Reaction of Ethyl 3-Chlorodifluoromethyl-4-chloro-4,4-difluorocrotonate (XII) with Diethyl Malonate.—Sodium (1.9 g., 0.08 atom) in 200 ml. of absolute ethanol, 24 g. (0.15 mole) of diethyl malonate and 40 g. (0.15 mole) of XII were allowed to react as described in the previous reaction, with the exception that addition occurred at 0° and that the mixture was then heated at 80–85° for 28 hours. Distillation gave 18.4 g. of a fraction boiling at 155–156° (17 mm.), $n^{20}\text{D}$ 1.4210, and 3.1 g. of a fraction boiling at 191–200° (17 mm.), $n^{20}\text{D}$ 1.4310. Both fractions had nearly identical infrared spectra, with absorptions at 3.35, 5.7, 6.8, 6.9, 9.8, 10.6, 11.7 and 13.45 μ. On repeated distillation of fraction 1 through a spinning band column, evolution of hydrogen chloride gas was observed. The gas chromatogram of the product showed mainly one peak with two small shoulders.

Anal. Calcd. for $C_{14}H_{17}O_6ClF_4$: C, 42.75; H, 4.33; Cl, 9.16; F, 19.34. Found: C, 43.12; H, 4.19; Cl, 5.70; F, 22.29.

The material (10.7 g.) was stirred at 110–120° with 100 ml. of 24% hydrochloric acid until the organic layer disappeared (37 hours). After concentration, extraction with ether, drying, removal of ether and recrystallization from benzene-ether, 3.4 g. of a white solid, m.p. 156–157°, was obtained (reptd.[18] for β-carboxyglutaric acid, m.p. 160°).

Anal. Calcd. for $C_6H_8O_6$: C, 40.91; H, 4.55; neut. equiv., 72. Found: C, 41.41; H, 4.70; neut. equiv., 68.

Ethyl 2,2-Difluoro-3-trifluoromethyl-3-methylglutarate (XVII).—Magnesium turnings (5 g., 0.2 g. atom) were placed in a flask equipped with a stirrer and nitrogen and hydrogen inlets. The system was flamed out under dry nitrogen, cooled, and 300 g. of mercury was added. After passing hydrogen gas for 15 minutes, the amalgam was stirred until the liberation of heat ceased. A solution of 12.4 g. (0.1 mole) of ethyl difluoroacetate and 18.2 g. (0.1 mole) of II in 200 ml. of anhydrous ether was added dropwise under vigorous stirring and cooling to 0°. After stirring for 12 hours at room temperature, the organic layer was decanted into 300 ml. of 3% sulfuric acid. The organic layer was separated and the aqueous layer extracted with ether. The combined organic portion was washed with 5% sodium bicarbonate, twice with distilled water, and dried over anhydrous magnesium sulfate. The ether was evaporated and the residue distilled under reduced pressure to give XVII which was purified by redistillation. The black viscous residue (15 g.) with a boiling range of 92–115° at 3 mm. was unidentifiable and probably polymeric.

2,4-Dimethyl-5,5,5-trifluoropent-3-en-2-ol (XVIII).—A solution of 0.45 mole of methylmagnesium iodide in 200 ml. of anhydrous ether was added at 0° to 25.2 g. (0.15 mole) of methyl 3-methyl-4,4,4-trifluorocrotonate. The mixture was stirred for 14 hours at that temperature and then refluxed for 3 hours. After hydrolysis with a saturated solution of ammonium chloride, the bulky precipitate was washed three times with ether and the organic portions combined and dried over anhydrous magnesium sulfate. Distillation and redistillation through a spinning band column gave pure XVIII. A Lucas test for a tertiary alcohol was positive (infrared, 2.9, 9.95 μ.)

Acknowledgments.—The financial support of the Westinghouse Electric Corporation and the Hooker Chemical Corporation is gratefully acknowledged.

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[18] German Chemical Society, "Beilstein, Handbuch der Organischen Chemie," Vol. II, p. 816.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY, LAFAYETTE, IND.]

The Kinetics of the Reaction between Polyfluoroalkyl Halides and Iodide Ion[1]

BY E. T. MCBEE, R. D. BATTERSHELL AND H. P. BRAENDLIN

RECEIVED DECEMBER 18, 1961

The rates of reaction of 2,2,2-trifluoro-1-bromoethane, 3,3,3-trifluoro-1-bromopropane, 2,2,3,3,4,4,4-heptafluoro-1-bromobutane, 3,3,4,4,5,5,5-heptafluoro-1-bromopentane, allyl chloride and *trans*-4,4,4-trifluorocrotyl chloride with potassium or sodium iodide in dry acetone have been measured and the energies of activation, entropies of activation and frequency factors calculated. The results are discussed in terms of steric and electronic effects exerted by the fluorine substituents.

There are numerous reports of the striking influence exerted on organic reactions by fluorine in the molecule. The electron-withdrawing inductive effect caused by these strongly electronegative substituents was recognized at an early stage to be a predominant factor. When perfluoroalkyl groups are spaced adjacent to reaction centers, a second major factor, a steric effect, is thought to play a significant role. However, the latter is usually obscured by the profound influence of inductivity, and the cases are few where a steric effect has been demonstrated unambiguously, especially with trifluoromethyl as substituent. Evidence for steric hindrance exerted by longer-chain perfluoroalkyl groups was provided by Bender[2] who obtained, according to the equilibrium $R_fCO_2Et + MeO^- \rightleftharpoons R_fC(OMe)(OEt)O^-$, an expected percentage increase of methoxide ion addition to ethyl fluoroacetates with increasing fluorine content, but observed a sharp decrease in percentage addition when substituting pentafluoropropionate or heptafluorobutyrate for trifluoroacetate. This was ascribed to F-strain in the larger molecules.

The influence of perfluoroalkyl groups is reduced considerably when a methylene unit separates the reaction center from the fluorine cluster; when two methylene units shield the functional group, the effects are almost negligible. This was demonstrated by comparison of the ionization constants of selected fluorinated alcohols and acids with non-fluorinated analogs.[3] The decrease in acidity with increasing distance between the perfluoroalkyl group and the reaction center cannot be interpreted solely on the basis of inductivity. In a recent review,[4] Lagowski showed convincing support for the assumption that trifluoromethyl is less electron withdrawing than fluorine. Calculated electronegativity values for trifluoromethyl obtained both from comparison of group influences on C=O and P=O infrared absorption frequencies and from bond dissociation data, were consistently

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[1] From a thesis submitted by R. D. Battershell to the Graduate School of Purdue University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] M. L. Bender, *J. Am. Chem. Soc.*, **75**, 5986 (1953).

[3] (a) A. L. Henne and C. J. Fox, *ibid.*, **73**, 2323 (1951); (b) A. L. Henne and R. L. Pelley, *ibid.*, **74**, 1426 (1952); (c) A. L. Henne and W. C. Francis, *ibid.*, **75**, 991 (1953); (d) E. T. McBee, O. R. Pierce and D. D. Smith, *ibid.*, **76**, 3722 (1954).

[4] J. J. Lagowski, *Quart. Revs.*, **13**, 233 (1959).

TABLE I

KINETIC DATA OF THE REACTION BETWEEN FLUOROALKYL BROMIDES AND POTASSIUM IODIDE

Bromide	$10^5 \times k$, liter mole^{-1} sec.$^{-1}$				Rel. k at 35°	Ea. kcal.	ΔS^*, e.u.	log B^a
	20°	35°	115°	160°				
$CH_3CH_2CH_2Br$	97.2	447^b			4.95	18.2	−12.1	10.6
$CF_3CH_2CH_2Br$	16.6	90.3			1.00	20.3	− 8.4	11.4
$C_3F_7CH_2CH_2Br$	14.0	73.3			0.81	19.8	−10.6	11.0
CF_3CH_2Br		0.0708^c	125	2500	.00078	22.2	−17.3	9.6
$C_3F_7CH_2Br$		0.00581	17.6	433	.000064	23.8	−17.0	9.7

^{a} B in liter mole^{-1} sec.$^{-1}$. ^{b} Fowden, Hughes and Ingold[6b] report $10^5 \times k = 450$. ^{c} Extrapolated values.

lower than for fluorine.[5] Hence, the electronegativities of fluoroalkyl groups should decrease in the order $CF_3 > C_2F_5 > C_3F_7 > CF_2H > CFH_2 > CF_3CH_2$, etc. This is supported by, for example, the facts that $CF_3(CH_2)_2CO_2H$ is more acidic than $C_3F_7(CH_2)_2CO_2H$,[3d] and that FCH_2CO_2H is more acidic than $CF_3CH_2CO_2H$,[3a] although in FCH_2CO_2H some mesomeric electron withdrawal may be a contributive factor in increasing its acidity. In contrast, the acidities increase with increasing size of the perfluoroalkyl group in $R_fCH_2CO_2H$ and R_fCO_2H ($R_f = CF_3, C_3F_7$).[3a] This suggests that such ionizations are dependent on additional factors, particularly in cases where the perfluoroalkyl group is adjacent to the reaction center. Steric, hydrogen bonding and field effects, etc., alone or in combination, may permit more facile proton release by acids with larger perfluoroalkyl substituents.

In an effort to gain greater insight into the relative importance of the steric and inductive effects exerted by perfluoroalkyl groups on chemical reactivity, the Finkelstein reaction, the bimolecular nucleophilic substitution of halogen in alkyl halides by iodide ion, was chosen. Selection of α,α-dihydro and $\alpha,\alpha,\beta,\beta$-tetrahydro halides, and the nature of the SN2 reaction, was reasoned to suppress largely the influences of mesomeric, hydrogen bonding and field effects. The reaction is known to be rather sensitive to spatial factors and should reveal any steric effects exerted by even the smallest perfluoroalkyl group, trifluoromethyl. In a recent series of papers, Hughes, Ingold, de la Mare and co-workers[6] observed very dramatic reductions in the rates of halogen substitution when the steric requirements of the alkyl halide were increased by an α- or β-methyl group.

The effect of α-halogen atoms on the chemical reactivity of halides in nucleophilic displacement reactions of the SN2 type has been the subject of kinetic studies by Hine, Thomas and Ehrenson[7] and McBee, Christman, Johnson and Roberts.[8] Methylene halides and haloesters, respectively, were subjected to potassium iodide in acetone, and in both systems the participation of both steric and inductive effects was indicated (*viz.*, the relative rates, $CH_3Br:CH_3CH_2Br:FCH_2Br:ClCH_2Br:BrCH_2Br = 257:1.9:1.0:0.1:0.03$).[7] The data available concerning the effect on SN2 reactivity of β-halogen substituents is rather slight. Hine and Brader have shown that vicinal halogen atoms have a retarding influence on the reaction of the highly nucleophilic sodium thiophenolate with 2-haloethyl bromides. Here, however, the relative retarding effects of the various halogen atoms are much less pronounced, the order of effectiveness being F > Br > Cl. Again the influence may stem from both inductive and steric factors.[9]

The results from this kinetic investigation of bimolecular nucleophilic substitution reactions between selected polyfluoroalkyl bromides with iodide ion in dry acetone are listed in Table I. 3,3,3-Trifluoro-1-bromopropane reacted about one-fifth as fast as 1-bromopropane; hence, as in the corresponding acid, trifluoromethyl in the β-position exerts a still noticeable influence on the nucleophilic displacement of halide ion. With 3,3,4,4,5,5,5-heptafluoro-1-bromopentane, a slight but perceptible further decrease in rate was observed. The greater rate-retarding influence of the C_3F_7 substituent when compared to the CF_3 substituent is a reversal of the relationship obtained primarily with the −I effect, as measured by the ionization constants of the corresponding acids.[3d] Hence, while inductive electron withdrawal is probably operative in both cases, a greater steric effect may be ascribed to the larger substituent. The energies of activation are not significantly different, whereas the decrease in activation entropy is sizable when comparing $CF_3CH_2CH_2Br$ and $C_3F_7CH_2CH_2Br$. A similar activation entropy difference has been suggested to arise from a steric effect.[9]

The second-order rates were profoundly affected when the perfluoroalkyl group was placed one methylene unit nearer to the reaction center. The decrease in rate, by a factor of 1280 with $R_f = CF_3$ and by 12,630 with $R_f = C_3F_7$, illustrates the considerable electronic and steric effects of perfluoroalkyl groups on adjacent reaction centers. Significantly, the ratio $k_{(CF_3CH_2Br)}/k_{(C_3F_7CH_2Br)}$ ($\sim$6:1) was relatively small; hence, also in compounds of the type R_fCH_2Br the rate-retarding influence of C_3F_7 is not much greater than that of CF_3. This indicates that the steric effect exerted by adjacent perfluoroalkyl groups on the SN2 transition state already approaches a maximum with trifluoromethyl.[10]

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[5] Both inductivity and total electron withdrawal, combining inductive and mesomeric effects, were approximated. Although true electronegativity values cannot be thus obtained since other factors participate in measurements of this nature, the approximations allow the conclusion that CF_3 is less electronegative than F.

[6] (a) E. D. Hughes, C. K. Ingold and J. H. D. Mackie, *J. Chem. Soc.*, 3173, 3177 (1955); (b) L. Fowden, E. C. Hughes and C. K. Ingold, *ibid.*, 3187, 3193 (1955); (c) P. B. D. de la Mare, *ibid.*, 3169, 3180, 3196 (1955); (d) P. B. D. de la Mare, L. Fowden, E. D. Hughes, C. K. Ingold and J. H. D. Mackie, *ibid.*, 3200 (1955).

[7] J. Hine, C. H. Thomas and S. J. Ehrenson, *J. Am. Chem. Soc.*, **77**, 3886 (1955).

[8] E. T. McBee, D. L. Christman, R. W. Johnson and C. W. Roberts, *ibid.*, **78**, 4595 (1956).

[9] J. Hine and W. H. Brader, *ibid.*, **75**, 3964 (1953).

[10] Comparison of the rates observed at 20° with FCH_2Br,[7] CF_3CH_2Br, CH_3Br[7] and CH_3CH_2Br[7] reveals the rate ratios $k_{(FCH_2Br)}/k_{(CF_3CH_2Br)}$ and $k_{(CH_3Br)}/k_{(CH_3CH_2Br)}$ to be about 5800 and 140, respectively, *i.e.*, the rate increase in the fluorocarbon series is about 40 times greater than in the hydrocarbon series when substituting CX_3

In contrast to its rate-retarding influence when present as an α- or β-substituent in saturated alkyl bromides, the trifluoromethyl group accelerates the Finkelstein reaction when present as a γ-substituent in an allylic chloride. This was established by Pegolotti and Young[11] in a very recent publication, appearing after completion of our experiments. Our rate data for *trans*-4,4,4-trifluorocrotyl chloride, agreeing with theirs after extrapolation, were determined at different temperatures. They are given with the energies of activation, entropies of activation and frequency factors, along with the data for allyl chloride. For *trans*-$CF_3CH{=}CHCH_2Cl$, $10^5 \times k$ (in liter mole^{-1} sec.$^{-1}$) was at 20° = 68.8, and at 35° = 358. Pegolotti and Young[11] report $10^5 \times k$ at 25° = 135_{av}. The energy and entropy of activation were 19.9 kcal. and −7.2 e.u., respectively, with a frequency factor log B = 11.7 liter mole^{-1} sec.$^{-1}$. For allyl chloride, the data, with the respective parameters, were: $10^5 \times k$ at 20° = 12.9,[12] at 35° = 18.5; $\Delta S^* = -15.2$; log B = 9.9. A comparison with the data known for *cis*- and *trans*-1-chloro-2-butene,[13] *cis*- and *trans*-1,3-dichloropropene[13] and *cis*- and *trans*-1-bromo-3-chloropropene,[14] all determined at 20°, establishes the relative rate ratios with the *cis* substituents as Br:Cl:CH_3:H = 21.3:9.29:9.02:1, and with the *trans* substituents as CF_3:Cl:CH_3:Br:H = 5.26:3.13:2.56:1.25:1.

trans-4,4,4-Trifluorocrotyl chloride was totally unreactive at room temperature toward silver nitrate in ethanol. It was necessary to heat a solution of the halide with silver tosylate in acetonitrile to 125° to cause formation of the tosyl ester at a reasonable rate. Oae and VanderWerf found crotyl chloride and *cis*- and *trans*-1,3-dichloropropene not only to react rapidly but also faster than allyl chloride with silver nitrate–ethanol at room temperature.[15] The mechanism is of the "pull–push" type and, since the silver cation is a strong pulling agent, whereas the weakly nucleophilic nitrate and tosylate anions are poor pushing agents, the reacting carbon atom will carry a partial positive charge. When the γ-substituents on allylic chlorides are hydrogen, methyl or chlorine, such a positive charge can be easily accommodated by resonance. With the trifluoromethyl substituent, on the other hand, not only is the carbon–chlorine bond shortened, requiring more pull, but also a positive charge would be accepted only very reluctantly in the transition state.

Experimental[16]

Procedures for Measuring Rates.—The procedures used were adaptations of that described by Conant and Kirner.[17] Our findings are in accord with those of Senior, Hetrick and Miller[18] who discovered that appreciable quantities of acetone obscure the end-point in the Andrews[19] titration of iodide ion. To void this difficulty the following procedures were developed.

Procedure A.—The reaction vessels were 11 cm. long test-tubes with 24/40 (outer) *standard-taper* ground joints capped with greased 24/40 S plugs held tightly in place by rubber bands. The reaction tubes were placed, at least 10 minutes before addition of the reagents, in a thermostat whose temperature variation was less than ± 0.05°. Solutions of known normality of potassium iodide in acetone and of alkyl halide in acetone had been previously prepared and stored in a thermostat maintained at 20 ± 0.02°. The potassium iodide solution (10 ml.) was pipetted into the reaction tube, and at zero time 5 ml. of the alkyl halide solution was added. The mixture was shaken for approximately 30 seconds, and after a given time interval the reaction was quenched by the addition of 5 g. of ice. The mixture was then quickly transferred to a 200-ml. round-bottom flask, containing 10 g. of ice, while taking care to rinse the emptied reaction tube well with distilled water. The flask and contents were attached, by means of a 15-cm. Pyrex extension tube, to a Rinco evaporator, and acetone and unreacted halide were removed under an aspirator vacuum in a period of 15 minutes. The residue was transferred to a 250-ml. erlenmeyer flask, along with 50 ml. of ice-cold concentrated hydrochloric acid, 5 ml. of chloroform and a Teflon covered magnetic stirring bar. The amount of unreacted iodide ion was determined by titration with a standard solution of potassium iodate according to the equation

$$2KI + KIO_3 + 6HCl \longrightarrow 3KCl + 3ICl + 3H_2O$$

The iodate solution was added rapidly, with stirring, causing a strong iodine color to develop which at the half equivalence point began to lighten. At this point, 30 g. of ice and the iodate solution again were added rapidly, with stirring, until the end-point was approached. The end-point was taken as the point at which the chloroform layer became colorless.

Procedure B.—The alkyl halide was sealed into tared thin-walled soft glass ampoules, prepared from 6-mm. soft glass tubing. The ampoule, 5 ml. of a standard solution of potassium or sodium iodide and a piece of 6/0.8 cm, glass rod were placed in a clean tube, 1.2 cm. × 30 cm. The tube was stoppered, cooled, the stopper removed, and the tube quickly sealed so that the free space above the liquid was approximately half the volume of the liquid. The upper portion of the tube remained attached to facilitate clamping of the tube to the bath and opening of the tube at the end of the reaction. The labeled tubes, placed in the thermostat 30 minutes prior to the reaction, were quickly withdrawn from the bath, given a swift shake at time zero to break the ampoule, and returned to the bath. The whole operation required less than 15 seconds. After a measured time interval the tube was withdrawn and plunged into a Dry Ice-bath and allowed to cool for at least 5 minutes, whereupon the tube was wiped clean, opened and the contents and washings poured into a 200-ml. round-bottom flask containing 15 g. of ice. From this point the procedure was identical with procedure A.

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by X (X = hydrogen or fluorine). Since it can be assumed that the decrease in steric requirement is greater on substitution of methyl by hydrogen than on substitution of trifluoromethyl by fluorine, the results indicate an electronic assistance in the relative rate acceleration by the fluorine substituent. Since this cannot be ascribed to a weaker inductive effect of fluorine, mesomeric electron release by the latter may take place.

(11) J. A. Pegolotti and W. G. Young, *J. Am. Chem. Soc.*, **83**, 3258 (1961). It has not been decided whether an S_N2 or S_N2' mechanism, or a combination thereof, prevails. In analogy to observations of these authors, our product revealed characteristic *trans*-ethylene absorption in the infrared. Hence, if an S_N2' process, $CF_3CH{=}CHCH_2Cl \rightarrow CF_3CHICH{=}CH_2$, is involved, product isomerization takes place.

(12) The following values for $10^5 \times k$ at 20° have been reported: L. F. Hatch, L. B. Gordon and J. J. Russ, *ibid.*, **70**, 1093 (1948), 13.9; M. Tamele, C. J. Ott, K. E. Marple and C. Hearne, *Ind. Eng. Chem.*, **33**, 119 (1941), 14.5; J. B. Conant, W. R. Kirner and R. E. Hussey, *J. Am. Chem. Soc.*, **47**, 488 (1925), 18.4.

(13) L. F. Hatch and S. S. Nesbitt, *ibid.*, **73**, 358 (1951).

(14) L. F. Hatch and K. E. Harwell, *ibid.*, **75**, 6002 (1953).

(15) S. Oae and C. A. VanderWerf, *ibid.*, **75**, 2724 (1953).

(16) All melting points and boiling points are uncorrected. Analyses were performed by Dr. C. S. Yeh, Purdue University. The infrared spectra were determined by Mrs. W. Dilling, Purdue University, on a Perkin–Elmer model 21 spectrophotometer. The vapor phase chromatograms were obtained with a Perkin–Elmer model 154 vapor fractometer, using copper columns packed with Carbowax on firebrick.

(17) J. B. Conant and W. R. Kirner, *J. Am. Chem. Soc.*, **46**, 232 (1924).

(18) K. L. Senior, R. R. Hetrick and J. G. Miller, *ibid.*, **66**, 1987 (1944).

(19) L. W. Andrews, *ibid.*, **25**, 756 (1903).

Procedure A was used for measuring the slower rates at 20° and 35°; procedure B was used for the faster rates at 20° and 35° and for the rates at higher temperatures. For the latter, it was necessary to employ sodium iodide since, at the concentrations used, potassium iodide precipitated out of solution. Most of the rate data were taken from the first 20–30% of the reactions, although several reactions were followed to 50–70% completion. No significant drifts in rate constants were observed.

The electric timer used was manufactured by the Standard Time Co. and was graduated in hundredths of a minute. The thermostat temperature regulators were set using a total immersion thermometer range 0 to 250°, graduated in 0.5°, calibrated by the U. S. Bureau of Standards.

The sample volumes varied from 5 to 15 ml.; N_{KIO_3} was 0.003082 for all reactions. The other concentrations varied, with N_{KI} or N_{NaI} between 0.015 and 0.025 and N_{KBr} between 0.05 and 0.1, accurate for 5 decimals.

The second-order rate constants were obtained from the equation $K = 1/t(a-b) \times \ln[b(a-x)/a(b-x)]$ which, with the appropriate substitutions, gives $k = 2.303/t(M-1) \times \log [M-Z/M[1-Z)]$, where Z = fraction of inorganic iodide consumed at time t, M = ratio of organic halide to inorganic iodide. A plot of *kt versus* time gave straight lines which passed through the origin and whose slopes were the velocity constants. The rates reported are the average values determined from not less than four separate runs.

Since the concentrations of the reagents were all based on a solvent temperature of 20°, corrections had to be made for the thermal expansion of acetone. The true value of k will be obtained by multiplying the calculated value by the factor obtained by dividing the volume of acetone at t° by the volume of acetone at 20°. This factor was measured in a capillary tube by meniscus difference.

The activation energies were calculated from the equation $E_a = 2.303 T_2T_1/(T_2 - T_1) \times \log k_2/k_1$ from which the activation entropies were obtained according to the expression $S^* = R \ln k_1 + E_a/T_1 - R \ln (R_2 + T_2)/2 \times k/(n - R)$, with $T_1 + T_2/2 = T_{av}$. After rearrangement and evaluation of constants, one obtains $S^* = 2.303 \log k_1 - E_a/T_1 - 2.303 R \log (2.084\ T_{av}) - 47.76$. The frequency factors B are given by the expression $\log B = \log k + 0.4342 E_a/RT$.

Reagents. Potassium iodide and sodium iodide (Baker analyzed) were recrystallized twice from distilled water, dried for 2 hours at 110°, and cooled in a desiccator.

Potassium iodate (Baker analyzed) was recrystallized twice from distilled water, dried for 2 hours at 140°, and cooled in a desiccator. Commercial **acetone** was purified by the method of Conant and Kirner[17]; although it is known that acetone thus purified still contains some water, the drying procedure was reproducible, as comparable results were obtained with different batches of acetone (see also Hine[9]). Commercially available **alkyl halides** were purified by rectification through a standard Todd column.

The following fluoroalkyl halides were prepared by known procedures: 3,3,3-trifluoro-1-bromopropane,[20] 3,3,4,4,5,5,5-heptafluoro-1-bromopentane,[21] 2,2,2-trifluoro-1-bromoethane[20] and 2,2,3,3,4,4,4-heptafluoro-1-bromobutane.[22]

***trans*-4,4,4-Trifluorocrotyl Chloride.**—A mixture of 4,4,4-trifluoro-2-butene-1-ol, (36 g., 0.29 mole) and tosyl chloride (60 g., 0.32 mole) was cooled to 0° in an ice-bath, and dry pyridine (45 g., 0.57 mole) was added dropwise with stirring. After continued stirring for 5 hours at 0°, the mixture was poured onto crushed ice and 30 g. of concentrated hydrochloric acid. The hydrolysis mixture was extracted 7 times with ether (emulsion), the ether extracts were dried over magnesium sulfate and the ether removed by distillation. Vacuum distillation of the residue gave a fraction boiling at 25–35° (39 mm.). Redistillation at atmospheric pressure gave 12 g. (29%) of *trans*-4,4,4-trifluorocrotyl chloride, b.p. 81–81.5°; $n^{20}\text{D}$ 1.3638,[23] d^{20}_4 1.2720.

Anal. Calcd. for $C_4H_4F_3Cl$: C, 33.25; H, 2.79; Cl, 24.54; M_D, 25.11. Found: C, 33.55; H, 2.96; Cl, 24.28; M_D, 25.22.

The product was shown to be isomerically pure by vapor phase chromatography; *trans* configuration was assigned on the basis of the infrared spectrum, with strong absorptions at 5.88 μ (1700 cm.$^{-1}$) and at 10.27 μ (974 cm.$^{-1}$).

Acknowledgment.—Financial support by the Hooker Chemical Corporation is gratefully acknowledged.

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(20) R. N. Haszeldine, *J. Chem. Soc.*, 3372 (1953).

(21) O. R. Pierce, E. T. McBee and R. E. Cline, *J. Am. Chem. Soc.*, **75**, 5618 (1953).

(22) E. T. McBee, D. H. Campbell and C. W. Roberts, *ibid.*, **77**, 3149 (1955).

(23) J. A. Pegolotti and W. G. Young, *ibid.*, **83**, 3256 (1961), report b.p. 82.5–83°, $n^{25}\text{D}$ 1.3610.

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Anionic Activation of C–H Bonds in Olefins. III. Solvent Effect on the Isomerization of 2-Methyl-1-pentene

BY A. SCHRIESHEIM AND C. A. ROWE, JR.

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The isomerization of 2-methyl-1-pentene was studied in a homogeneous medium consisting of potassium *tert*-butoxide in dimethyl sulfoxide. It was found that the use of dimethyl sulfoxide allowed the double bond isomerization to take place with ease and high selectivity at moderate temperatures. The reaction is first order in olefin and of varying order in base. Activation parameters are E_a = 22 kcal./mole, $\Delta H^{\ddagger}$ = 21.6 kcal./mole and $\Delta S^{\ddagger} = -16.7$ e.u. It was also determined that 2-methyl-1-pentene and 2-methyl-2-pentene rapidly interconvert, but that the 4-methyl-1-pentene isomers are only formed at very long contact times. This is interpreted on the basis of different stabilities of the anionic intermediates.

A recent communication reported that dimethyl sulfoxide was an effective medium for the potassium *tert*-butoxide catalyzed isomerization of olefins.[1] This reaction technique is of some importance since it represents a tool for activating weakly acidic C–H bonds in a variety of molecules. As an example, Price and Snyder[2] have recently reported the use of the same system for the rearrangement of allyl ethers, and Cram, *et al.*, have speculated on the use of similar systems for a variety of base-catalyzed reactions.[3]

Anionic activation of C–H bonds in olefins is a relatively unexplored area. The reason for the lack of information in this area has been due to the use of strong base systems that are relatively difficult to handle and reproduce.[4] Olefin isomerization has been accomplished with sodium-organosodium catalysts prepared *in situ*[5] and alkyl-sodium com-

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