(13,000), and 312 (16,000)]; nmr ($CDCl_3$), δ 7.0–7.8 (6 H multiplet, aryl CH), 6.78 (1 H doublet of doublets, J = 2.5 and 8.5 cps, C-2 aryl CH), 3.77 (3 H singlet, OCH_3), and 3.69 (2 H singlet, benzylic CH_2); mass spectrum, molecular ion at m/e 196, abundant fragment peaks at m/e 181, 165, 153, and 152. The sample was identified with an authentic sample,[18] mp 76–78°,[19] by a mixture melting point determination and comparison of infrared spectra.

For comparison, a sample of 2-methoxyfluorene (**32**) was synthesized from the known[20] methoxyhexahydrofluorenone **31**. Wolff–Kisner reduction of 0.27 g of this ketone **31** with 0.6 g of KOH, 1.0 ml of aqueous 85% hydrazine, and 24 ml of diethylene glycol at 175–220° yielded 0.20 g of the crude hexahydrofluorene derivative which was mixed with 0.10 g of a 30% palladium-on-carbon catalyst and heated to 235° under a stream of nitrogen for 2.5 hr. The resulting mixture was extracted with chloroform and the resulting extract was filtered through Celite and concentrated under reduced pressure. The residual four-component mixture[21] (0.20 g, mp 95–99°) was chromatographed on silicic acid. The fractions (0.11 g, mp 97–101°, two components[21]) eluted with an ether–hexane (1:50 v/v) mixture were recrystallized from methanol to separate 30 mg of the pure 2-methoxyfluorene (**32**) as white needles: mp 107–108° (lit. mp 110–111°,[22a] 109°[22b,c]); uv maxima, 207 mμ (ε 35,500), 272 (22,100), 303 (6750), and 314 (6580); uv maxima ($CHCl_3$), 276 mμ (ε 19,400), 304 (7070), and 315 (6950) [lit.[23] uv maxima, 271 mμ (ε 22,000), 303 (6500), and 314 (6200); lit.[17] uv maxima ($CHCl_3$), 272 mμ (ε 20,000), 306 (6300), and 314 (6300)]; nmr ($CDCl_3$), δ 6.7–7.7 (7 H multiplet, aryl CH) and 3.74 (5 H singlet, OCH_3 and benzylic CH_2); mass spectrum, molecular ion at m/e 196, abundant fragment peaks at m/e 181, 153, and 152. The material was identified with a commercial sample[24] of the 2-methoxy isomer **32** by a mixture melting determination and comparison of infrared spectra. The spectra of the isomeric methoxyfluorenes **30** and **32** are distinctly different.

Registry No.—**4,** 15378-00-4; **6,** 6771-54-6; **7a,** 15378-01-5; **8,** 15378-02-6; **9,** 15378-03-7; **10a,** 15378-04-8; **10b,** 15378-05-9; **11,** 15378-06-0; **13,** 15378-07-1; **14,** 15378-08-2; **16,** 15378-09-3; **17,** 15378-10-6; **19b,** 15378-11-7; **20,** 15378-12-8; **21** (less highly substituted), 15378-13-9; **21** (more highly substituted), 15378-14-0; **22** (less highly substituted), 15378-15-1; **22** (more highly substituted), 5796-60-1; **28a,** 15412-43-8; **28b,** 15378-17-3; **29,** 15378-18-4; **33a,** 15378-19-5; **33b,** 15378-20-8; **34,** 15378-21-9.

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[18] This sample was purchased from K & K Laboratories, Inc., Plainview, N. Y.

[19] The compound has been reported to melt at (a) 84–85° [N. Ishikawa and M. Okuzaki, *Yuki Gosei Kagaku Kyokai Shi*, **16**, 610 (1958); *Chem. Abstr.*, **53**, 3168 (1959)]; (b) 82–83° [W. S. P. Neish, *Rec. Trav. Chem.*, **69**, 207 (1950)]; and (c) 81–82° [W. D. Zahler and R. Huisgen, *Chem. Ber.*, **96**, 765 (1963)]. C. J. Collins and B. M. Benjamin [*J. Amer. Chem. Soc.*, **75**, 1644 (1953)] have reported the same compound to melt at 101–101.5°. This discrepancy may be attributable to the isolation of a second crystalline form of the 3-methoxyfluorene.

[20] W. G. Dauben and J. W. Collette [*ibid.*, **81**, 967 (1959)] report mp 99–100°. A sample, mp 98–99°, was prepared by Mr. T. M. Bare in our laboratories.

[21] A thin layer chromatography plate coated with silicic acid and eluted with a benzene–petroleum ether (bp 30–60°) mixture was employed for this analysis.

[22] (a) N. Ishikawa and M. Okazaki, *Yuki Gosei Kagaku Kyokai Shi*, **16**, 467 (1958); *Chem. Abstr.*, **52**, 18340 (1958). (b) G. W. Gray, J. B. Hartley, and A. Ibbutson, *J. Chem. Soc.*, 2686 (1955). (c) J. D. Dickinson and C. Eaborn, *ibid.*, 2337 (1959).

[23] E. Sawicki, *J. Org. Chem.*, **21**, 271 (1956).

[24] Purchased from the Aldrich Chemical Co., Inc., Milwaukee, Wis.

Solvents of Low Nucleophilicity. X. Inductive and Participation Effects in the Addition of Trifluoroacetic Acid to Cyclopropanes[1]

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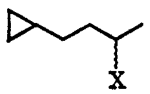
We have studied the carbonium ion formation which, formally, occurs in the ring-opening reactions of butylcyclopropane, 4-cyclopropyl-2-chlorobutane, and 4-cyclopropyl-2-butyl trifluoroacetate with trifluoroacetic acid. Cyclopropanes reacted approximately 300 times faster than comparable alkenes. Cyclopropane openings showed similar inductive effects but smaller effects of chlorine participation and (probably) hydrogen participation, compared with additions to unbranched alkenes and solvolyses of secondary tosylates.

Since quantitative information concerning the rates and products of electrophilic reactions of simple, substituted cyclopropanes is lacking, we have studied the reaction of trifluoroacetic acid with three substituted cyclopropanes carefully chosen to elucidate the role of hydrogen shifts and of inductive and participation effects in such reactions. The significance of the present study is that, by comparison with our previous studies, it provides the first comparison of carbonium ion formation *via* the following three different pathways: (1) cyclopropane opening, (2) additions to alkenes, and (3) tosylate solvolyses.

Increased interest in electrophilic ring-opening reactions of cyclopropanes has resulted from studies indicating the intermediacy of equilibrating edge- and/or end-protonated cyclopropane intermediates[2] and of the corresponding species derived from electrophilic attack of bromine[3] or acyl cations.[4] Although it is not yet known whether indications of unusual mechanisms will be confined to reactions of cyclopropane itself, the ring-opening reactions of substituted cyclopropanes take on new interest for comparison purposes. The presently reported study, however, has no direct connection with the question of unusual intermediates in reactions of cyclopropanes.

Description and Results

The compounds chosen for study were butylcyclopropane (**1a**), 4-cyclopropyl-2-chlorobutane (**1b**), and



1a, X = H
b, X = Cl
c, X = $OCOCF_3$
d, X = OH

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[1] Supported in part by St. Louis University. Use of equipment furnished *via* National Science Foundation Grants GP2917 and GP20904 is gratefully acknowledged.

[2] R. L. Baird and A. A. Aboderin, *J. Amer. Chem. Soc.*, **86**, 252 (1964).

[3] N. C. Deno and D. N. Lincoln, *ibid.*, **86**, 252 (1964); **89**, 5357 (1966).

[4] H. Hart and R. L. Schlosberg, *ibid.*, **88**, 3347 (1966).

4-cyclopropyl-2-butyl trifluoroacetate (**1c**). Preparation of **1a** from hexene by the Simmons-Smith reaction posed no difficulty, but the comparable reaction with 5-chloro-1-hexene and 5-hexen-2-ol failed. Fortunately the modified procedure of Ginsig and Cross[5] gave excellent conversion of 5-hexen-2-ol into **1d**, from which **1b** and **1c** were prepared.

Butyl cyclopropane was found to react rapidly with trifluoroacetic acid, but fortunately at a rate ($t_{1/2}$ = 191 sec) just within the range measurable by conventional methods at 0°. By another fortunate circumstance the rates of cyclopropane ring openings were just sufficiently fast that the reactions could be followed by titration of the alkenes formed in the reactions, without interference due to addition of trifluoroacetic acid to the alkenes. As a third fortuitous circumstance, the cyclopropanes were *unreactive* toward the iodine monobromide reagent which quantitatively reacts with alkenes in the titrimetric analysis! Rates and percents of elimination, determined in the same experiment, are given in Table I.

TABLE I

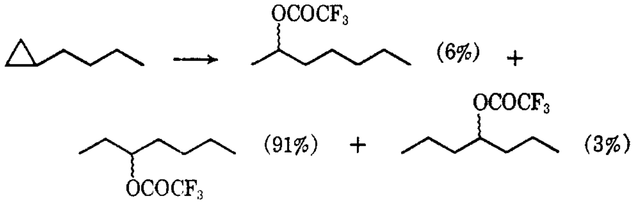
RATES OF REACTION OF TRIFLUOROACETIC ACID WITH SUBSTITUTED CYCLOPROPANES AT 0° AND PERCENTAGES OF ELIMINATION

Compd	X	$k \times 10^6$, sec^{-1}	Elimination, %
1a	H	3260	39.2
1b	Cl	98.1	32.2
1c	$OCOCF_3$	10.2	27.7

The substitution products obtained by reaction of butylcyclopropane consisted of 3-heptyl trifluoroacetate, the expected product of Markovnikov ring opening, along with smaller amounts of products arising from hydride shift as given in Scheme I. 4-Cyclopropyl-2-chlorobutane was expected possibly to react in part *via* a path involving a 1,4-chlorine shift. Analogous chlorine shifts and/or other indications of chlorine participation have now been observed in the addition of trifluoroacetic acid to alkenes[6a] and alkynes[6b] and in the trifluoroacetolysis, formolysis, and acetolysis of secondary tosylates.[6c] The products which might be formed from 4-cyclopropyl-2-chlorobutane (**1b**) by "normal," "H shift," and "chloronium ion" paths are shown in Scheme II. The nmr spectrum of the isolated chloroheptyl trifluoroacetates obtained from **1b** showed a doublet at δ 1.51 (CH_3CHCl–) and a partially obscured doublet at 1.34 ($CH_3CHOCOCF_3$–) whose areas were indicative of the percentage ratio 84:14. The latter doublet could arise from **4**, the product of chlorine shift, or **3a**, the product of hydrogen shift. Since only 6% out of the 14% would be expected to arise from hydrogen shift, based on the result found for the reaction of butylcyclopropane, the nmr analysis was indicative of 8% 1,4-chlorine shift (16% chloronium ion formation, assuming equally probable formation of **4** and **2** from the chloronium ion). The assumption that the presence of chlorine does not affect the per cent of hydrogen shift is of course open to question. However, confirmation of the per cent of 1,4-chlorine shift was obtained by pyrolysis of the chlorotrifluoroacetates, followed by hydrogenation of the resulting unsaturated chlorides, to give 2-chloroheptane (from **2**, **3a**, and **3b**) and 3-chloroheptane (from **4**). Comparison of the nmr spectrum of the chloroheptane mixture with spectra of authentic mixtures indicated the presence of 11% 3-chloroheptane, in reasonable agreement with the earlier estimate.

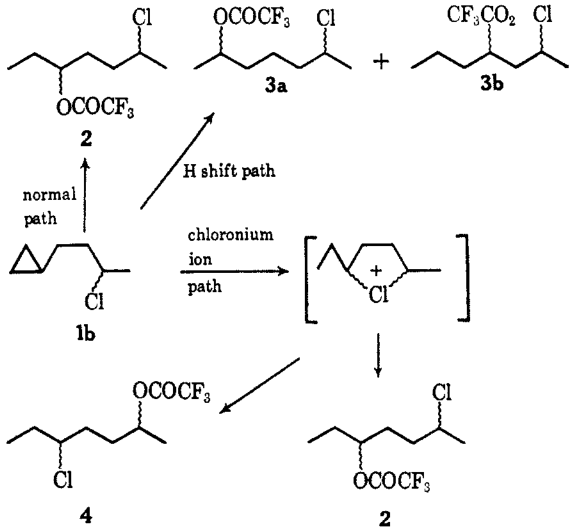
SCHEME I

ESTERS FORMED FROM BUTYLCYCLOPROPANE



SCHEME II

REACTION PATHS OF 4-CYCLOPROPYL-2-CHLOROBUTANE

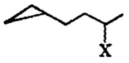
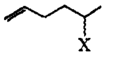
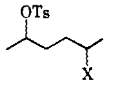


Discussion

In Table II the cyclopropane ring-opening reactions which we studied are compared with other carbonium ion-forming reactions in the same solvent (trifluoroacetic acid). Formally, the tosylate and alkene reactants compared in Table II may yield the same carbonium ion, whereas the cyclopropanes give closely

TABLE II

COMPARISON OF TRIFLUOROACETOLYSIS OF CYCLOPROPANES, ALKENES, AND TOSYLATES

	H shift, %, X = H	Elimination, %, X = H	k_Δ/k_s, (Cl shift)	ρ_I
	6, 3	19.5, 19.5?	0.25	−3.50
	10[a]	24[a]	11[b]	−3.43
	22[c]	86[c]	65, 99[b]	−3.30[b]

[a] See ref 13. [b] See ref 6c. [c] See P. E. Peterson, *J. Amer. Chem. Soc.*, **82**, 5834 (1960).

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(5) R. Ginsig and A. D. Cross, *J. Am. Chem. Soc.*, **87**, 4629 (1965).

(6) (a) P. E. Peterson, C. Casey, E. V. P. Tao, A. Agtarap, and G. Thompson, *ibid.*, **87**, 5163 (1965). (b) P. E. Peterson and J. E. Duddey, *ibid.*, **88**, 4990 (1966). (c) P. E. Peterson, R. J. Bopp, D. M. Chevli, E. L. Curran, D. E. Dillard, and R. J. Kamat, *ibid.*, **89**, 5902 (1967).

comparable secondary ions which, however, differ in that an ethyl substituent is present in place of methyl. We assume that this structural difference is not the major factor which leads to the marked reaction trends to be discussed below. Subject to some additional ambiguities of interpretation (to be discussed) the first three reaction characteristics—per cent hydrogen shift, per cent elimination, and tendency for 1,4-chlorine participation—exhibit somewhat similar trends as the substrate varies in this sequence: cyclopropane, alkene, tosylate. All of the reactions exhibit similar and notably large inductive rate retardations of electron-attracting substituents as reflected in the Taft–Hammett ρ_I values.

The trends shown in Table II fit very well into a concept introduced in a recent paper from our laboratories concerning the nature of inductive and participation effects.[6c] Specifically a reaction type (*e.g.*, cyclopropane ring opening, as reported here) is postulated to exhibit a *characteristic participation tendency* which is reflected not only in the tendency for halogen participation (column 3, Table II) but also in the tendency for hyperconjugation of carbon and/or hydrogen in the carbonium ion transition state. According to our concept[6a] the increasing percentages of hydrogen shift shown in the first column of Table II reflect an increasing tendency for hydrogen hyperconjugation as secondary carbonium ions are formed from cyclopropanes, alkenes, and tosylates, respectively. The carbonium ion formed from butylcyclopropane can, of course, undergo a hydrogen shift in two directions (*cf.* Scheme I), and our discussion is based on the reasonable hypothesis that the two processes should be considered separately. Also it may be noted that the percentages of hydrogen shift have been determined only in the substitution product in each case.

The increasing percentages of elimination shown in the second column of data in Table II are likewise conveniently ascribed to increasing hydrogen hyperconjugation in the order shown. Again there is some question concerning the treatment of the cyclopropane data, since the intermediate cation may eliminate in two directions to give *cis*- or *trans*-2-heptene and *cis*- or *trans*-3-heptene. In the absence of an analysis for the four elimination products it seems most appropriate to assume that the observed 39% of elimination products is divided equally in the two directions. Direct comparison is then appropriate with the data for 1-hexene, which represents elimination in one direction (isomerization) in competition with substitution at the cationic carbon. The 86% elimination for 2-heptyl tosylate may be presumed to represent predominant elimination in one direction (to give *cis*- and *trans*-2-hexene) although the per cent elimination is so large as to make the direction a less important consideration.

Finally there is some question as to whether the ratio of rate constants for the reactions proceeding with 1,4-chlorine participation to those for normal solvolysis (k_Δ/k_s) should be judged from reaction rates, from the per cent halogen shift, or from the per cent of solvolysis with net retention of configuration (for tosylates). Regardless of the choice, however, the trend is that shown in Table II.

If increasing participation tendency with change of reactant is a reflection of increasing electron deficiency in the transition state, it would appear that an increasing magnitude of the respective ρ_I values would be found, reading down in the last column, Table II. It may be seen that no such trend is observed. In our paper dealing with the origin of inductive and participation effects[6c] we hypothesized that a chloroalkyl tosylate (considered as a typical example) shows substantial ground-state destabilization arising from dipole–dipole repulsion between the substituent and the reaction site. This ground-state interaction would decrease the absolute magnitude of ρ_I, since the latter quantity reflects only the additional interaction between the substituent and the reaction site upon going from the ground state to the transition state. Since alkenes are probably strongly hydrogen bonded in trifluoroacetic acid, leading to a larger than usual σ_I value for the double bond,[7] it is not unreasonable to postulate that moderate ground-state destabilization similarly affects the alkene reactions (Table II). Cyclopropanes would presumably show the least effect. According to this view, then, for the reaction in Table II, increasing positive charge in the transition state is found for reactions of cyclopropanes, alkenes, and tosylates, respectively, leading to increased participation, although concomitantly increasing ground-state destabilization in electronegatively substituted starting materials leads to relatively constant ρ_I values.

The argument outlined need not be regarded as more than a working hypothesis which originally was used to compare reactions of alkenes, alkynes, and tosylates, and which has now been extended to cyclopropane reactions. Some difficulties of this generalized theory of inductive and participation effects are, in fact, evident. Trends are not quantitatively parallel, for example. Furthermore ground-state effects would not appear to differ enough in alkenes and in cyclopropanes to account for the large difference in the chlorine participation tendency for reactions of these compounds. Certainly specific (and presently unpredictable) steric effects may be expected to be present in the reactions occurring by a halogen participation path. Despite these difficulties, the concept of participation tendency as a reaction parameter which may be determined experimentally, and which reaches a minimum in cyclopropane reactions (among those we have compared), provides a useful correlation of our results and a highly suggestive guide to further studies.

It is worth noting that cyclopropane ring openings have proved to be the *most suitable carbonium ion reactions for studies of inductive effects* in aliphatic, and presumably certain other systems, owing to their relative freedom from complications due to participation. Furthermore their relatively fast rates assure freedom from side reactions in many instances, including, as we have mentioned, freedom from interference due to additions to alkenes formed in the ring openings. A comparison of cyclopropane and alkene reactivities is made in Table III. Also listed there are values of k_H/k_X, the ratios of the rate constants for reaction of unsubstituted and substituted cyclopropanes, respectively, and other related quantities. Table III represents the first quantitative comparison of cyclopropane and alkene reactivities. In this con-

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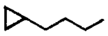
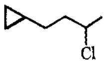
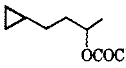
(7) For references to such hydrogen bonding, see R. C. Fahey and D.-J. Lee, *J. Amer. Chem. Soc.*, **80**, 2780 (1967).

TABLE III

REACTIVITY OF CYCLOPROPANES TOWARD TRIFLUOROACETIC ACID. COMPARISON WITH ALKENES. SUBSTITUENT EFFECTS

	$k_{\text{cyclopropane}}{}^a$		Log (k_H/k_X)	
Cyclopropane	k_{alkenes}	k_H/k_X	3.5	σ_I
	332	1.0	0	0
	54	33.3	0.43	0.47[b]
	307	319	0.72	0.72[b]

[a] Calculated using data in ref 13. [b] For values, see ref 10a and b.

nection we note that LaLonde and Tobias have said, "That the acid-promoted addition of acetic acid to olefins is slower than the addition to cyclopropanes has been demonstrated."[8a]

In the present work the cyclopropane ring is seen to be approximately 300-fold more reactive than alkenes toward trifluoroacetic acid, the smaller ratio (54) for the chlorosubstituted compounds being attributable to halogen participation in the alkene reaction. The previously mentioned much greater reactivity of alkenes toward iodine bromide in carbon tetrachloride–acetic acid constitutes a striking reversal of the reactivity toward acids. A possible correlation with hard and soft acid–base behavior[9] is suggested, cyclopropanes representing the harder base which combines preferentially with hard (protonic) acids. Finally, it may be noted from the third and fourth columns in Table III that the three cyclopropane reactivities studied give a satisfactory Hammett–Taft correlation, using σ_I values presumably appropriate to trifluoroacetic acid.[10] The slight deviation from the line exhibited by the chloro substituent is approximately of the magnitude expected, based on the observed percentage of halogen participation (*cf.* Table II).

Experimental Section

Chemicals.—Butylcyclopropane[11] was obtained in 26% yield in our study by the Simmons–Smith reaction[12] of 1-hexene. Trifluoroacetic acid (Allied Chemical) was distilled through a 3-ft, helix-packed column, and the center cut retained.

4-Cyclopropyl-2-butanol.—5-Hexen-2-ol (36.8 g, 0.5 mole, from sodium borohydride reduction of commercial allyl acetone) was added over a period of 30 min to a stirred mixture of 93.6 g of zinc–copper couple, 500 ml of dry ether, 316 g (1.15 mole) of methylene iodide, and several crystals of iodine. As previously recommended,[5] the mixture was distilled to half of the original volume, made up to the original volume with dry ether, and heated at 85–90° for 6–7 hr in a high pressure vessel. The ether layer was decanted, and combined with two 50-ml ether washings of the couple. The ether layer was washed with ten 50-ml portions of saturated sodium bicarbonate (until the water layer did not contain a white precipitate of zinc salts). Washing (saturated sodium chloride), drying (magnesium sulfate), and spinning-band distillation of the ether layer gave 31.2 g (55%) of gas chromatographically pure (6-ft diethylene glycol succinate on firebrick) 4-cyclopropyl-2-butanol: bp 75° (20 mm); nmr multiplets, δ −0.17 to +0.92.

Anal. Calcd for $C_7H_{14}O$: C, 73.63; H, 12.36. Found: C, 73.62; H, 12.25.

4-Cyclopropyl-2-chlorobutane.—4-Cyclopropyl-2-butanol (30.0 g, 0.26 mole) was mixed with 20.8 g (0.26 mole) of dry pyridine, and 31.4 g (0.26 mole) of thionyl chloride was added over a period of 35 min. The mixture was heated to 80–90° for 7 hr. The resulting pyridine hydrochloride was dissolved in a minimum amount of water. Distillation of an ether extract gave 4.4 g (bp 73°, 50 mm) of pure material and other less pure fractions which were preparatively gas chromatographed (8-ft diethylene glycol adipate column) to give a total of 9.1 g (26%) of 4-cyclopropyl-2-chlorobutane with nmr multiplets at δ −0.12 to +0.83.

Anal. Calcd for $C_7H_{13}Cl$: C, 63.39; H, 9.91. Found: C, 63.55; H, 9.88.

4-Cyclopropyl-2-butyl Trifluoroacetate.—An ice-cold mixture of 4-cyclopropyl-2-butanol (9.29 g, 0.081 mole) in 35 ml of ether was added during 15 min to an ice-cold mixture of 25.6 g (0.12 mole) of trifluoroacetic anhydride in 50 ml of ether. After 6 min, isolation by extraction was begun (water, aqueous sodium bicarbonate, aqueous sodium chloride). The ether extract gave 11.4 g (67%) of gas chromatographically pure (6-ft diethylene glycol adipate) 4-cyclopropyl-2-butyl trifluoroacetate: bp 70° (29 mm); nmr multiplet, δ −0.19 to +0.88.

Anal. Calcd for $C_9H_{13}F_3O_2$: C, 51.43; H, 6.23. Found: C, 51.47; H, 6.23.

Kinetic Method.—Sufficient cyclopropane compound to make a 0.1 *M* solution was weighed in a 25-ml volumetric flask, brought to 0.00 ± 0.05°, and diluted to 25 ml with trifluoroacetic acid, 0.125 *M* in sodium trifluoroacetate, also at 0.00°. Aliquots (2 ml) were withdrawn at intervals and analyzed for alkene concentration by the iodine monobromide titrimetric method described previously.[13]

Products of Reaction of Butylcyclopropane with Trifluoroacetic Acid.—Butylcyclopropane (10.0 g) was cooled to 0.0° and diluted to 100 ml with trifluoroacetic acid, 0.125 *M* in sodium trifluoroacetate, also at 0°. After 97 min (86% reaction, measured by titration of an aliquot), the mixture was poured into 200 ml of ice cold water and 100 ml of ether. Extraction and distillation gave 2.37 g of alkene, bp 52–62° (61%, based on 39.2% "elimination," measured in a kinetic run), and 9.31 g (39%, based 60.8% "substitution") of trifluoroacetate esters, bp 72–78.5° (55 mm). The esters were analyzed on a 150-ft capillary Dow-Corning 550 silicone column (*cf.* Scheme I) by comparison with authentic 2-, 3-, and 4-heptyl trifluoroacetates.

Products of Reaction of 4-Cyclopropyl-2-chlorobutane.—The procedure was similar to that used in the reaction of butylcyclopropane except that 7.00 g of 4-cyclopropyl-2-chlorobutane was allowed to react in a volume of 100 ml for 12.3 hr (96.9% reaction, by titration). Distillation gave a chloroheptene fraction of 1.32 g (59% based on 32% elimination: bp 51–60°, (30 mm), nmr multiplet, δ 5.31–5.68) and an ester fraction of 5.72 g (62% based on 68% substitution).

The ester 4.16 g was pyrolyzed in a 20 × 2 cm glass column packed with glass helices. The ester (mixed chloroheptyl trifluoroacetates) was dropped into the tube, which was heated to 410° and through which dry nitrogen was passed, over a period of 5 min. The products were collected in a Dry Ice–acetone cold trap.[14] The product was diluted to twice its original volume

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[8] (a) R. T. LaLonde and M. A. Tobias, [*J. Amer. Chem. Soc.*, **86**, 4068 (1964)] studied the cyclopropane ring opening of *exo*-7-methylbicyclo[4.1.0]heptane and *exo*-6-methylbicyclo[3.1.0]hexane in glacial acetic acid, 0.09 *N* in sulfuric acid, at 47° for 36 and 24 hr, respectively. Their contention that their reaction products did not arise to an appreciable extent from addition of acetic acid to first-formed alkenes on the basis of the "slower addition of acetic acid to olefins" appears to deserve further comment.[8b] (b) P. E. Peterson and E. V. P. Tao, [*J. Org. Chem.*, **29**, 2322 (1967)] have shown that *branched* alkenes reach equilibrium with the corresponding tertiary acetates in 0.0145 *M* toluene-sulfonic acid hydrate in acetic acid at 35° in a few days. It seems certain, therefore, that the 1-ethylcyclohexene (22% of the 53% olefin yield) and 1-methylcycloheptene (13% of 53%) formed from *exo*-7-methylbicyclo[4.1.0]heptane *did react* in the experiment of LaLonde and Tobias, although the equilibrium yield of tertiary acetates may have been small. Although quantitative data are not yet available, it seems likely that branched alkenes will be found to react faster with acids (to give tertiary carbonium ions) than those cyclopropanes which can give only secondary carbonium ions, contrary to the assumptions of LaLonde and Tobias.

[9] R. G. Pearson and J. Songstad, *ibid.*, **89**, 1827 (1967).

[10] (a) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Anderson, and G. T. Davis, *ibid.*, **85**, 709 (1963). (b) P. E. Peterson and G. Allen, *J. Org. Chem.*, **27**, 2290 (1962).

[11] J. T. Grogson, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *ibid.*, **20**, 275 (1955).

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[13] P. E. Peterson and G. Allen, *J. Org. Chem.*, **27**, 1505 (1962).

[14] In a prior control experiment 5-chloro-2-hexyl trifluoroacetate was shown to undergo loss of trifluoroacetic acid without loss of hydrogen chloride under these conditions.

with ether, washed, dried, and hydrogenated over prereduced platinum oxide. Removal of ether (spinning-band column) and preparative gas chromatography (3 ft × 0.25 in., 20% diethylene glycol adipate column) gave 0.43 g of pure material having the retention time of 2- and 3-chloroheptane. Since these chloroheptanes were not separated on four different capillary columns, the mixture from pyrolysis and hydrogenation was analyzed by comparison of the nmr spectrum (neat) with spectra of quantitatively prepared mixtures of 2- and 3-chloroheptane. The spectrum was identical with that of a mixture prepared from 100 μl of 2-chloroheptane and 12 μl of 3-chloroheptane (corresponding to 10.7 mole % 3-chloroheptane). Assuming that our procedure did not result in selective product formation from the original mixture, or in chlorine migration, during pyrolysis (both assumptions seem to be reasonably good) the above-mentioned percentage is a measure of the chlorine shifted products in the cyclopropane ring-opening reaction.

Registry No.—**1a**, 930-57-4; **1b**, 15451-38-4; **1c**, 15451-39-5; **1d**, 15451-40-8; trifluoroacetic acid, 76-05-1.

Solvents of Low Nucleophilicity. XI. Modified Aromatic σ Values in the Addition of Trifluoroacetic Acid to Phenylbutenes[1]

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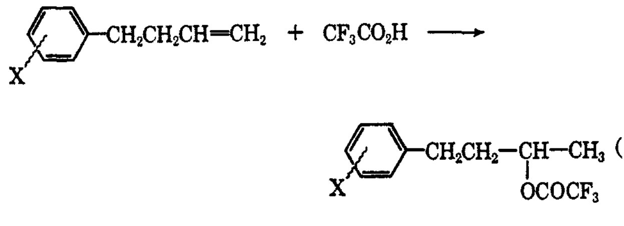
Rates of addition of trifluoroacetic acid to 4-phenyl-1-butenes substituted in the *meta* and *para* positions of the benzene ring were determined. Oxygen- and nitrogen-containing substituents were more electron attracting than expected from the σ^0 values of the substituents, owing to hydrogen bonding of the solvent to the substituents. The solvent modification of aliphatic and aromatic σ values is compared.

In connection with studies of enhanced inductive effects in trifluoroacetic acid attributable to hydrogen bonding between trifluoroacetic acid and oxygen- or nitrogen-containing groups,[2] we were prompted to examine the effect of such hydrogen bonding on aromatic substituent effects.

The reaction of substituted phenylbutenes with trifluoroacetic acid (eq 1) appeared to be ideally suited for such a study. The desirable absence of phenyl participation in this system may be inferred from the studies of Heck and Winstein.[3] Also, the potential cationic carbon in the carbonium ion intermediate which may be envisioned for the reaction of eq 1 is just far enough from the phenyl group to prevent rearrangement to a more stable benzyl cation by hydrogen shift in the rate-determining step.[4] Finally the large effects of distant substituents upon reaction rates for addition of trifluoroacetic acid to alkenes suggests that rate effects should be large compared to experimental errors, despite the relative remoteness of the substituents in the phenylbutenes. Actually there are only a few studies of aromatic substituent effects in cases where there is no possible conjugation between the substituent and the reaction site, and the discovery of additional reactions suitable for such studies is of interest itself.



(1)

Results

The phenylbutenes were obtained as a gift (for a reference, see the Acknowledgment), or synthesized as described in the Experimental Section. The rates of reaction with trifluoroacetic acid, measured at 60.0°, are given in Table I. Also listed are "effective σ_I" values to be discussed later. It is interesting that the rate constants vary over a range of 40-fold (for p-methyl and p-cyano) despite the distance of seven carbons between the substituent and the reaction site (counting the cationic carbon as 1). A Hammett plot of the data, using σ^n values[5] is shown in Figure 1. The correlation line is drawn through the points for nonhydrogen-bonding substituents. The substantially increased electron-attracting effect of oxygen- and nitrogen-containing substituents, ascribable to hydrogen bonding of the solvent to the substituent, is immediately apparent.

TABLE I

RATES OF ADDITION OF TRIFLUOROACETIC ACID TO 4-PHENYL-1-BUTENES AT 60.0°

Substituent	10^6k, sec^{-1}	Effective σ_I[a]
$p\text{-CH}_3$	408	0.063
$m\text{-CH}_3$	353	0.080
H	257	0.1[b]
$p\text{-OCH}_3$	218	0.112
p-Cl	93.5	0.168
$m\text{-OCH}_3$	87.4	0.181
p-Br	84.5	0.176
m-Cl	71.7	0.206
$p\text{-CO}_2\text{CH}_3$	31.2	0.259
$p\text{-COCH}_3$	18.0	0.300
p-CN	10.5	0.341

[a] Values of σ_I for the substituted phenyl groups, calculated according to eq 11 (*cf.* discussion section). [b] From ref 12.

Present Status of Solvent Modified σ Values.—Before proceeding to a closer examination of solvent-

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[2] P. E. Peterson, C. Casey, E. V. P. Tao, A. Agtarap, and G. Thompson, *J. Amer. Chem. Soc.*, **87**, 5163 (1965).

[3] R. Heck and S. Winstein, *ibid.*, **79**, 3105 (1957).

[4] Similar direct formation of a phenylethyl-type bridged cation cannot be ruled out *a priori*.

[5] The origin and applicability of σ^n values, which differ slightly from the Hammett σ values, is reviewed in the next section.