylbenzene with nitric acid and acetic anhydride in methylene chloride at 25° produced, in 43% yield, a 90:10 mixture of 3-nitro-2,6-dimethylcyclopropylbenzene (mp 32–22°) and 4-nitro-2,6-dimethylcyclopropylbenzene (mp 71–73°). The nmr spectra of the 3 isomer, 0.30–0.70 (2 H, m), 0.85–1.25 (2 H, m), 1.40–1.85 (1 H, br m), 2.45 (6 H, d, J = 3 Hz), 6.94 (2 H, d, J = 8.5 Hz), 7.42 (2 H, d, J = 8.5 Hz), and the 4 isomer, 0.20–0.75 (2 H, m), 0.75–1.35 (2 H, m), 1.35–1.95 (1 H, m), 2.5 (6 H, s), 7.75 (2 H, s), distinguished these compounds which had identical mass charge ratios; mass spectrum, calcd (for $C_{11}H_{13}NO_2^+$), 191.0946; found (for the 3 and 4 isomers), 191.0938 and 191.0952, respectively.

Nitro-(1-methylcyclopropyl)benzene. The nitration of (1-methylcyclopropyl)benzene with nitric acid and acetic anhydride in methylene chloride at 0–5° produced, in 30% yield, a 50:30 mixture of 2-nitro-(1-methylcyclopropyl)benzene (mp 27.5–28.5° after vacuum sublimation) and 4-nitro-(1-methylcyclopropyl)benzene (mp 53–55° after vacuum sublimation). The nmr spectra of the 2 isomer, 0.89 (4 H, s), 1.49 (3 H, s), 7.1–7.7 (4 H, m), and the 4 isomer, 0.89 (4 H, br s), 1.45 (3 H, s), 7.3 (2 H, d, J = 8.5 Hz), 8.08 (2 H, d, J = 8.5 Hz) distinguished these compounds; mass spectrum, calcd (for $C_{10}H_{11}NO_2^+$), 177.0790; found (for the 2 and 4 isomers), 177.0800 and 177.0804, respectively.

Nitro-*syn*-(*cis*-2,3-dimethylcyclopropyl)benzene. The nitration of *syn*-(*cis*-2,3-dimethylcyclopropyl)benzene at −15 to 0° produced, in 25% yield, a 1:1 mixture of the known[38] 2-nitro-*syn*-(*cis*-2,3-dimethylcyclopropyl)benzene (mp 29–32° after sublimation) and

(34) P. Warrick, Jr., and W. H. Saunders, *J. Amer. Chem. Soc.*, 84, 4095 (1962).

(35) G. L. Closs and D. L. Schober, unpublished results; D. L. Schober, Thesis, The University of Chicago Library, 1969.

(36) This compound and the other isomeric nitro derivatives of spiro(cyclopropane-1,1′-indan) have been prepared and characterized by Hahn and his associates, ref 7.

(37) C. F. Koelsch and C. D. LeClaire, *J. Org. Chem.*, 6, 516 (1941).

(38) G. L. Closs and S. H. Goh, unpublished results; S. H. Goh, Thesis, The University of Chicago Library, 1968.

4-nitro-*syn*-(*cis*-2,3-dimethylcyclopropyl)benzene (mp 43–45° after sublimation). The nmr spectra of the 2 isomer, 0.80 (6 H, d, J = 5 Hz), 1.0–1.5 (2 H, br m), 2.20 (1 H, t, J = 8 Hz), 7.25 (3 H, s), 7.55–7.82 (1 H, m), and the known 4 isomer, 0.8 (6 H, d, J = 5 Hz), 1.0–1.5 (2 H, br m), 2.20 (1 H, t, J = 8 Hz), 7.25 (3 H, s), 7.55–7.82 (1 H, m), distinguished the reaction products.

Nitro-*anti*-(*cis*-2,3-dimethylcyclopropyl)benzene. The nitration of *anti*-(*cis*-2,3-dimethylcyclopropyl)benzene at −15 to 0° produced, in near quantitative yield, an 80:20 mixture of the known[38] 2-nitro-*anti*-(*cis*-2,3-dimethylcyclopropyl)benzene, a yellow liquid, and 4-nitro-*anti*-(*cis*-2,3-dimethylcyclopropyl)benzene (mp 109–110° after sublimation). These compounds were also distinguished by the characteristic nmr spectra of the 2 isomer, 1.2 (8 H, s), 1.65 (1 H, d, J = 4.5 Hz), 6.95–7.45 (3 H, m), 7.61–7.83 (1 H, m), and the known 4 isomer, 1.23 (9 H, s), 7.05 (2 H, d, J = 8.5 Hz), 8.06 (2 H, d, J = 8.5 Hz).

Relative Rates. In a typical competitive experiment cyclopropylbenzene (0.118 g, 1.00 mmol) and toluene (0.920 g, 9.98 mmol) were weighed into a flask. Methylene chloride was added to bring the volume to 10 ml. In another flask, anhydrous nitric acid (0.061 g, 0.963 mmol, previously distilled from a twofold excess of sulfuric acid in a glass apparatus *in vacuo*) was added to acetic anhydride (0.151 g, 1.48 mmol) which had been purified by fractionation. This latter solution was maintained at ambient temperature for 15 min for the conversion of starting materials to acetyl nitrate. The solution was then diluted to 10-ml volume with methylene chloride. Both flasks were cooled to −25°. The contents of the flasks were then mixed in a third flask prechilled to −25°. The reaction was allowed to proceed 12 hr. An analytical reference compound, 3-nitro-1,2-dimethylbenzene (0.028 g, 0.210 mmol), was added to the reaction mixture. The solution was poured into water (500 ml). The organic layer was separated. The aqueous phase was extracted with three portions of ether (50 ml). The organic layers were combined and the solution was washed with distilled water (three 25-ml portions) prior to drying over magnesium sulfate. The solution was concentrated by removal of the solvents *in vacuo*. The product-rich residue was analyzed by vpc on a Carbowax 20M column (10 ft × $^1/_4$ in.) operated at 200° with a helium flow of 100 ml/min.

Prior analytic work established that 2- and 4-nitrocyclopropylbenzene were not decomposed or otherwise fractionated in the isolation procedure. Thermal conductivity response factors were determined by the chromatography of three known mixtures containing 3-nitro-1,2-dimethylbenzene, the three isomeric nitrotoluenes, and the two major nitrocyclopropylbenzenes. The nitro compounds used in these calibration experiments were isomerically pure. At least two analyses of each mixture were carried out and the results averaged. The areas under the curves were measured by triangulation or by recorder integration. Both methods gave sensibly identical results.

Analysis of the product mixture described above revealed 62% conversion of nitric acid to nitroaromatic compounds. The Ingold–Shaw rate expression was used to assess the relative rate $k_{C_6H_5C_3H_5}/k_{C_6H_5CH_3}$ = 10.3 on the measured formation of 0.315 mmol of nitrotoluenes and 0.282 mmol of nitrocyclopropylbenzenes. A second experiment indicated the relative rate was 10.1.

The isomer distributions were determined in separate experiments conducted under the conditions of the kinetic experiments. The pure isomers were used to identify the reaction products and to determine the vpc response factors. In the course of this study Hahn and his students communicated the isomer distributions for spiro(cyclopropane-1,1′-indan) and 3′,4′-dihydrospiro(cyclopropane-1,1′(2*H*′)-naphthalene). Preliminary experiments indicated that three products were obtained in significant amounts in the nitration of the spiroindan. The 5-nitro derivative constituted 83% of these products. This result was combined with the results of Hahn and his associates to yield the values reported in Table II. The isomer distribution for the nitration of the spirotetralin was established in the same way.

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Mechanisms of Ion–Molecule Reactions of Propene and Cyclopropane[1]

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Abstract: Ion–molecule reaction of the $C_3H_6\cdot^+$ ion from propene proceeds *via* a "four-center" mechanism to a $C_6H_{12}\cdot^+$ ion capable of 1,2- and 1,4-hydrogen migrations but not 1,3-hydrogen migration. The $C_6H_{12}\cdot^+$ ion can rearrange *via* structures **6**, **7**, and **8**. Decomposition to ethylene proceeds *via* a "four-center" cleavage of the dimethylcyclobutane ion **6**. The $C_3H_6\cdot^+$ ion from cyclopropane can be distinguished from that formed from propene. The $C_6H_{12}\cdot^+$ ion formed on reaction of propene and cyclopropane is different from that formed from propene alone; it undergoes facile cleavage with loss of ethylene. By study of ion–molecule reactions of CD_3CH-$CH_2\cdot^+$ formed at energies below the appearance potential of fragment ions a small amount of isotopic scrambling has been observed in the $CD_3CHCH_2\cdot^+$ ion in accord with predictions based on quasiequilibrium theory. Part of the $C_3H_3^+$ ions formed from propene are unusually unreactive at high pressures with propene and may have the cyclopropenium ion structure.

The ion–molecule reactions in unsaturated systems, particularly hydrocarbon systems, offer an excellent opportunity to study in detail the mechanisms and kinetics of an important class of condensation phenomena. Most studies have been carried out using standard high-pressure mass spectroscopy although more recently time of flight, tandem techniques, and ion cyclotron resonance (icr) techniques have become more widely used. In our studies, the icr technique has been employed.[2]

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