$\times 10^{-6}$ is obtained from eq 1 of Swain and Brown.[2] A factor of 31.6 is thus estimated as being due simply to the position effect, well within the expected range.

It is perhaps worth mentioning that if one plots $\xi_{x,y}$ *vs.* the log of reactivity for the catalysts of Menger, appending a point corresponding to $\xi_{x,y} = 0$ and reactivity of 31.6 times that of *n*-butylamine, the correlation coefficient is 0.964 and is, despite only a single degree of freedom, significant at the 0.1 level.

Swain and Brown[2] made a single measurement using 8-hydroxyquinoline as catalyst and found a k_1 of only 20×10^{-6} for a concentration of 0.25 *M*. The exceedingly low activity of this compound is associated with a coupling index of −0.0126.

In evaluating the results reported here, one must bear in mind the approximate nature of the method used and the fact that certain effects, such as the involvement of the π system of the substrate, are beyond the scope of the Hückel approximation. Further work, both experimental and theoretical, is clearly called for. It seems safe to conclude, however, that electronic coupling is a factor in bifunctional catalysis. If the reactions of Swain and Brown and of Menger are to be taken as a basis for models of enzyme catalysis, it would seem that such models should include provision for the possibility of coupling through the protein molecule. Further work, using more complete molecular orbital methods, is in progress.

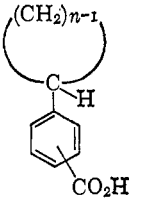
Electrical Effects of Cycloalkyl Groups[1]

Roger C. Hahn, Thomas F. Corbin, and Harold Shechter

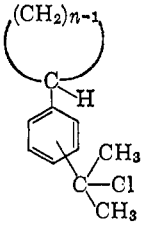
Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, and the Department of Chemistry, Syracuse University, Syracuse, New York 13210. *Received December 26, 1967*

Abstract: A study has been made of (1) the syntheses and ionization constants of *m*- and *p*-cyclopropyl-, -cyclobutyl, -cyclopentyl-, -cyclohexyl-, -(1-cyclopentenyl)-, and -(1-cyclohexenyl)benzoic acids and (2) the syntheses and unimolecular hydrolysis rates of *m*- and *p*-cyclopropyl-, -cyclopentyl-, -cyclohexyl-, and *p*-cyclobutylphenyldimethylcarbinyl chlorides in 90% aqueous acetone. The effects of ring size on the ionization constants of the *m*-(1-cycloalkenyl) and *m*-cycloalkylbenzoic acids and on the rates of hydrolysis of *m*-cycloalkylphenyldimethylcarbinyl chlorides are small and are interpreted primarily on the basis of electron release of substituents in the order: cyclohexenyl > cyclopentyl > cyclobutyl > cyclopropyl > 1-cyclohexenyl > 1-cyclopentenyl. *p*-Cycloalkylphenyldimethylcarbinyl chlorides solvolyze more rapidly than do their *meta* isomers; hydrolysis of *p*-cyclopropylphenyldimethylcarbinyl chloride is much faster than that of its *p*-cycloalkyl homologs. The marked reactivity of *p*-cyclopropylphenyldimethylcarbinyl chloride is attributed to stabilization of the reaction transition state through the large π character of the cyclopropyl carbon–carbon bonds. The fact that *p*-cyclopropylbenzoic acid is weaker than its homologous *p*-cycloalkylbenzoic acids provides additional evidence for the electron-donor abilities of a cyclopropyl group.

The reactivities of cycloalkyl derivatives are markedly affected by ring size. In order to divorce electrical effects from classical steric factors and to avoid complications arising from carbon skeleton rearrangement of alicyclic substituents, a study has been made of the ionization constants of homologous *m*- and *p*-cycloalkylbenzoic acids **1**, **2**, **3**, and **4**, and the rates of solvolysis of *m*- and *p*-cycloalkyl-*t*-cumyl chlorides **34**, **35**, **36**, and **37**.[2,3] The objectives are to determine the electrical effects of cycloalkyl groups in the systems of interest. Synthetic routes to the compounds studied are summarized in Charts I, II, and III. The present paper also includes comments on the unusual isomer distribution in nitration of cyclopropylbenzene.



1, $n = 3$
2, $n = 4$
3, $n = 5$
4, $n = 6$
p, para; m, meta



34, $n = 3$
35, $n = 4$
36, $n = 5$
37, $n = 6$
p, para; m, meta

Syntheses

Cyclopropylbenzoic Acids. Cyclopropylphenyldimethylcarbinols. Synthesis of the desired cyclopropylbenzene derivatives involved (a) ring closure of substituted benzenoid intermediates and (b) preparation, nucleophilic substitution, and subsequent transformations of cyclopropylbenzene. While the former method allowed nuclear-substituted phenylcyclopropanes (*p*-bromocyclopropylbenzene was obtained from 1-bromo-

(1) (a) Abstracted in part from the Ph.D. dissertation of R. C. Hahn, The Ohio State University, Columbus, Ohio, 1960; *Dissertation Abstr.*, 21, 2891 (1961); University Microfilms, Inc., Ann Arbor, Mich., Library of Congress Card No. Mic 61–911; *Chem. Abstr.*, **55**, 18632 (1961). (b) Presented at the 139th National Meeting of the American Chemical Society, St. Louis, Mo., March 21, 1961, Abstracts of Papers, 35-O.

(2) L. B. Jones and V. K. Jones, *Tetrahedron Letters*, 1493 (1966), have reported a large rate acceleration in solvolysis of *p*-cyclopropylphenyldimethylcarbinyl chloride in 90 vol % acetone as compared to *p*-alkylphenyldimethylcarbinyl chlorides. These authors were not aware of our studies[1] of these systems upon initial submittal of their communication (footnote d).

(3) H. C. Brown and J. D. Cleveland, *J. Am. Chem. Soc.*, **88**, 2051 (1966), have used the present research as an initial basis for their elegant study of steric inhibition of interaction of a cyclopropyl substituent with the electron-deficient center in solvolysis of *t*-cumyl derivatives.

Chart I

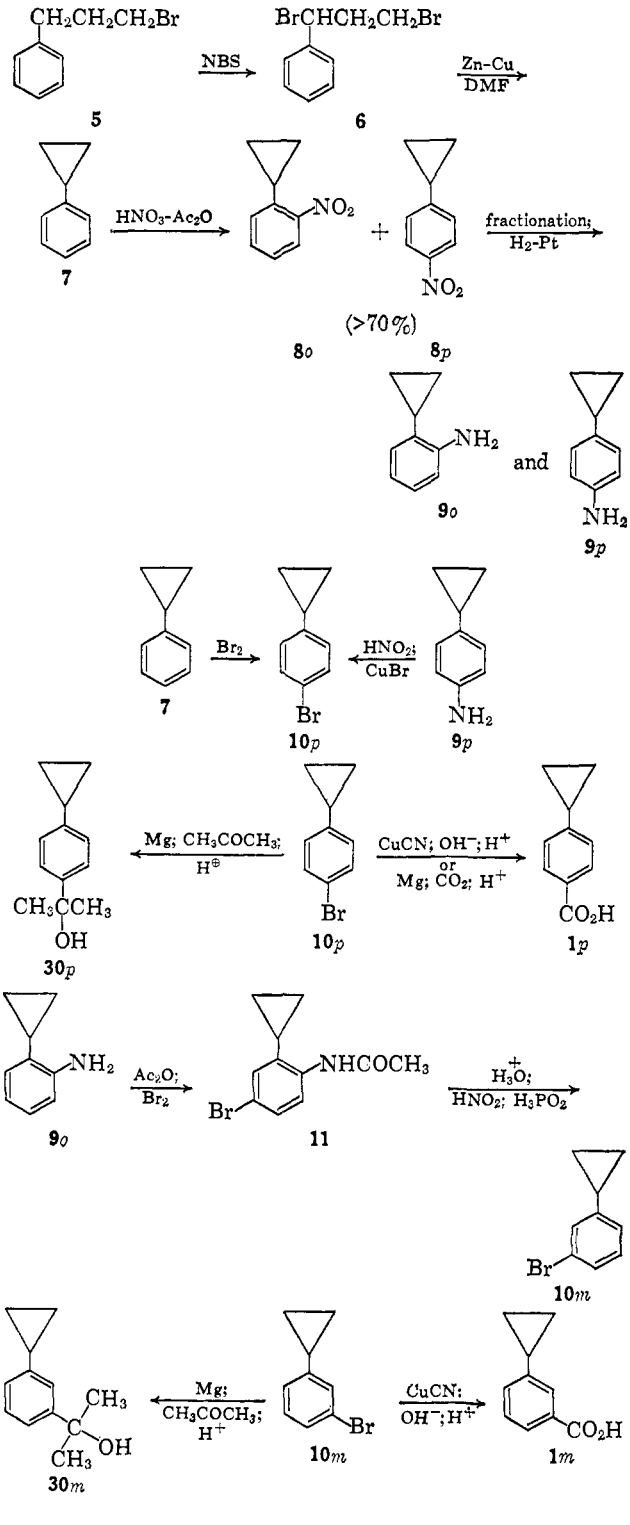
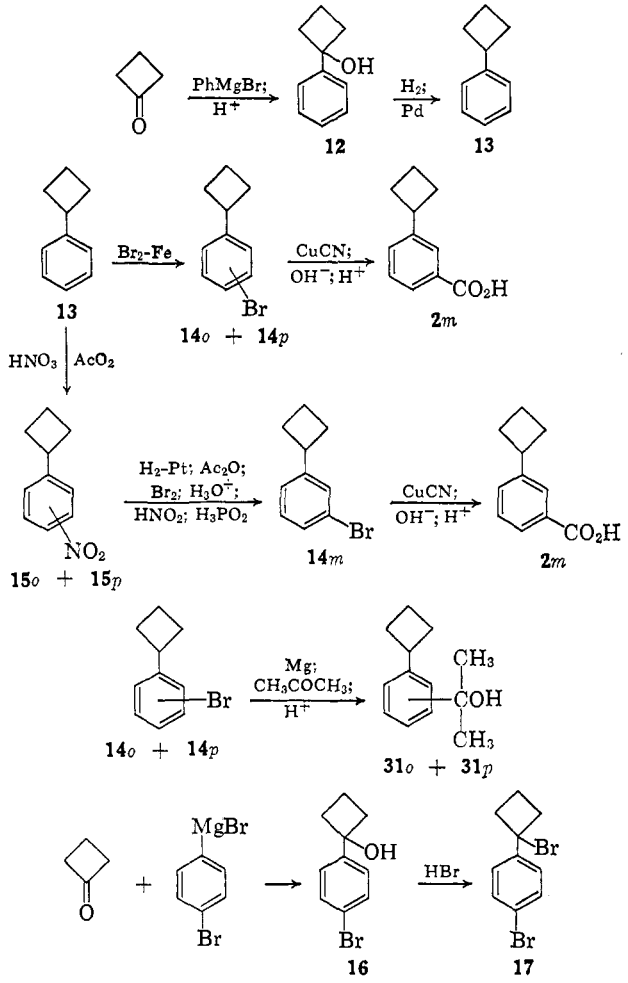


Chart II



1-(*p*-bromophenyl)-3-chloropropane and zinc; see Experimental Section), this route was abandoned for the latter, more convenient method outlined in Chart I. Development of a convenient preparation of high-purity cyclopropylbenzene (**7**) from 1-bromo-3-phenylpropane (**5**) by cyclization of its subsequent derivative, (1,3-dibromopropyl)benzene (**6**), with zinc–copper couple[4] in dimethylformamide was a key step in the syntheses.[5]

Nitration of cyclopropylbenzene (**7**) with nitric acid and acetic anhydride at 10–20° gave over 95% conversion to *o*-cyclopropylnitrobenzene (**8***o*) and *p*-cyclopropylnitrobenzene (**8***p*) in a ratio greater than 2.5. The over-all *ortho*:*para* ratios for nitration of cyclopropylbenzene range from 2.0 to 4.7[6] depending on the nitrating reagent and experimental conditions. These ratios are significantly larger than those for methyl- (1.78 and 1.57, respectively), ethyl- (0.9), isopropyl- (0.4), and *t*-butylbenzenes (0.1),[7] and indicate an unusual ability of the cyclopropyl group to activate *ortho* nitration. Survey of orientations in nitration of homologous cycloalkylbenzenes further emphasizes the selectivity in nitration of cyclopropylbenzene; *ortho*:*para* ratios for cyclobutylbenzene (0.56),[8a] cyclo-

(4) (a) G. F. Hennion and J. J. Sheehan, *J. Am. Chem. Soc.*, **71**, 1964 (1949); (b) R. S. Shank and H. Shechter, *J. Org. Chem.*, **24**, 1825 (1959).

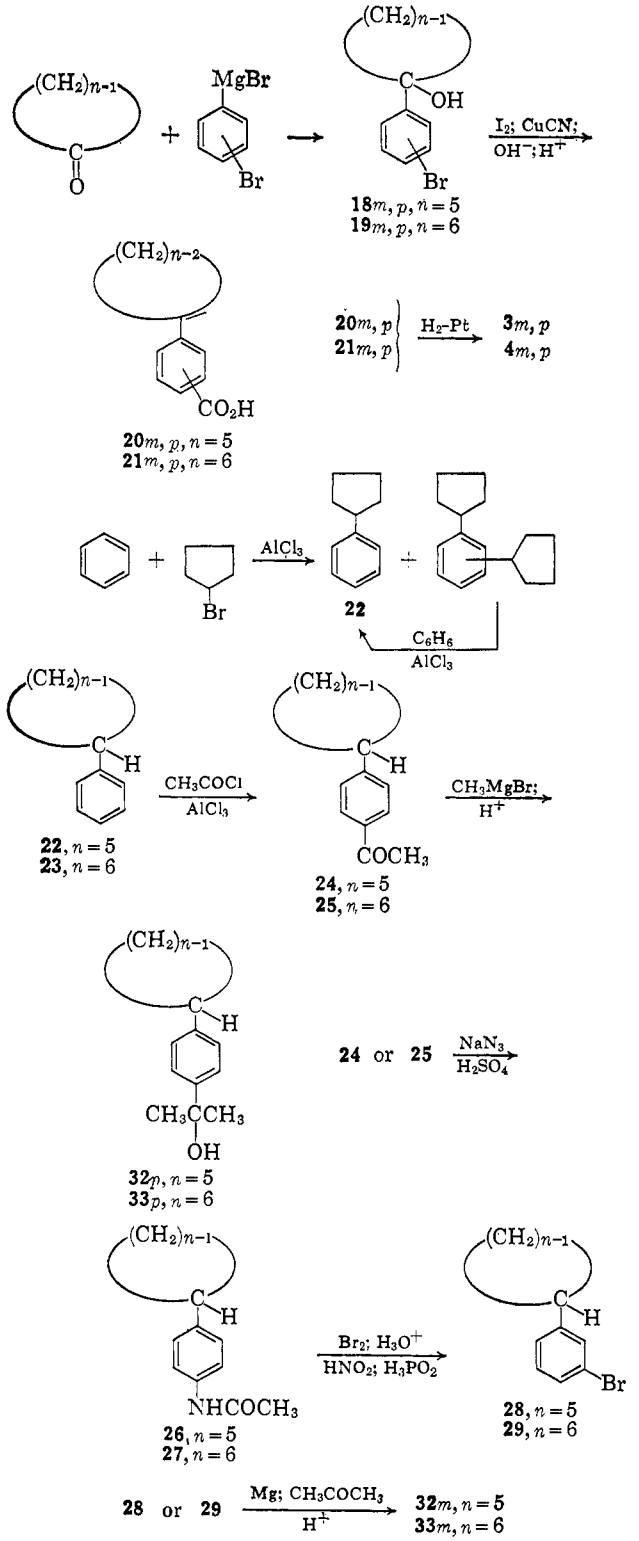
(5) T. F. Corbin, R. C. Hahn, and H. Shechter, *Org. Syn.*, **44**, 30 (1964).

(6) (a) In research subsequent to the present,[1] R. Ketcham, R. Cavestri, and D. Jambotkar, *J. Org. Chem.*, **28**, 2139 (1963), found that nitration of cyclopropylbenzene with concentrated nitric–sulfuric acids or with nitric acid–acetic anhydride yields *o*-cyclopropylnitrobenzene as the principal product. The *ortho*:*para* ratios for nitration in their experiments were 2.1 and 2.0–4.7, respectively. (b) Yu. S. Shabarov, V. K. Potapov, and R. Ya. Levina, *J. Gen. Chem. USSR*, **34**, 3171 (1964), in a study of the reaction of cyclopropylbenzene with nitric acid–acetic anhydride at −50° report an *ortho*:*para* ratio of 4.2.

(7) (a) J. R. Knowles, R. O. C. Norman, and G. K. Radda, *J. Chem. Soc.*, 4885 (1960); (b) H. C. Brown and W. H. Bonner, *J. Am. Chem. Soc.*, **76**, 605 (1954). (c) The *ortho*/*para* ratios for nitration of toluene by nitronium tetrafluoroborate in tetramethylene sulfone, nitronium perchlorate in tetramethylene sulfone, and nitryl chloride–silver tetrafluoroborate in nitromethane are 2.05, 2.18, and 2.33, respectively,[7d] (d) G. A. Olah and S. J. Kuhn in "Friedel–Crafts and Related Reactions," Vol. III, Part 2, G. A. Olah, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, pp 1460–1461.

(8) (a) Nitration by 70% nitric acid in acetic anhydride at 25°; see Experimental Section. (b) Nitration by 100% nitric acid in acetic an-

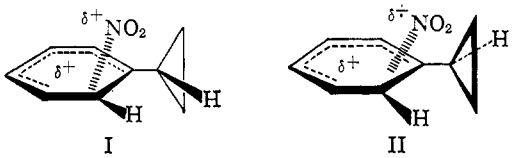
Chart III



pentylbenzene (0.45),[8b] and cyclohexylbenzene (0.29, 0.28)[8b,c] are considerably smaller than that for cyclopropylbenzene. Activation by the cyclopropyl group of the *ortho* positions in nitration is the largest yet found for a hydrocarbon substituent[6a,9] and thus merits discussion.

Nitration of cyclopropylbenzene is of particular interest in that the *ortho*:*para* ratios for the nitrating reagents investigated (nitric and sulfuric acids and nitric acid–acetic anhydride) are 2 or greater. It is thus clear that these substitution systems do not suffer relative diminished reactivity at *ortho* positions as is usual for other electrophilic aromatic processes. It has been suggested that nitrations resulting in enhanced *ortho* substitution result from complexation of the nitration agent with the aromatic substituent and subsequent *ortho* attack *via* a cyclic or related path.[6a,10] In the present discussion such concepts have been modified or extended upon consideration of the structures of the product-forming transition states on the basis of steric, conformational and electrical factors in cyclopropyl groups along with steric features of the nitrating reagents.

Considerable evidence has been obtained that cyclopropyl groups, along with their unsaturated properties, prefer *cis*-bisected conformations when attached to trigonally substituted carbon.[11] Such stereochemistry allows maximum overlap of the intracyclic bonds of the cyclopropane ring with a p orbital of the carbon substituent. Reaction of cyclopropylbenzene with nitronium ions, as derived from the nitric–sulfuric acid mixtures, leading to *o*-nitrocyclopropylbenzene may thus be expected to favor product-forming transition states such as I and II[12] in which there is significant delocalization through the cyclopropyl and the phenyl groups. In either I or II, steric restriction to *ortho* substitution should not be large because of the small effective volume of the cyclopropyl group; in I steric



I II

interference to *ortho* nitration involves only partial eclipsing with hydrogen substituents. It is thus suggested that nitration of cyclopropylbenzene by nitronium ion processes gives an *ortho*:*para* ratio of 2.0–2.1 because transition states I (preferred) and II are stabilized by *extended* conjugation as deterred by small steric and inductive effects whereas that, III, from *para* attack primarily involves lesser effective *crossed*-conjugative stabilization.[13]

Cyclopropylbenzene reacts with nitric acid–acetic anhydride to give *ortho*:*para* ratios (2.5–4.2) larger than those obtained from mixtures of nitric and sulfuric acids. The nitration reagents derived from nitric

hydride at *ca.* 0°; see Experimental Section. (c) The 0.28 ratio is based on separation of 75% of the mononitration product into pure *ortho* and *para* isomers: O. Neunhoeffer, *J. Prakt. Chem.*, **133**, 95 (1932).

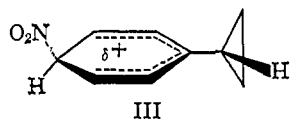
(9) F. G. Bordwell and E. W. Garbisch, Jr., *J. Org. Chem.*, 27, 2322 (1962), found that *o*-nitrostyrene is the principal nuclear substitution product in the reaction of styrene with nitric acid–acetic anhydride. The *ortho*:*para* ratio was not reported however.

(10) See J. R. Knowles and R. O. C. Norman, *J. Chem. Soc.*, 3888 (1961); R. O. C. Norman and G. K. Radda, *ibid.*, 3030 (1961); and Yu. S. Shabarov, D.Sc. Dissertation, Moscow University, Moscow, USSR, 1964, and references therein.

(11) See ref 3; G. L. Closs and H. B. Klinger, *J. Am. Chem. Soc.*, **87**, 3265 (1965); C. V. Pittman, Jr., and G. A. Olah, *ibid.*, **87**, 5123 (1965), and the many references therein.

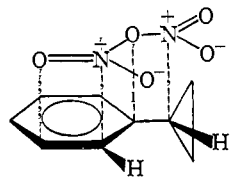
(12) The σ character of transition states such as I and II depends on the extent of penetration of the π cloud of cyclopropylbenzene by the nitrating agent.

(13) (a) The significance of extended and crossed conjugation in aromatic substitution processes in which steric factors are small will be discussed in other manuscripts from these laboratories. (b) M. J. S. Dewar, *J. Chem. Soc.*, 463 (1949), has calculated by molecular orbital methods that electrophilic substitution will occur more rapidly at each *ortho* position than in the *para* position in benzene derivatives containing electron-donating substituents which do not effect steric retardation.

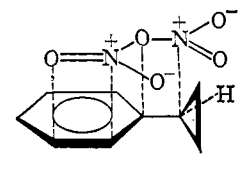


III

acid–acetic anhydride apparently depend on reaction temperature and time[10,14a] and appear to be dinitrogen pentoxide and/or possibly complexed nitronium nitrate, acetyl nitrate, and protonated acetyl nitrate.[10,14] These species are anticipated to be less nucleophilic than are nitronium ion reagents and should lead to transition states having more σ character and which make greater use of stabilization by extended conjugation than do nitronium ion reactants when there is no strong steric prohibition. The enhanced *ortho* substitution effected by such reagents may be derived from structural features in electron-deficient, product-forming transition states such as IV and V which reflect the favorable geometry, the small space-volume require-



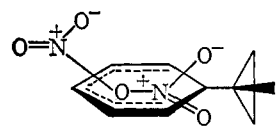
IV



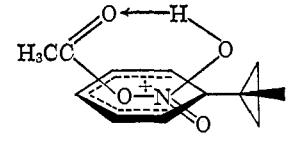
V

ments, and the electron-donor properties of the cyclopropyl group along with the expected π-coordination abilities of the nitrating agent.[15]

It is also possible that transition states of the type VI and VII in which there is overlap of the nitration reagent with the aromatic ring rather than with the cyclopropyl group can lead to enhanced *ortho* reactivity since steric



VI



VII

repression should be minimal and the contributions of extended *vs.* crossed conjugation can be realized.[13] These concepts in which nitration of cyclopropylbenzene occurs by broadside attack on its unsaturated systems with minor steric retardation are consistent with the structures and steric requirements of the nitrating agents and are analogous to that proposed for *cis* addition of dinitrogen pentoxide, nitric acid–acetic anhydride,[14a] and dinitrogen tetroxide to olefins in which coordination is not restricted sterically.[16b]

Reaction of bromine and cyclopropylbenzene (**7**) in acetic acid–potassium acetate at 10° gave *p*-bromocyclopropylbenzene (**10***p*, 47%); considerable cleavage of the cyclopropane ring occurred under these conditions.[17] *p*-Bromocyclopropylbenzene was also obtained from *p*-cyclopropylaniline by diazotization and replacement methods and from zinc and 1-bromo-1-(*p*-bromophenyl)-3-chloropropane.

Chart I summarizes the reactions used for converting (a) *p*-bromocyclopropylbenzene (**10***p*) to *p*-cyclopropylbenzoic acid (**1***p*) and *p*-cyclopropylphenyldimethylcarbinol (**30***p*)[18] and (b) *o*-cyclopropylaniline (**9***o*) to *m*-cyclopropylbenzoic acid (**1***m*) and *m*-cyclopropylphenyldimethylcarbinol (**30***m*). The sequence *o*-cyclopropylaniline (**9***o*) to *m*-bromocyclopropylbenzene (**10***m*) is efficient and provided access to a variety of *m*-cyclopropylbenzene derivatives. *p*-Cyclopropylacetanilide, prepared by acetylation of **9***p* or Schmidt reaction of *p*-cyclopropylacetophenone,[19] could not be advantageously brominated. This result is in contrast to the satisfactory conversion of **9***o* to **11** and **7** to **10***p*.

Cyclobutylbenzene, Cyclobutylbenzoic Acids, Cyclobutylphenyldimethylcarbinols. Cyclobutylbenzene (**13**), prepared by hydrogenolysis of 1-phenylcyclobutanol (**12**), was converted to *p*- and *m*-cyclobutylbenzoic acids (**2***p*,*m*) by the sequences in Chart II. Bromination of cyclobutylbenzene (**13**) gave a mixture of bromocyclobutylbenzenes (13% **14***o* and 87% **14***p*) which could not be separated preparatively; the subsequent *p*-cyclobutylbenzoic acid (**2***p*) was purified by recrystallization. *m*- and *p*-(1-cyclobutenyl)benzoic acids were not prepared because of the instability of *p*-bromo-(1-cyclobutenyl)benzene obtained from dehydration of 1-(*p*-bromophenyl)cyclobutanol (**16**). Reaction of *p*- and *o*-cyclobutylphenylmagnesium bromides (from **14***p* and **14***o*) with acetone yielded *p*-cyclobutylphenyldimethylcarbinol (**31***p*) containing approximately 14% of the *ortho* isomer.[20] The mixture of *p*- and *o*-carbinols could be used in the solvolysis study without further purification. Synthesis of *m*-cyclobutylphenyldimethylcarbinol was not undertaken because of the limited availability of initial materials and the very small solvolysis effects observed in the *meta* series.

C_5 and C_6 Cycloalkyl- and (1-Cycloalkenyl)benzoic Acids. C_5 and C_6 Cycloalkylphenyldimethylcarbinols. Reactions of *m*- and *p*-bromophenylmagnesium bromide with cyclopentanone and cyclohexanone afforded efficient entry to the corresponding *m*- and *p*-(1-cyclopentenyl)-, -(1-cyclohexenyl)-, -cyclopentyl-, and -cyclohexylbenzoic acids: **20**(*m*,*p*), **21**(*m*,*p*), **3**(*m*,*p*), and **4**(*m*,*p*), as summarized in Chart III. *m*- and *p*-cyclopentyl- and -cyclohexylphenyldimethylcarbinols, **32**(*p*, *m*) and **33**(*p*,*m*), were prepared as illustrated (Chart III) from cyclopentylbenzene (as obtained from benzene and cyclopentyl bromide or from di(poly)cyclopentylbenzenes in the presence of aluminum chloride) and cyclohexylbenzene.

Cycloalkyl-*t*-cumyl Chlorides. All carbinols were converted to the corresponding chlorides by reaction

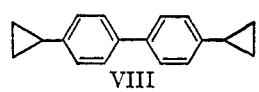
(14) (a) F. G. Bordwell and E. W. Garbisch, Jr., *J. Am. Chem. Soc.*, **82**, 3588 (1960); (b) G. A. Olah, S. J. Kuhn, S. H. Flood, and J. C. Evans, *ibid.*, **84**, 3687 (1962).

(15) For discussion of the relatively small steric effects in aromatic nitration which led to the concepts of the present manuscript, see ref 8d, p 1441–1485.

(16) (a) T. E. Stevens and W. D. Emmons, *J. Am. Chem. Soc.*, **79**, 6008 (1957); (b) H. Shechter, J. J. Gardikes, T. S. Cantrell, and G. V. D. Tiers, *ibid.*, **89**, 3005 (1967).

(17) R. Ya. Levina and P. A. Gembitskii, *J. Gen. Chem. USSR*, **31**, 3242 (1961), report that bromine reacts with cyclopropylbenzene in chloroform at −75° to give *p*-bromocyclopropylbenzene (**10***p*) in 80% yield.

(18) In conversions of **10***p* to acid **1***p* or carbinol **30***p* *via* the Grignard reagent, *p*,*p*′-bicyclopropylphenyl (VIII) is a minor product; see Experimental Section.



VIII

(19) H. Hart and G. Levitt, *J. Org. Chem.*, **24**, 1261 (1959).

(20) Formation of *p*,*p*′-bicyclobutylphenyl from the Grignard reaction is analogous to that for *p*,*p*′-bicyclopropylphenyl obtained similarly.

Table I. Ionization Constants and pK_a Values of *m*- and *p*-Cycloalkylbenzoic Acids in 50% Aqueous Ethanol at 25 ± 0.15°

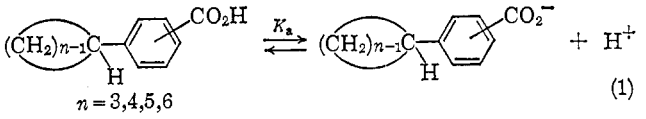
Group	*meta* $K_i \times 10^6$	pK_a	*para* $K_i \times 10^6$	pK_a
Hydrogen[a]	2.01	5.70	2.01	5.70 (5.71,[b] 5.73[c])
Isopropyl	...	...	1.30	5.89 (5.88[b])
Cyclohexyl	1.18	5.93	1.28	5.89
Cyclopentyl	1.20	5.93	1.28	5.89
Cyclobutyl	1.29	5.89	1.30	5.89
Cyclopropyl	1.41	5.85 (5.80[c])	1.22	5.91 (5.96,[b] 5.94[c])
Isopropenyl	...	...	2.75[b]	5.56[b]
1-Cyclohexenyl	1.42	5.85	1.52	5.82
1-Cyclopentenyl	1.63	5.79	1.59	5.80

[a] pK_a values reported for benzoic acid in 50% aqueous ethanol are: 5.72, O. Exner, *Collection Czech. Chem. Commun.*, **31**, 65 (1966); 5.73, F. G. Bordwell and G. D. Cooper, *J. Am. Chem. Soc.*, **74**, 1058 (1952); 5.75, J. D. Roberts, E. A. McElhill, and R. Armstrong, *ibid.*, **71**, 2923 (1949). [b] Reference 25a reports the indicated values as adjusted for change in solvent, assuming a Hammett ρ value of 1.52 (D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958)). [c] These pK_a values are given in ref 42 (Experimental Section), as adjusted for solvent change, on the assumption that the Hammett ρ is 1.52 (see McDaniel and Brown, footnote *b*).

with hydrogen chloride by established procedures[21] (see Experimental Section).

Discussion of Results

Ionization Constants. The apparent ionization constants of the *m*- and *p*-cycloalkylbenzoic acids in 50% aqueous ethanol (eq 1) were determined by potentio-



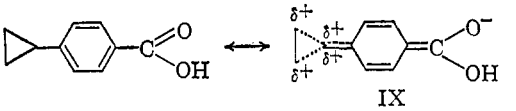
(1)

titrimetric methods (see Experimental Section). The results are summarized in Table I.

In the series of *m*-cycloalkylbenzoic acids, the differences in acid strengths are small, and in some cases are possibly within experimental error; however, the excellent reproducibility of the data (±0.01–0.02 pK_a unit), and the consistent trends with changing ring size encourage interpretation within existing theories. Introduction of any of the cycloalkyl groups, C_3–C_6, into the *meta* position weakens the acid (60–70% decrease in K_i; Table I) relative to benzoic acid; as the ring size of the *m*-cycloalkyl substituent increases from C_3 to C_6, the acid strength diminishes. These effects can be explained in terms of greater electron release of cycloalkyl groups relative to hydrogen and as ring size of the cycloalkyl groups is increased. The increase in acidity of *m*-cycloalkylbenzoic acids with decreasing ring size can also be rationalized on the basis of decreasing steric interference to solvation with decreasing ring size.[22] It is not yet possible to assess the relative influences of electronic and solvation effects of substituents for most of the cycloalkylbenzoic acids studied. However since most of the equilibrium data along with the kinetic results for solvolysis of the cycloalkyl-*t*-cumyl chlorides can be more readily rationalized in terms of substituent electronic effects, emphasis in the present discussion is placed on the effects of ring size on the inductive and conjugative properties of the cycloalkyl substituents. Thus for the carbocyclic rings (C_6–C_3), a decrease in ring size is presumably accompanied by an increase in the s character of the exocyclic bonding of the carbon atoms and in the electronegativities of the orbitals involved,[23] resulting in acid strengthening.

Acid strength continues to increase for the series: *m*-cyclopropyl- to *m*-(1-cyclohexenyl)- to *m*-(1-cyclopentenyl)benzoic acids. Electronic effects can account for this ordering on the basis of electron-withdrawing properties of vinyl substituents and the increase in s character and the electronegativity of exocyclic orbitals as ring size is decreased.

The effects of C_4–C_6 *p*-cycloalkyl substituents on the strengths of benzoic acids are similar to that for these substituents in *meta* positions. Within the series of *p*-cycloalkylbenzoic acids only the ionization constant of *p*-cyclopropylbenzoic acid is measurably different from that of its higher homologs. *p*-Cyclopropylbenzoic acid is slightly weaker than its homologous *p*-cycloalkylbenzoic acids, clearly weaker than *m*-cyclopropylbenzoic acid, and clearly weaker than either *p*-(1-cyclohexenyl)- or *p*-(1-cyclopentenyl)benzoic acids (Table I). This relative weakness of *p*-cyclopropylbenzoic acid finds little rationalization in inductive or solvation effects. The result is compatible however on the basis of conjugative interaction between intracyclic orbitals of the cyclopropyl group[24] and an adjacent electron-deficient π system. The weakness of *p*-cyclopropylbenzoic acid also supplements previous evidence that the cyclopropane ring, unlike the carbon–carbon double bond, can donate but cannot readily accept electrons when adjacent to an unsaturated center.[25] The electron-donor effect of the cyclopropyl group in *p*-cyclopropylbenzoic acid is formulated in structure IX.[26] Interaction of the cyclopropane ring as in IX can account for the reduced acidity of *p*-cyclopropylbenzoic



IX

acid relative to that of the *meta* isomer and the other *p*-cycloalkylbenzoic acids.

(21) H. C. Brown, J. D. Brady, M. Grayson, and W. H. Bonner, *J. Am. Chem. Soc.*, **79**, 1897 (1957).

(22) W. A. Sweeney and W. M. Schubert, *ibid.*, **76**, 4625 (1954); W. A. Sweeney and W. M. Schubert, *J. Org. Chem.*, 21, 119 (1956).

(23) A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949); J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, **84**, 540 (1962).

(24) For a summary of theories of bonding of cyclopropanes see W. A. Bernett, *J. Chem. Educ.*, **44**, 17 (1967), and references therein.

(25) (a) Alkaline hydrolysis of ethyl *p*-cyclopropylbenzoate in 86% ethanol at 40° is about four times faster than that of its *p*-isopropenyl analog: R. Ya. Levina, P. A. Gembitskii, L. P. Guseva, and P. K. Agasyan, *J. Gen. Chem., USSR*, **34**, 144 (1964); (b) R. H. Eastman and J. C. Selover, *J. Am. Chem. Soc.*, **76**, 4118 (1954).

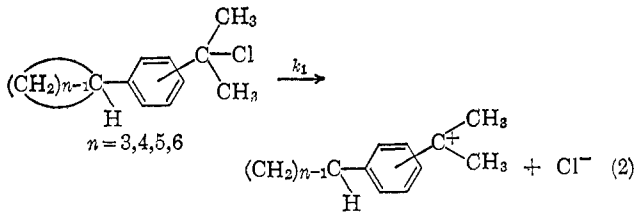
(26) For other representations of delocalization in cyclopropylcarbonium ions, see P. von R. Schleyer and G. W. Van Dine, *ibid.*, **88**, 2321 (1966).

Table II. Rate Constants and Derived Data for Solvolysis of Cycloalkyl-*t*-cumyl Chlorides in 90% Aqueous Acetone[a]

Alkyl Group	Rate constant, $k \times 10^5$ sec^{-1} −5.38°	0°	15°	25°	Rel rate, 25°	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	σ^+ [d]
Hydrogen				12.4	1.00	18.8	−12.4[b]	(0.00)
p-Methyl				327	26.4	17.3[b]	−12.0[b]	−0.311[b]
p-Cyclopropyl	60.5	117	577	1550[c]	125[c]	16.7	−10.6	−0.462[e]
p-Cyclobutyl		16.5	87.1	257	20.7	17.3	−12.4	−0.290
p-Cyclopentyl		18.5	102	294	23.7	17.4	−11.6	−0.303
p-Cyclohexyl		14.7	85.1	243	19.6	17.6	−11.6	−0.285
p-Isopropyl				233[b]	18.8[b]	17.4[b]	−12.2[b]	−0.280[b]
m-Cyclopropyl		0.89	5.87	19.0	1.53	19.3	−10.9	−0.041
m-Cyclohexyl		1.03	6.93	21.9	1.77	19.2	−10.9	−0.054
m-Isopropyl				23.2[b]	1.87[b]	19.4[b]	−10.2[b]	−0.060[b]

[a] Solvent was adjusted to give 12.4 ± 0.3 × 10^{-5} sec^{-1} for k_1 (25°) for *t*-cumyl chloride. [b] Reference 21. [c] Obtained by extrapolation of plot (log k/T *vs.* $1/T$). [d] On the assumption that $\rho = -4.54$; *cf.* ref 30. [e] Other values reported are: −0.410, ref 2; −0.484, calculated from data in ref 3, assuming a ρ value of −4.54.

Kinetics of Solvolysis. The rates of ionization (k_1, eq 2) of the cycloalkyl-*t*-cumyl chlorides were determined in 90 vol % aqueous acetone.[21] The rate con-



(2)

stants, kinetic parameters, and σ^+ for the systems are given in Table II.

Introduction of any of the cycloalkyl groups, C_3–C_6, into the *meta* position increases the rate of solvolysis of the *t*-cumyl chloride (~70% increase in k_1; Table II) relative to the parent compound. These effects are again as expected from inductive electron release of the cycloalkyl groups (relative to hydrogen) to the reaction center. As the ring size of the *m*-cycloalkyl substituent decreases from C_6 to C_3, the rate of solvolysis of the *t*-cumyl chloride decreases. This decrease cannot be explained readily in terms of usual solvation effects but is rationalizable on the basis of decreased inductive electron-donating ability with decreasing ring size, as related to extracyclic orbital hybridization of the respective α-carbon atoms.

m-Cyclopropyl-*t*-cumyl chloride is the slowest to solvolyze and *m*-cyclopropylbenzoic acid is the strongest acid in their respective homologous series. These facts fit with previous evidence that exocyclic cyclopropane orbitals possess considerable sp^2 character[24] and increased electronegativity. Kinetic evidence has been recently obtained[3] that the *p*-cyclopropyl group, when sterically hindered from assuming the geometry needed for significant overlap of intracyclic orbitals with an electron-deficient system, is less electron donating than is (*e.g.*) an isopropyl group. This effect provides both a contrast and a supplement to the present results in that, in *meta* systems, significant conjugative interaction of the cyclopropane ring is prevented by the inherent nature of the molecular orbital system, rather than by steric effects.

In the *para* position, cycloalkyl substituents produce more than a 10-fold increase in the rates of solvolysis relative to the *meta* isomers, and a 20-fold increase relative to the parent *t*-cumyl chloride. This acceleration cannot be solely an inductive effect.[27] Similar rate accelerations in solvolysis of *p*-alkyl-*t*-cumyl chlorides have been attributed to hyperconjugative stabilization of the transition states, and a rationalization of this type is applicable for the *p*-cycloalkyl-*t*-cumyl chlorides. Such hyperconjugative interaction is not effective for *meta* substituents.[28]

Solvolysis of *p*-cyclopropyl-*t*-cumyl chloride at 25° is ~6 times faster than that of its *p*-cycloalkyl homologs and 125 times faster than that of the parent *t*-cumyl chloride. This rate enhancement is the largest observed in the present study and the largest known for a hydrocarbon substituent. It is compatible with experimental results reported for other cyclopropyl systems[26] and with theories of demands of reaction centers,[29] hybridization of cyclopropyl bonds, and conjugative abilities used to explain previous observations in the present study. This is believed to be the first kinetic demonstration of the conjugative ability of the cyclopropane ring transmitted through an aromatic system.[2] No rearrangement of the cyclopropyl group was noted in the present solvolytic experiments.

Correlation of Solvolyses and Aromatic Nitrations. Because of the large differences in the effects of the *m*- and *p*-cyclopropyl groups (the *least* and *most* rate-enhancing hydrocarbon substituents of the present study) on solvolyses of *t*-cumyl chlorides, these rate data have been correlated with the isomer distribution from mononitration of cyclopropylbenzene (74% *ortho*, 0.1% *meta*, and 26% *para*).[8b] If σ^+ *meta* and σ^+ *para* values of the cyclopropyl substituent are assumed to be the same for nitrations as for solvolyses[30] (specifically solvolyses of *t*-cumyl chlorides in 90% aqueous acetone), and are known from solvolysis data, the *meta* and *para* partial rate factors for nitration can be calculated, using

$$\log p_f = \rho_{\text{nitration}}\sigma^+_{para} \quad (3a)$$

and

$$\log m_f = \rho_{\text{nitration}}\sigma^+_{meta} \quad (3b)$$

(27) R. W. Taft, Jr. has calculated that the inductive effect is nearly the same for alkyl groups in the *meta* and *para* positions: "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, pp 594–597.

(28) *Cf.* J. W. Baker, "Hyperconjugation," Oxford University Press, London, 1952, p 48.

(29) (a) M. F. Hawthorne, *J. Org. Chem.*, 21, 1523 (1956); (b) R. Fuchs, C. A. Kaplan, J. J. Bloomfield, and L. F. Hatch, *ibid.*, 27, 733 (1962).

(30) For discussion of the basis for this assumption see L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, 1, 89 (1963).

Knowledge of the isomer distribution for nitration of cyclopropylbenzene and σ^+ values for the cyclopropyl group, plus ρ for the nitration reaction, allows calculation of the relative reactivity of cyclopropylbenzene in nitration.

Stock and Brown have calculated $\rho_{\text{nitration}}$ to be -6.0, using a variety of substituents which include the "ordinary" alkyl groups (Me, Et, *i*-Pr, *t*-Bu).[30] On the basis of $\rho_{\text{solvolysis}}$ as -4.54, use of log (p_t/m_t) for cyclopropyl[31] (eq 4) gives a value of $= -6.45$ for nitration of cyclopropylbenzene, in reasonable agreement with calculated values of ρ for nitration of other monosubstituted benzenes.[30] This agreement indicates that the change in response of the cyclopropyl group to electron deficiency in the *meta* or *para* position parallels that of many other groups in going from solvolysis of the *t*-cumyl chlorides to aromatic nitration. Thus, for the cyclopropyl substituent, log p_t and log m_t values may be calculated with some assurance of meaning. Use of eq 3a and 3b leads to partial rate factors of 1.8 and 950, respectively, for *meta* and *para* nitration of cyclopropylbenzene. Using an *ortho*:*para* nitration ratio of 2.8, calculation indicates a partial rate factor of 1.3×10^3 for *ortho* nitration and a total reactivity of cyclopropylbenzene of *ca.* 700 times that of benzene under the specified experimental conditions. This prediction, however, is to be taken with some reservation, primarily because of its sensitivity to the amount of *m*-nitro isomer produced in nitration of cyclopropylbenzene.[32] Thus, a change of the *meta* percentage to 0.2% changes the ρ value for nitration to -5.73 (still in reasonable agreement with other nitrations), and changes the total relative reactivity of cyclopropylbenzene to *ca.* 350. On the assumption that a linear free energy correlation exists for nitration of cyclopropylbenzene, a reactivity several hundred times that of benzene may be expected; experimental investigation of this prediction is to be initiated.

$$\log (k_p/k_m)/\rho_{\text{solvolysis}} = \log (p_t/m_t)/\rho_{\text{nitration}} \qquad (4)$$

Experimental Section[1]

(1,3-Dibromopropyl)benzene (6). A stirred mixture of 1-bromo-3-phenylpropane (257 g, 1.29 mol), N-bromosuccinimide (238 g, 1.33 mol), and benzoyl peroxide (3.0 g, 0.012 mol) in carbon tetrachloride (1200 ml) was heated cautiously until reflux was spontaneous. After reaction had subsided[33] heating was resumed until hydrogen bromide was evolved. Solids were filtered and washed with carbon tetrachloride; the washings were combined with the filtrate. The bulk of solvent was distilled at partial aspirator pressure at a pot temperature below 50°. Residual solvent was removed by vacuum evaporation (no heat applied); the orange-yellow residue (362 g, 101%) was used without further treatment in the next step. Distillation of an aliquot of the residue from a similar experiment gave dibromide **6**, bp 100° (1 mm), n^{27}D 1.5893 [lit.[34] nD 1.5935]; attempts to distil large quantities usually caused evolution of hydrogen bromide.

Cyclopropylbenzene (7). Crude dibromide **6** (359 g, 1.29 mol) was added to a stirred, chilled suspension of zinc–copper couple[4a,b] (135 g, 2 mol) in redistilled dimethylformamide (500 ml) at a rate sufficient to maintain the temperature at 7–12°. After addition was complete, the mixture was stirred for 15 min, poured into water (1 l.), and steam distilled until the condensate was homogeneous. The separated organic layer was washed with water, then dried over magnesium sulfate. Distillation at atmospheric pressure gave hydrocarbon **7** (140 g, 92%) as a colorless liquid, bp 169–172°, n^{20}D 1.5323 [lit.[35,36] nD 1.5302], essentially pure as analyzed by vapor phase chromatography.

Reaction of **6** with magnesium in ethyl ether at 25–30° gave **7** (*ca.* 40% yield) contaminated by *trans*-1-phenylpropene.[37,38]

p*-Bromocyclopropylbenzene (10*p*) (Method 1).** Cyclopropylbenzene (11.8 g, 0.10 mol) was added to potassium acetate (11 g, 0.11 mol) in glacial acetic acid (100 ml). Upon cooling the stirred mixture to 5° it became semisolid;[39] bromine (16 g, 0.10 mol) was then added dropwise in 0.5 hr. The mixture was kept at 5° for 5 hr and 10° for 2 hr. Potassium bromide separated. The organic layer and the ether extracts of the aqueous layer were combined and successively washed with water, aqueous sodium bisulfite, water, and saturated sodium chloride. Concentration of the dried solution left a yellow residue; distillation gave a light yellow liquid (11.5 g), bp 70–80° (1 mm). Redistillation afforded crude **10*p as a near-colorless liquid (9.3 g, 47%), bp 66–70° (1 mm), mp *ca.* 12°. The product, on being shaken 12 hr with excess 2% aqueous potassium permanganate and decolorized with sodium bisulfite, gave a colorless distillate, bp 61–63° (1 mm), mp *ca.* 15°, n^{20}D 1.5749 [lit.[17] bp 116° (15 mm), mp 15°, n^{20}D 1.5752, d^{20} 1.3920]. The infrared spectrum of this material indicated the absence of *meta* isomer (no absorption at 12.8 μ).

Anal. Calcd for C_9H_9Br: C, 54.86; H, 4.60; Br, 40.55. Found: C, 54.67; H, 4.66; Br, 40.48.

The product gave silver bromide (*ca.* 2% of theory) after having been shaken with excess alcoholic silver nitrate. Recrystallization of the distillate gave a product whose ir spectrum had a more intense band at 13.4 μ (*para* substitution) and was almost void of a weak band at 14.4 μ present in the spectrum of the unrecrystallized liquid.[38]

Method 2. *p*-Cyclopropylaniline (32 g, 0.24 mol, bp 81–85° (1–2 mm), n^{24}D 1.5828, obtained in 89% yield by platinum-catalyzed hydrogenation of *p*-nitrocyclopropylbenzene) was stirred at -3 to -5° with 48% hydrobromic acid (100 g, 0.6 mol), and a solution of sodium nitrite (18 g, 0.26 mol) in water was slowly added. After 1 hr, the mixture was poured rapidly into a stirred suspension of cuprous bromide (50 g, 0.35 mol) in water (300 ml) at 75°; 48% hydrobromic acid (100 ml) was added at once. Work-up[40] gave 29 g of a pale green liquid, bp 58–61° (1 mm). Its infrared absorption at 10.4 μ indicated the presence of unsaturation; two treatments with aqueous potassium permanganate afforded olefin-free **10*p*** (17.5 g, 37%), spectrally identical with purified **10*p*** prepared by direct bromination (above).

Method 3. Synthesis of **10*p*** was also effected[38] by reaction of *p*-bromophenylmagnesium bromide with 3-chloropropionaldehyde to give 1-(*p*-bromophenyl)-3-chloro-1-propanol (22% crude, bp 120–135° (1 mm), n^{35}D 1.5445), reaction of the product with hydrogen bromide to yield 1-bromo-1-(*p*-bromophenyl)-3-chloropropane (32% crude, bp 122–125° (1 mm), n^{31}D 1.5971), and cyclization of this intermediate by reaction with zinc in dimethylformamide at 0°. The physical constants of the final colorless liquid (25%) were bp 69–71° (1–2 mm), n^{20}D 1.5750, d^{25}_4 1.3915, mp *ca.* 15°.

Anal. Calcd for C_9H_9Br: C, 54.86; H, 4.60. Found: C, 54.65; H, 4.56.

p*-Cyclopropylbenzoic Acid (1*p*) (Method 1).**[41] A stirred mixture of **10*p (15.22 g, 0.077 mol), cuprous cyanide (4.48 g, 0.050 mol), and dimethylformamide (10 ml) was refluxed for 3.5 hr. The cooled red mixture was poured into water (50 ml) containing ferric chloride hexahydrate (20 g, 0.073 mol) and hydrochloric acid (5 ml). The mixture was shaken and extracted with benzene at 60–70° and the extract filtered through sodium sulfate. Removal of benzene and

(31) Although the partial rate factors are not known for nitration of cyclopropylbenzene, log (p_i/m_i) for cyclopropyl is readily calculated from the isomer distribution.

(32) The reservations needed in using experimental data and linear free energy correlations for nitration reactions have been discussed previously in ref 30.

(33) Further heating was omitted if only a small amount of unreacted N-bromosuccinimide remained. The N-bromosuccinimide was easily discerned.

(34) M. Lespieau, *Compt. Rend.*, **190**, 1129 (1930).

(35) G. S. Hammond and R. W. Todd, *J. Am. Chem. Soc.*, **76**, 4081 (1954).

(36) M. T. Rogers, *ibid.*, **69**, 2544 (1947).

(37) P. J. C. Fierens and J. Nasielski, *Bull. Soc. Chim. Belges*, 71, 187 (1962).

(38) For greater detail see T. F. Corbin, Ph.D. Dissertation, The Ohio State University, 1956.

(39) The yield of 10*p* was not significantly different when the reaction was effected homogeneously in 50% acetic anhydride–acetic acid.

(40) J. S. Buck and W. S. Ide, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p 132.

(41) The general procedure of L. Friedman and H. Shechter, *J. Org. Chem.*, **26**, 2522 (1961).

distillation gave *p*-cyclopropylbenzonitrile slightly contaminated by **10***p* (9.28 g, 84%), bp 74–85° (1–2 mm, mostly at 84°), n^{20}D 1.5639 [lit.[42] bp 150° (14 mm), n^{20}D 1.5639].

The *p*-cyclopropylbenzonitrile (4.19 g, 0.0284 mol) was refluxed with potassium hydroxide (10 g) and 50% aqueous ethylene glycol (50 ml) until evolution of ammonia had virtually ceased (*ca.* 12 hr). The mixture was poured into water, filtered, and extracted with ether. Acidification of the filtrate gave colorless acid **1***p* (3.9 g, 85%), mp 157–159° [lit.[42] 161–162°]. Recrystallizations from ethanol–water afforded an analytical sample, mp 163.6–164.2°, which gave no manganese dioxide on being shaken 12 hr with excess 2% aqueous potassium permanganate or in 0.5 hr when made homogeneous with sodium hydroxide.

Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.05; H, 6.22; neut equiv, 162. Found: C, 73.88; H, 6.27; neut equiv, 162.

Stirring with 15% potassium permanganate at 90° converted **1***p* into terephthalic acid (sublimed *ca.* 290–300°) in 35% yield.

Method 2. The Grignard reagent resulting from addition of bromide **10***p* (5.14 g, 0.026 mol) to magnesium (0.62 g, 0.255 g-atom) in anhydrous ether (15 ml) was poured onto crushed Dry Ice (*ca.* 50 g) in anhydrous ether. Hydrolysis of the mixture with dilute hydrochloric acid at 25–30° yielded **1***p* (2.4 g crude, 57%), mp (recrystallized from ethanol–water) 163.6–164.2°.

A neutral product (0.20 g), obtained from the ether solution and recrystallized from ethanol–water as thin, colorless plates, mp 127–128°, was assigned the structure *p,p'*-bicyclopropylphenyl (VIII).

Anal. Calcd for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.19; H, 8.00.

p*-Cyclopropylphenyldimethylcarbinol (30*p*).** Bromide **10p* (10.9 g, 0.055 mol) in dry ether (50 ml) was added slowly to magnesium turnings (1.5 g, 0.06 g-atom) stirred in tetrahydrofuran (15 ml) under nitrogen. Reaction started immediately. After the addition had been completed, the mixture was heated 15 min with steam and cooled, and acetone (10 ml, *ca.* 0.13 mol) was added dropwise. The mixture was stirred 1 hr and poured into concentrated aqueous ammonium chloride. The separated organic layer and combined ether extracts of the aqueous layer were washed with saturated aqueous sodium chloride, dried over potassium carbonate–magnesium sulfate, filtered, and concentrated. The residue, combined with similar material from another run, was fractionated to give carbinol **30***p* (11.6 g, 51%) as a colorless liquid, bp 99–100° (1–2 mm), n^{22}D 1.5394, λ_{max}^{film} 2.9 (s), 9.9 (s) μ; redistillation provided an analytical sample.

Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.24; H, 8.73.

The solid residue from the above fractionation was recrystallized from ethanol to give *p,p'*-bicyclopropylphenyl (VIII), identical with the material isolated from carboxylation of the Grignard reagent from **10***p*.

2-(*p*-Cyclopropylphenyl)propene. Methylmagnesium bromide (67 ml, 3 *M* solution in ether) was added slowly to a stirred solution of *p*-cyclopropylacetophenone (20 g, 0.125 mol) in ether (50 ml). The mixture was poured into dilute hydrochoric acid and extracted with ether, and the combined organic portions were dried over potassium carbonate and filtered. Solvent removal followed by fractionation of the residue yielded a colorless middle fraction (14 g, 71%), bp 84–85° (1–2 mm), n^{22}D 1.5612, λ_{max}^{film} 6.1–6.2 (s, twin) μ, none for —OH or >C=O.

Anal. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 90.23; H, 9.71.

Nitration of Cyclopropylbenzene (7) (Method 1). Nitric acid (70 ml, 16 *N*, *ca.* 1.1 equiv) was added dropwise to a stirred solution of **7** (118 g, 1.0 mol) in acetic anhydride (400 ml) at 10–20°. Stirring of the yellow homogeneous mixture was continued for 1 hr at 10°. The solution was poured into water and neutralized with cold, concentrated sodium hydroxide. The organic layer and ether extracts of the aqueous layer were combined, washed with excess aqueous potassium carbonate, dried, and concentrated. The yellow residue (156 g, 96%) was combined with 25 g of mononitrated **7** from another run and distilled (*ca.* 3 mm) through a glass-helix column in three principal fractions: I (*o*-cyclopropylnitrobenzene, **8***o*), bp 99–100°, n^{25}D 1.5590, 120.7 g; II, bp 100–115°, 20.6 g; III (*p*-cyclopropylnitrobenzene, **8***p*), bp 115–116°, mp 30–31°, 37.0 g. A mixture of **8***o* and **8***p* (bp 81–96° (1–2 mm)) from simple distillation of the nitration product was analyzed.

Anal. Calcd for $C_9H_9NO_2$: C, 66.24; H, 5.56. Found: C, 66.12; H, 5.37.

Structural assignments were supported by ir spectra; fraction I and *o*-ethylnitrobenzene showed distinctive absorption near 15.2, 14.3, and 12.8 μ, while fraction III and *p*-ethylnitrobenzene absorbed near 14.5 and 9.0 μ (sharp). Vapor phase chromatography (5-ft silicone column, 197°) and ir spectra each indicated slightly incomplete separation of **8***o* and **8***p* in fractions I and III; purer **8***p*, mp 32–33° (lit.[6a] 32–33°), was obtained by recrystallization of III from petroleum ether (30–60°). Vpc analysis (100-ft squalene capillary column, 140°) of fraction II showed only a trace of *m*-cyclopropylnitrobenzene; vpc analysis of the unrectified nitration product gave an **8***o* to **8***p* area ratio of 71:29.

Oxidation of a portion of fraction III with excess 20% nitric acid in phosphoric acid (44 *N*) gave *p*-nitrobenzoic acid, mp and mmp 230–235°.

Method 2. A solution of 100% nitric acid (0.315 g, 0.005 mol) in acetic anhydride (0.510 g, 0.005 mol) was added dropwise with stirring to a solution of cyclopropylbenzene (1.2 g, 0.01 mol) in acetic anhydride (10 ml) kept at 0–10°. After 1–2 hr, water and ether were added to the reaction mixture. The separated ether solution was washed with aqueous sodium hydroxide, dried, and concentrated. Gas chromatography of the resulting mixture (Aerograph Hy-Fi Model 600-C) on a 5-ft silicone rubber column at 180° gave peaks attributable to the isomeric mononitration products. The peak for the *meta* isomer was obtained by injecting a sample size determined to give maximum on-scale *ortho* and *para* peaks at minimum sensitivity and switching to maximum sensitivity for the *meta* peak. Retention volumes were assumed equal, and isomer ratios were determined by weighing Xerox cutouts of the vpc scans. Isomer distributions for six runs averaged 26 ± 5% *ortho* and 74 ± 5% *para;* four of these runs included *meta* determinations, which averaged 0.1 ± 0.1%.

o*-Cyclopropylacetanilide.** A mixture of platinum oxide (0.1 g), **8o* (50 g, 0.306 mol), and absolute ethanol (40 ml) was shaken under 2–3 atm of hydrogen until practically the theoretical amount had been absorbed. After the catalyst had been filtered and the mixture concentrated at reduced pressure, the residue was distilled to yield *o*-cyclopropylaniline (**9***o*) (38.8 g, 95%), bp 74–77.5° (2–3 mm), n^{20}D 1.5780. Acetylation (acetic anhydride) gave *o*-cyclopropylacetanilide, mp 113–114° (recrystallized from ethanol–water), in 92% yield.

Anal. Calcd for $C_{11}H_{13}NO$: C, 75.40; H, 7.48. Found: C, 75.22; H, 7.37.

Amine **9***o* was similarly converted to benz-2-cyclopropylanilide, mp 147–148° (lit.[6b] 146–147°).

4-Bromo-2-cyclopropylacetanilide (11). A solution of bromine (32 g, 0.20 mol) in glacial acetic acid (150 ml) was poured into *o*-cyclopropylacetanilide (34 g, 0.194 mol) in acetic acid (200 ml). The initial mildly exothermic reaction soon subsided, and crystals formed; after 4 hr the product was filtered, washed with ether, and dried to give crude **11** (47 g, 95%). Recrystallization (ethanol) yielded a colorless sample, mp 135–136°.

Anal. Calcd for $C_{11}H_{12}NOBr$: C, 52.00; H, 4.76; Br, 31.46. Found: C, 51.87; H, 4.73; Br, 31.29.

***p*-Cyclopropylacetanilide.** Sodium azide (14 g, 0.209 mol) was added in portions to *p*-cyclopropylacetophenone[19] (33 g, 0.206 mol) in 70% sulfuric acid (300 ml) stirred at 15–20°. Nitrogen was evolved rapidly. After 15 min, the mixture was poured into iced water (1 kg). A yellow gum was formed which was taken up in chloroform and dried over potassium carbonate. Most of the solvent was removed at reduced pressure; dilution of the remaining solution with petroleum ether (30–60°) produced pale yellow crystals (29 g, 81%), mp 115–120°. Recrystallization from benzene afforded a colorless sample of *p*-cyclopropylacetanilide, mp 120–121°; admixture with material obtained from acetylation of *p*-cyclopropylaniline produced no depression of melting point.

Anal. Calcd for $C_{11}H_{13}NO$: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.61; H, 7.63; N, 8.16.

***m*-Bromocyclopropylbenzene (10*m*).** Sodium nitrite (19 g, 0.275 mol) in cold water (75 ml) was added slowly to a stirred mixture of 4-bromo-2-cyclopropylaniline hydrochloride (62 g, 0.25 mol, mp 223–225° dec, prepared from **11** in 89% yield[43]), concentrated hydrochloric acid (75 ml), and water (200 ml) at 5–10°. Cold hypophosphorous acid (30%, 560 g, 2.3 mol) was added and the mixture allowed to warm slowly to 25–30°. When evolution of nitrogen had ceased, the red organic layer was separated, the aqueous layer was extracted with ethylene dichloride, and the combined organic

(42) J. Smejkal, J. Jonas, and J. Farkas, *Collection Czech. Chem. Commun.*, **29**, 2950 (1964).

(43) The procedure used for diazotization was essentially that of C. S. Marvel, H. W. Johnston, J. W. Meier, T. W. Mastin, J. Whitson, and C. M. Himel, *J. Am. Chem. Soc.*, 66, 914 (1944).

portions were dried over potassium carbonate. After the solution had been filtered and solvent removed, the residue was combined with similar material from other runs and distilled to give colorless bromide **10***m* (128 g, 94% based on 172 g of amine hydrochloride), bp 63–64° (1–2 mm), n^{25}D 1.5735, d^{25}_4 1.3888 [lit.[42] bp 98–100° (14 mm), n^{20}D 1.5758]. A vapor phase chromatogram (5-ft silicone column, 219°) showed a single peak containing 99% of the total area.

Anal. Calcd for C_9H_9Br: C, 54.86; H, 4.60; Br, 40.55. Found: C, 54.69; H, 4.92; Br, 40.57.

m*-Cyclopropylbenzoic Acid (1*m*).** A stirred mixture of **10m* (9.87 g, 0.050 mol), cuprous cyanide (5.36 g, 0.060 mol), and dimethylformamide (15 ml) was heated at 140° for 1 hr and refluxed for 2 hr. Colorless, slightly impure (contaminated with starting material) *m*-cyclopropylbenzonitrile (5.97 g, 84%), bp 83–85° (1–2 mm), n^{20}D 1.5540, was isolated from the red-brown mixture by the procedure described for *p*-cyclopropylbenzonitrile. After the nitrile had been refluxed 19 hr with 50% ethylene glycol–water (30 ml) containing potassium hydroxide (7.0 g), acid **1***m* was isolated as near-colorless crystals (mp 118–120°, 92% yield) upon acidification. A sequence of recrystallization (ethanol–water), sublimation, and recrystallization yielded colorless needles, mp 121.2–122.0° (lit.[42] 119–120°), neut equiv calcd 162, found 163, inert to 2% aqueous potassium permanganate (25–30°).

Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.05; H, 6.22. Found: C, 74.05; H, 6.35.

m*-Cyclopropylphenyldimethylcarbinol (30*m*).** Treatment of bromide **10m* (67 g, 0.34 mol) by the method used for preparation of **30***p* from **10***p* produced carbinol **30***m* (41.5 g, 69%), bp 91.5–96° (1–2 mm). A central fraction [bp 95–96° (1–2 mm), n^{22}D 1.5358] was analyzed.

Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.44; H, 8.98.

1-Phenylcyclobutanol (12). Cyclobutanone (33.5 g, 0.48 mol) in anhydrous ether (50 ml) was added to a stirred ether solution (300 ml) of phenylmagnesium bromide (0.50 mol) under nitrogen at 0–5°. Additional ether (50 ml) facilitated the stirring. After the reaction mixture had been hydrolyzed with aqueous ammonium chloride, the combined ether decantate and residue extract was dried and concentrated at reduced pressure. The partly solid residue was distilled at 75–91° (1–2 mm) and the solid distillate recrystallized (petroleum ether, 30–60°) to give large, colorless prisms (44 g, 62%) of alcohol **12**, mp 39.0–39.8° (lit. 40–41°,[44] 39–40°[45]).

Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 81.27; H, 8.24.

Cyclobutylbenzene (13). Alcohol **12** (15 g, 0.10 mol) in absolute ethanol (50 ml) was hydrogenated over 10% palladized charcoal (*ca.* 5 g) at 45 psi. After 1 equiv of hydrogen had been absorbed, the mixture was filtered and concentrated and the residue distilled to yield colorless **13** (11.5 g, 89%), bp 88.5–89.5° (30 mm), n^{20}D 1.5269, d^{25} 0.9366 [lit.[46] by 101–102° (41 mm), n^{20}D 1.5277, d^{20}_4 0.9378; lit.[45] bp 89–91° (25 mm), n^{20}D 1.5267]. Vapor phase chromatographic analysis (5-ft silicone column, 155°) showed 99% of the area under a single peak.

Bromination of Cyclobutylbenzene. Bromide (14.1 g, 0.088 mol) was added in 2 hr to a stirred mixture of **13** (11.5 g, 0.087 mol) and iron filings (0.1 g) at 0°. After the red mixture had been stirred 2 hr, aqueous sodium hydroxide–sodium sulfite (100 ml) was added. The organic layer and an ether extract of the aqueous layer were combined, washed with saturated aqueous sodium chloride, dried over anhydrous magnesium sulfate, and distilled to give colorless monobromocyclobutylbenzene (15.7 g, 86%), bp 78–80° (1–2 mm), nD 1.5670, d^{25}_4 1.3470. Vpc analysis (100-ft squalene capillary column, 150°) of the bromocyclobutylbenzene showed two peaks having an approximate area ratio of 13:87 attributable to *ortho* and *para* isomers **14***o* and **14***p*, respectively. The infrared spectrum of the mixture contained a strong band at 12.2 μ (**14***p*) and a shoulder at 13.25 μ (**14***o*).

Anal. Calcd for $C_{10}H_{11}Br$: C, 56.89; H, 5.25; Br, 37.86. Found: C, 56.95; H, 5.25; Br, 37.67.

p*-Cyclobutylbenzoic Acid (2*p*).** Acid **2p* was prepared from bromide **14***p* in 39% over-all yield as depicted in Chart II, by the methods described for conversion of bromide **10***m* to acid **1***m*. Properties of the products are given in Table I.

p*-Cyclobutylphenyldimethylcarbinol (31*p*). *p,p'*-Bicyclobutylphenyl.** A mixture of bromides **14o* and **14***p* from bromination of **13** (15.7 g, 0.074 mol) was converted to carbinols **31***o* and **31***p* by the process used to prepare **30***p* from **10***p*. The product mixture (10.0 g, 71%) boiled at 100–102° (1 mm). Analysis by vpc (5-ft silicone column, 165°) showed peaks attributable to *ortho* and *para* isomers with an area ratio of *ca.* 14:86. Fractionation through a Nester spinning-band column (1 × 25 cm) produced no detectable separation of isomers; a middle fraction was analyzed.

Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 81.83; H, 9.58.

The solid pot residue from the spinning-band fractionation was recrystallized from ethanol as colorless plates, mp 109–111°; this product was assigned the structure *p,p'*-bicyclobutylphenyl.

Anal. Calcd for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 91.75; H, 8.41.

1-(*p*-Bromophenyl)cyclobutanol (16). Cyclobutanone (17.5 g, 0.25 mol) in ether (15 ml) was added in 45 min to a stirred equivalent amount of *p*-bromophenylmagnesium bromide at 0°. The mixture was stirred at 25–30° for 2 hr and then hydrolyzed with saturated aqueous ammonium chloride. The yellow decantate and the ether washings of the residue were combined, dried, concentrated, and distilled to give colorless, impure alcohol **16** (42.6 g, 75%), bp 90–135° (1–2 mm), which subsequently solidified, and an unidentified yellow residue (8 g). Redistillation at 105–108° (1–2 mm) and recrystallization from petroleum ether (30–60°) gave colorless crystals of **16**, mp 43.5–44.5°.

Anal. Calcd for $C_{10}H_{11}OBr$: C, 52.88; H, 4.88. Found: C, 52.88; H, 4.96.

1-(*p*-Bromophenyl)cyclobutyl Bromide (17). Alcohol **16** (7.83 g, 0.0345 mol) and hydrobromic acid (48%, 50 ml) were shaken at 70–75° for 15 min. The initial crystals soon formed a red-brown oil which crystallized at 25–30°. Extraction with petroleum ether (30–60°) and recrystallization at 0–5° gave **17** (7.32 g, 73%). Recrystallization from petroleum ether furnished an analytical sample, mp 62–63°, which evolved hydrogen bromide on storage for several days.

Anal. Calcd for $C_{10}H_{10}Br_2$: C, 41.55; H, 3.49; Br, 55.30. Found: C, 41.40; H, 3.54; Br, 55.16.

Nitration of Cyclobutylbenzene (13). Nitric acid (4.8 ml, 70%) was added in 15 min to a stirred solution of **13** (6.28 g, 0.0476 mol) in acetic anhydride (33 ml) at 25°. After the mixture had been stirred 1 hr at 24°, the yellow product (7.07 g, 84%) was isolated as described previously in nitration of **7**: bp 91–102° (1–2 mm), n^{20}D 1.5617. The crude nitration product was rectified (Nester spinning-band column); six fractions were collected over the range 102–117° (2–3 mm). Refractive indices and infrared spectra indicated that fractions 1 and 6 were nearly pure *o*-cyclobutylnitrobenzene (**15***o*), bp 102–104.8° (2–3 mm), n^{20}D 1.5541, and *p*-cyclobutylnitrobenzene (**15***p*), bp 114.5–117° (2–3 mm), n^{20}D 1.5660, respectively. A twice distilled but unrectified sample of similarly nitrated material had bp 87–88° (1–2 mm), n^{20}D 1.5587, d_4^{25} 1.1306. The mixture corresponded to a 36:64 *ortho*:*para* ratio on the basis of its refractive index.

Anal. Calcd for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.26. Found: C, 67.65; H, 6.41.

o*- and *p*-Cyclobutylanilines.** A distilled sample of the mixture of **15o* and **15***p* (11.80 g, 0.0667 mol) in absolute ethanol (40 ml) was hydrogenated at 40 psi over 10% palladized charcoal (*ca.* 4 g) at a maximum temperature of 45°. Three equivalents of hydrogen was absorbed. The mixture was filtered and the filtrate poured into water and extracted with ether. The extract was washed with water and saturated sodium chloride, dried, concentrated, and distilled twice to give a near-colorless liquid, primarily *o*- and *p*-cyclobutylanilines (8.29 g, 84%), bp 78–91° (1–2 mm), n^{28}D 1.5700. A middle fraction was analyzed.

Anal. Calcd for $C_{10}H_{13}N$: C, 81.58; H, 8.90. Found: C, 81.75; H, 9.17.

Hydrogenation of a similar mixture over platinum oxide in ethanol gave *o*- and *p*-cyclobutylanilines in 92% yield, bp 80–91° (1–2 mm).

2(4)-Bromo-4(2)-cyclobutylacetanilides. Potassium acetate (5.9 g, 0.060 mol) in acetic acid (30 ml) and acetic anhydride (22 ml) was added slowly to a stirred mixture of *o*- and *p*-cyclobutylanilines (8.05 g, 0.0547 mol) at 0°. The mixture warmed to *ca.* 25°. Bromine (8.8 g, 0.055 mol) in acetic acid (15 ml) was added in 10 min (stirring) at 0–4°. The red-orange mixture was stirred for 3.5 hr while being warmed to 22–25°. Dilution with water precipitated an amorphous solid (12.98 g, 89%) which on recrystallization (ethanol–water) afforded a mixture of 2-bromo-4-cyclobutylacetanilide

(44) J. W. Wilt and D. D. Roberts, *J. Org. Chem.*, 27, 3430 (1962).
(45) Yu. S. Shabarov, N. A. Donskaya, and R. Ya. Levina, *J. Gen. Chem. USSR*, 33, 3360 (1963).
(46) F. H. Case, *J. Am. Chem. Soc.*, 56, 715 (1934).

Table III. Physical Constants and Analyses of Cycloalkyl and Cycloalkenylbenzene Derivatives

Compound	Bp, °C (1–2 mm)	Mp, °C	n^tD	Calcd, % C	Calcd, % H	Found, % C	Found, % H	Neut equiv Calcd	Neut equiv Found
p-Cyclobutylbenzonitrile[a]	83–85		1.5499[b]						
p-Cyclobutylbenzoic acid		134.0–134.5		75.0	6.9	74.8	7.0	176	176
m-Cyclobutylbenzonitrile[a]	88–92		1.5478[b]						
m-Cyclobutylbenzoic acid		68.5–69.0		75.0	6.9	75.0	7.1	176	175
1-(*p*-Bromophenyl)cyclopentene	120–125	96–97		59.2	5.0	59.4	5.2		
p-(1-Cyclopentenyl)benzonitrile	100–116	72–73		85.2	6.6	85.1	6.5		
p-(1-Cyclopentenyl)benzoic acid		236–255[c]		76.6	6.4	76.6	6.6	188	189
p-Cyclopentylbenzoic acid		196.5–198.5		75.8	7.4	76.1	7.3	190	189
2-Bromo-4-cyclopentylacetanilide[d]		143–145		55.3	5.7	55.8	6.0		
m-Bromocyclopentylbenzene	110–111		1.5634[e]	58.7	5.8	58.6	5.9		
1-(*m*-Bromophenyl)cyclopentene	86		1.6600[b]	59.2	5.0	59.1	5.0		
m-(1-Cyclopentenyl)benzoic acid		181.5–182.2[f]		76.6	6.4	76.4	6.6	188	188
m-Cyclopentylbenzoic acid		93.4–94.2		75.8	7.4	75.7	7.4	190	190
1-(*p*-Bromophenyl)cyclohexanol	128–131	75–76		56.5	5.9	56.5	5.8		
1-(*p*-Bromophenyl)cyclohexene	125–130	76–77		60.8	5.3	60.9	5.4		
p-(1-Cyclohexenyl)benzonitrile[a]	123–135	67.0–67.8		85.2	7.2	85.2	7.3		
p-(1-Cyclohexenyl)benzamide		228–229		77.6	7.5	77.5	7.3		
p-(1-Cyclohexenyl)benzoic acid		203–207 dec		77.2	7.0	77.5	6.6	202	202
p-Cyclohexylbenzoic acid		196.5–198.5[h]		76.4	7.9	76.1	7.7	204	205
m-Bromocyclohexylbenzene	124–126.5[i]		1.5591[e]						
1-(*m*-Bromophenyl)cyclohexanol	120–130	51.5–52.0		56.5	5.9	56.4	6.1		
1-(*m*-Chlorophenyl)cyclohexanol	130–136		1.5578[b]	68.4	7.2	68.7	7.3		
1-(*m*-Bromophenyl)cyclohexene	102		1.5994[b]	60.8	5.5	61.0	5.5		
1-(*m*-Chlorophenyl)cyclohexene	97		1.5789[b,j]	74.8	6.8	74.6	6.8		
m-(1-Cyclohexenyl)benzonitrile[a]	106		1.5798[e]						
m-(1-Cyclohexenyl)benzoic acid		135.5–136.5[f]		77.2	7.0	77.2	6.9	202	202
m-Cyclohexylbenzoic acid		122.4–123.6[k]		76.4	7.9	76.3	8.0	204	205
p-Cyclopentylphenyldimethylcarbinol	110–114	53.5–54.5		82.3	9.9	81.9	9.4		
m-Cyclopentylphenyldimethylcarbinol	100.5–101.5		1.5324[e]	82.3	9.9	81.6	9.7		
p-Cyclohexylphenyldimethylcarbinol	130–138	72.5–73.5		82.5	10.2	82.4	9.7		
m-Cyclohexylphenyldimethylcarbinol	119–121	34.5–35.5		82.5	10.2	82.2	9.4		

[a] Slightly contaminated with the parent bromide; not analyzed. [b] t = 20°. [c] Turned yellow at *ca.* 225°, evolved carbon dioxide at *ca.* 250°. [d] *Anal.* Calcd for Br: 28.3. Found: 27.4. [e] t = 25°. [f] Sealed capillary under nitrogen. [g] *Anal.* Calcd for N: 7.6. Found: 7.5. [h] Lit. mp 197°: D. Bodroux and R. Thomassin, *Bull. Soc. Chim. France*, [5] **6**, 1411 (1939). [i] 4–5 mm. [j] Lit. bp 78–89° (0.1 mm), n^{24}D 1.5782: M. T. Davies, D. F. Dobson, D. F. Hayman, G. B. Jackman, M. G. Lester, V. Petrow, O. Stephenson, and A. A. Webb, *Tetrahedron*, **18**, 751 (1962); bp, 104–107° (1.2 mm), n^{20}D 1.5783: E. W. Garbisch, Jr., *J. Org. Chem.*, **26**, 4165 (1961). [k] Lit. mp 123–124°: J. W. Lynn and L. W. Newton, *Chem. Ind.* (London), 159 (1958).

and 4-bromo-2-cyclobutylacetanilide as colorless, cotton-like crystals in two crops: (1) 10.46 g, 71%, mp 110–180°, and (2) 0.39 g, mp 110–125°. Further recrystallizations did not completely separate the isomers.

m*-Bromocyclobutylbenzene (14*m*).** The mixture of 2(4)-bromo-4(2)-cyclobutylacetanilides (8.76 g, 0.0327 mol) was refluxed 10 hr with 95% ethanol (75 ml) and concentrated sulfuric acid (6 ml). Solid sodium nitrite (6.0 g, 0.087 mol) and then water (5 ml, after 0.5 hr) were added at 25–30°. On addition of copper powder (2.5 g, 0.039 mol) in small portions at 35°, gases (acetaldehyde, but no nitrogen dioxide) were vigorously evolved. After the mixture had been refluxed for 15 min, bromide **14*m (4.33 g, 63%) was isolated, bp 67–87° (1–2 mm), as described for the homologous **10*m***. Treatment with 2% aqueous potassium permanganate and redistillation afforded colorless **14*m***, bp 68° (1–2 mm), n^{20}D 1.5665, d^{25}_4 1.3426, infrared bands at 10.9 μ (cyclobutane) and 12.8 μ (strong, broad; *meta* substitution), none at 12.2 μ (*para* substitution).

Anal. Calcd for $C_{10}H_{11}Br$: C, 56.80; H, 5.25; Br, 37.86. Found: C, 56.92; H, 5.27; Br, 37.73.

m*-Cyclobutylbenzoic Acid (2*m*).** Acid **2*m was prepared from **14*m*** in 63% over-all yield as depicted in Chart II by the procedures described for the conversion of bromide **10*m*** to acid **1*m***. Products and properties are given in Table III.

1-(*p*-Bromophenyl)cyclopentene. Cyclopentanone (84 g, 10 mol) in ether (100 ml) was added to a stirred equivalent of *p*-bromophenylmagnesium bromide (prepared under nitrogen at −15 to −10° from magnesium, *p*-dibromobenzene, and 40:60 ether–benzene)[47] at 0°. The viscous addition complex on warming to 25–30° was hydrolyzed with ice and dilute hydrochloric acid. The ether layer and ether extracts of the aqueous layer were combined, extracted with water and with saturated aqueous sodium chloride, filtered through sodium sulfate, and concentrated. The residue was diluted with benzene (200 ml), iodine (0.5 g) was added, and 200 ml of distillate was collected. This process was repeated, replacing benzene with toluene (200 ml); a total of 7 ml (50% of theory) of water was azeotroped. Distillation of the residue (bp 120–125°, 2 mm) and crystallization of the solid distillate from ethanol gave the olefin as near-colorless plates (110 g, 50%).

An attempt to isolate 1-(*p*-bromophenyl)cyclopentanol (**18*p***) by the subsequent procedure for **18*m*** gave a mixture containing principally 1-(*p*-bromophenyl)cyclopentene.

1-(*m*-Bromophenyl)cyclopentene. *m*-Dibromobenzene (59 g, 0.25 mol) in ether (50 ml) was added dropwise to a stirred suspension of magnesium (6.1 g, 0.25 mol) in ether (100 ml) under nitrogen at 0°. (Reaction was initiated at 25–30°.) Cyclopentanone (21 g, 0.25 mol) was added dropwise to the stirred dark brown solution of *m*-bromophenylmagnesium bromide at 0°. After the mixture had been hydrolyzed with aqueous ammonium chloride, the ether decantate and the ether washings of the solid residue were filtered through sodium sulfate and distilled to yield crude light yellow 1-(*m*-bromophenyl)cyclopentanol (**18*m***) (35.5 g, 59%), bp 110–120° (2–3 mm). Subsequent redistillations of successive middle fractions gave a final middle fraction (analyzed), bp 117° (2–3 mm), n^{20}D 1.5834, d^{25}_4 1.3922, whose infrared spectrum contained a strong hydroxyl band.

Anal. Calcd for $C_{11}H_{13}OBr$: C, 54.89; H, 5.43. Found: C, 55.78; H, 6.14.

Weak absorption bands at 5.9 and 6.1 μ and analytical data suggested that the product contained small amounts of 2-cyclopentylidenecyclopentanone (from base-catalyzed condensation of cyclopentanone) and 1-(*m*-bromophenyl)cyclopentene. It was of advantage to dehydrate the slightly impure product. The method described for dehydration of alcohol **18*p*** was applied to yield an initial product (18.5 g, 84%), bp 80–100° (1–2 mm). Three redistillations of middle fractions gave colorless 1-(*m*-bromophenyl)-

(47) This preparation of *p*-bromophenylmagnesium bromide is a modification of the method of H. S. Pink, *J. Chem. Soc.*, **123**, 3418 (1923).

cyclopentene which had infrared absorption at 6.1 μ (C=C), none for hydroxyl. Physical constants are given in Table III.

1-(*p*-Bromophenyl)cyclohexene and 1-(*m*-Bromophenyl)cyclohexene. Reaction of cyclohexanone and *p*-bromophenylmagnesium bromide as described for preparation of alcohol **18***p* (Chart III) gave 1-(*p*-bromophenyl)cyclohexanol (**19***p*) in 49% yield. Dehydration of **19***p* as described for the cyclopentanol analog yielded 1-(*p*-bromophenyl)cyclohexene (97%). In like manner, 1-(*m*-bromophenyl)cyclohexene was obtained in 55% over-all yield from reaction of cyclohexanone with *m*-bromophenylmagnesium bromide and subsequent dehydration. Physical constants of the products are given in Table III.

p*-(1-Cyclopentenyl)benzoic Acid (20*p*); *m*-(1-Cyclopentenyl)-benzoic Acid (20*m*); *p*-(1-Cyclohexenyl)benzoic Acid (21*p*); *m*-(1-Cyclohexenyl)benzoic Acid (21*m*).** Acids **20p*, **20***m*, **21***p*, **and 21***m* were prepared from the corresponding 1-(bromophenyl)cycloalkenes as indicated in Chart III, by the processes used to convert bromide **10***m* to acid **1***m* (Chart I). Over-all yields ranged from 46% (**19***p* to **21***p*) to 72% (**18***m* to **20***m*); physical constants and analyses of isolated intermediates are summarized in Table I. Acid **21***p* was also synthesized by carbonation of *p*-(1-cyclohexenyl)-phenylmagnesium bromide. Attempted synthesis of acid **21***m via* reaction of *m*-chlorophenylmagnesium bromide with cyclohexanone and subsequent transformations as in Chart III gave 1-(*m*-chlorophenyl)cyclohexanol (78%) and 1-(*m*-chlorophenyl)cyclohexene (85%) (Table III), but the latter was converted to the nitrile only in poor yield.

p*- and *m*-Cyclopentylbenzoic Acids (3*p*, 3*m*). *p*- and *m*-Cyclohexylbenzoic Acids (4*p*, 4*m*).** In a typical procedure, *p*-(1-cyclopentenyl)benzoic acid (2.3 g, 0.012 mol) in dimethylformamide (5.5 ml) was hydrogenated at *ca.* 40 psi over 10% palladium on charcoal (*ca.* 5 g). The mixture absorbed only 1 equiv of hydrogen. After the mixture had been filtered and the catalyst washed, the filtrate was poured into water. Acid **3p* separated as a near-colorless amorphous solid (2.3 g, ≈100%), mp 191–195°. Crystallization from ethanol–water, treatment with charcoal, and recrystallization gave colorless needles, mp 196.5–198.5°. Similarly, acids **20***m*, **21***p*, and **21***m* were hydrogenated to give acids **3***m*, **4***p*, and **4***m* in yields of 90, 84, and 90%, respectively. Physical constants of the products are given in Table III.

Cyclopentylbenzene (22). Reaction of bromocyclopentane (151 g, 1.01 mol) and benzene (360 ml, *ca.* 4.5 mol) in the presence of anhydrous aluminum chloride (1 g) at 25° and subsequent work-up yielded **22** (115 g, 77%), bp 217–218.5° (lit. 213–215°,[48] 215–217°[49]).

The high-boiling residues (307 g, 1.43 mol based on dicyclopentylbenzene[49,50]) from several alkylations were combined and refluxed 1 hr with benzene (*ca.* 6 mol) and anhydrous aluminum chloride (5 g) to give 308 g (73.5%) of **22**, identical with material obtained by the previously described method.

***p*-Cyclopentylacetophenone (24).** Ketone **24** was prepared from acetyl chloride (173 g, 2.2 mol) and **22** (292 g, 2.0 mol) in ethylene dichloride (1 l.) in the presence of aluminum chloride (280 g, 2.1 mol) at 3–4°. The purified product had bp 130–141° (3–4 mm) [lit.[51] bp 131–135° (6 mm)]. Vpc analysis (5-ft silicone column, 219°) indicated a purity of *ca.* 99%.

p*-Cyclopentylphenyldimethylcarbinol (32*p*).** To a stirred solution of ketone **24** (53 g, 0.28 mol) in dry ether (200 ml) was added 3 *M* methylmagnesium bromide (*ca.* 100 ml, 0.3 mol) in ether. The mixture was stirred 1 hr and slowly poured into concentrated aqueous ammonium chloride. The organic layer was washed with aqueous ammonium chloride, then with water, dried over anhydrous potassium carbonate, filtered, and concentrated. The residue was distilled at 1–2 mm to give **32p* as a pale yellow solid (36 g, 62.6%), bp 110–114°, mp 46–49°. Recrystallization from petroleum ether (30–60°) afforded colorless needles, mp 53.5–54.5°.

Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 81.90; H, 9.42.

***p*-Cyclohexylphenyldimethylcarbinol (33*p*).** Reaction of ketone **25**[52,53] and methylmagnesium bromide as described for the cyclopentyl analog **24** afforded *p*-cyclohexylphenyldimethylcarbinol in 82% yield. Physical constants are given in Table III.

m*-Cyclopentyl- and *m*-Cyclohexylphenyldimethylcarbinols (32*m* and 33*m*).** Carbinols **32m* and **33***m* were prepared in 18 and 20% over-all yields, respectively, from ketones **24** and **25** as depicted in Chart III; experimental procedures were those used in the analogous cyclopropyl series. Properties of isolated intermediates are summarized in Table III.

Nitration of Cyclopentylbenzene and Cyclohexylbenzene. These nitrations were conducted as described for cyclopropylbenzene (method 2). For cyclopentylbenzene, four runs averaged 30 ± 3% *ortho*, 3.0 ± 0.5% *meta*, and 67 ± 3% *para;* for cyclohexylbenzene, three runs averaged 22 ± 1% *ortho*, 2.3 ± 0.8% *meta*, and 75.7 ± 0.3% *para* isomers.

Ionization Constants. Benzoic acid (ACS Reagent Grade) and *p*-isopropylbenzoic acid were recrystallized from ethanol–water; analytical samples of the cycloalkyl- and cycloalkenylbenzoic acids were used.

The titration cell was a tall 300-ml beaker covered with a polyethylene sheet through which protruded two electrodes, the tips of three burets, and a gas inlet tube which led through two gas washing bottles containing 50% ethanol–water to a tank of nitrogen. Two of the burets (50 ml) had Teflon valves and were used for triple distilled water and absolute ethanol; the third buret (10 ml) was used for aqueous sodium hydroxide (carbonate free, 0.02 *N*). The burets were protected by Ascarite and were filled from the bottom through a side arm of polyethylene and glass tubing using dry nitrogen-pressure techniques. The titration cell was immersed in a water bath mounted over a magnetic stirrer and maintained at 25 ± 0.15°. A Model G Beckman pH meter with glass and reference calomel electrodes (Beckman No. 1190–80 and 1170, respectively) was used for the titrations.

A sample (30–45 mg) of the acid was put into the titration cell; the weighing bottle was rinsed with ethanol. The remainder of a given amount (usually 25 ml) of ethanol was delivered to the mounted cell from the buret, an equal volume of water was added, and the cell was flushed with solvent-saturated nitrogen. After the cell had been equilibrated thermally (10–15 min), the initial pH was determined. A small amount of base was then added, followed by an equal volume of ethanol so that the initial solvent composition was maintained; the solution was stirred for 30 sec and allowed to sit *ca.* 15 sec, and the pH was recorded. In each titration 15 to 25 readings were made up to pH 11.

The pH meter and electrodes were standardized periodically against a pH 7 buffer and checked against a pH 4 buffer (within 0.02 pH unit). Usually adjustment of 0.01–0.02 pH unit was sufficient at the middle and end of each day.

The pH was plotted *vs.* added base, and the pK_a calculated at one-third, one-half, and two-thirds neutralization using eq 5,[54] in

$$pH = pK_a + \log [A^-]/[HA] + \log A^-/HA \quad (5)$$

which $[A^-]$ and [HA] are the concentrations of the anion and undissociated acid, respectively, and A^- and HA are the activity coefficients of these species. The activity coefficients were assumed to be nearly unity in the dilute solutions used, so that

$$pH = pK_a + \log [A^-]/[HA] \quad (6)$$

The constant pK_a values obtained indicate the validity of this assumption. It was assumed also that the pH reading is equal to the logarithm of the reciprocal of the hydrogen ion concentration; no correction was made for liquid-junction potential. Results are summarized in Table I.

Kinetic Measurements. The solvent was acetone–water (90:10 by volume); temperatures were controlled to ±0.05° or better. Solvent from the stock solution was brought to reaction temperature (2–3 hr). Approximately 1 ml of the tertiary chloride (2 ml in some experiments) was added, the solution was mixed thoroughly, and 5-ml aliquots were removed at appropriate intervals. The aliquots were run into 100 ml of cold (*ca.* 5°), dry acetone to stop the reaction, and the liberated hydrogen chloride was titrated with 0.03 *N* sodium hydroxide, using as indicator a solution of three parts of brom cresol green and two parts of methyl red in ethanol. The reaction solution was allowed to stand at least ten times the calculated half-life to obtain aliquots for the "infinity" titer. Rate constants were calculated by the usual first-order expression, k_1 =

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$(2.303/t) \log (a - x_0)/(a - x)$, and were generally reproducible to $\pm 2\%$.

Enthalpies and entropies of activation were calculated from the expression,[55] $k_1 = kT/h(e^{-\Delta H^{\pm}/RT})(e^{\Delta S^{\pm}/R})$. A plot of $\log k_1/T$ *vs.* $1/T$ was made, and the slope of the best visual straight line (three points) were used to calculate $\Delta H^{\pm}$. Entropies of activation were calculated at all three temperatures and the values averaged; variations between extremes did not exceed 0.1 eu. Relative free energies of activation at 298.16°K were calculated from the relationship, $\Delta F^{\pm} - \Delta F^{\pm}_{H} = RT \ln (k_1/k_{1_H})$.

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Proton Transfers in Dipolar Aprotic Solvents. IV. Solvent Effects on the Rates of Proton Transfers Involving Hydrocarbons

Calvin D. Ritchie and R. E. Uschold

Contribution from the Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214. *Received December 13, 1967*

Abstract: The rates and equilibria of several acid–base reactions involving hydrocarbons have been measured in DMSO solution. The rates of the reactions and Brønsted correlations of the data are compared with similar data for methanol solution reactions. It is concluded that the rates of proton transfer reactions in DMSO solution are greater than those for reactions with the same equilibrium constant in methanol solution. The faster rates are attributed to two factors. (1) In methanol solution, oxygen bases, such as methoxide ion, must be partially desolvated before they can accept a proton from a hydrocarbon acid. (2) The slopes of the Brønsted relationships for reactions in DMSO undergo change from zero to unity in a narrower range of strength of the donor to acceptor than they do in methanol. This indicates that the actual proton transfer step can take place faster in DMSO than in methanol, and the behavior is attributed to solvent reorganization contributions to the free energy of activation.

Although it has generally been found that the proton transfers between oxygen or nitrogen acids and bases take place at diffusion-controlled rates,[1,2] the situation is often entirely different for carbon acids or bases. For example, the carbon protonation of trifluoroacetylacetonate by hydronium ion occurs with a rate constant of $7.5 \times 10^2\ M^{-1}\ \text{sec}^{-1}$, and the analogous protonation of nitromethyl anion has a rate constant of $6.8 \times 10^2\ M^{-1}\ \text{sec}^{-1}$ in aqueous solutions.[1] For some proton transfers to strongly basic carbanions from alcohols in DMSO solution, however, a variety of studies[3-5] indicate diffusion-controlled rates.

In order to provide data concerning the sources of the slow rates of reactions of carbon acids in hydroxylic solvents and to investigate the relationship between changes in rates and equilibria resulting from changes in solvent, we have initiated several studies of the reactions of carbon acids in DMSO solution. In a separate series of papers[6] we have reported the measurements of equilibrium constants, and in the present series of papers[7] we have already reported the rates of reactions of triphenylmethane with alkoxides and dimsyl ion and some preliminary results of a study of the proton transfer from 9-methylfluorene to 4,5-methylenephenanthryl anion.

In the present paper we report the results of studies of the rates of reactions of a series of benzoate ions with fluoradene and 9-carbomethoxyfluorene and of several fluorenyl-type anions with 9-methylfluorene.

Results

All of the reactions reported here have been studied by the stop-flow technique using spectrophotometric detection.[8] The general techniques have been detailed previously,[7,8] and are summarized in the Experimental Section.

Rate constants for the hydrocarbon acid–hydrocarbon base reactions are reported in Table I, and those for other types of acids and bases are in Table II. Some isotope effects which have been measured are included in the tables.

The rates of the reactions were measured in only one direction, and the rate constants for the reverse direction were calculated from the known equilibrium constants for the reactions.[6]

The rate constants obtained in this study are not of high precision because of the sensitivity of reactants or products to various impurities, primarily oxygen, and because of the rapidity of the reactions. We estimate a precision and accuracy of *ca.* $\pm 20\%$ for the rate constants and of $\pm 50\%$ for the isotope ratios, k_H/k_D.

In addition to the reactions reported in Tables I and II, investigations of the systems shown in Table III have revealed that these reactions occur at rates too great to follow on the stop-flow apparatus. From a conservative estimate of *ca.* 5 msec for mixing time[8] and observations on dilute solutions, we can confidently

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