Chemistry of Bromine Trifluoride. The Fluorination of Bromofluoroethanes[1,2]

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Bromine trifluoride in bromine solution has been found to react smoothly with bromofluoroethanes to give a relatively clean, progressive substitution of the bromine by fluorine. Under normal reaction conditions (0–50°) no replacement of hydrogen is observed and coupled products have not been found. The relative ease of replacement of bromine in various groups appears to be $CBr_3 > CBr_2F > CHBr_2 > CF_2Br > CHBrF > CH_2Br$. A mechanism for the reaction is postulated.

Bromine trifluoride (I) is well known as an extremely powerful fluorinating agent that can react with explosive violence with organic compounds. Consequently, its use as a fluorinating agent has been limited. An excellent critical review of previous work has been made by Musgrave.[3]

Nutting and Petrie[4] employed bromine trifluoride to replace selectively from one to four of the chlorine atoms in carbon tetrachloride by varying the reaction conditions. Later Emeléus and co-workers[5] extended this reaction to carbon tetrabromide and carbon tetraiodide and Haszeldine[6] employed bromine trifluoride to replace the iodine in a series of perfluoroalkyl iodides. McBee and co-workers[7] reported in a series of patents the reaction of bromine trifluoride with a number of polyhaloaromatic and polychlorinated hydrocarbons. The aromatic compounds yielded complex mixtures of bromochlorofluorocyclohexanes containing bromine atoms that could not be removed by further treatment with bromine trifluoride. Reaction of the polychlorinated hydrocarbons with bromine trifluoride gave mixed products which showed indiscriminate substitution of both hydrogen and chlorine by fluorine, as well as introduction of bromine into the molecule.

We became interested in the potential use of bromine trifluoride as a fluorinating agent for polyfluoroalkyl bromides, since the antimony fluorides are unsatisfactory agents for the fluorination of bromine-containing compounds. While the antimony fluorides react readily with bromine-containing compounds, the complex antimony fluorobromides cannot be regenerated with anhydrous hydrogen fluorides.[8] In addition the complex salts frequently precipitate in the reaction mixture and cause serious corrosion problems with metal equipment.

We have found that bromine trifluoride reacts rapidly with polyfluoroalkyl bromides in bromine solution at temperatures between 0 and 50° to give excellent yields of products formed by the stepwise substitution of the bromine atoms and without substitution of hydrogen atoms in the molecule.

Results and Discussion

A series of polyfluoroethyl bromides was fluorinated with bromine trifluoride in bromine solution with the results shown in Table I. In general, the reactions were carried out at atmospheric pressure in Monel equipment by carefully adding, with vigorous stirring, the alkyl bromide to the appropriate amount of bromine trifluoride (I)[9a] dissolved in liquid bromine. The stoichiometry of the reaction is given in eq A. The

TABLE I

REACTIONS OF BROMINE TRIFLUORIDE WITH FLUOROALKYL BROMIDES

Fluoroalkyl bromide	Product	Yield, %	Organic recovery, %
CF_3CHBr_2 (II)	CF_3CHBrF (III)	86	86
	CF_3CHF_2 (IV)	Trace	
CF_3CHBr_2[a] (II)	CF_3CHBrF (III)	91.7	96.8
	CF_3CHF_2 (IV)	5.1	
$CBrF_2CHBr_2$[b] (V)	$CBrF_2CHBrF$ (VI)	58.9	69
	CF_3CHBrF (III)	Trace	
$CBrF_2CHBr_2$ (V)	CF_3CHBrF (III)	77.1	78
	CF_3CHF_2 (IV)	Trace	
CF_3CH_2Br (VII)	CF_3CH_2F (VIII)	76	80.5
$CBrF_2CBr_3$[b] (IX)	$CF_2BrCFBr_2$ (X)	78.6	88.5
	CF_2BrCF_2Br (XI)	4.1	
$CBr_2FCHBrF$ (XII)	CF_3CHBrF (III)	65.2	71
	CF_3CHF_2 (IV)	5.7	

[a] BrF_3 prepared from ClF_3. [b] BrF_3–Br_2 solution added to organic in bromine.

$$3\ -\overset{|}{\underset{|}{C}}-Br + BrF_3 \longrightarrow 3\ -\overset{|}{\underset{|}{C}}-F + 2Br_2 \qquad (A)$$

total amount of bromine used as a solvent is preferably between 50 and 85 mole % of the final reaction mixture. The use of less bromine makes the reaction difficult to control and increases the probability of hydrogen substitution. While temperatures below 0° can be employed, the use of lower temperatures can bring about phase separation which markedly raises the explosion potential of the solution.

In our work the reaction temperature was generally controlled at about 25° by means of a water bath during the addition and then raised slowly to 50–60°

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[1] Presented in part at the 148th National Meeting of the American Chemical Society, Chicago, Ill., 1964, Abstracts of Papers, p 15K.

[2] R. A. Davis and E. R. Larsen, Canadian Patent 704,494 (1965).

[3] W. K. R. Musgrave, *Advan. Fluorine Chem.*, **1**, 12 (1960).

[4] H. S. Nutting and P. S. Petrie, U. S. Patent 1,961,622 (1934).

[5] A. A. Banks, H. J. Emeléus, R. N. Haszeldine, and V. Kerrigan, *J. Chem. Soc.*, 2188 (1948).

[6] (a) R. N. Haszeldine, *ibid.*, 3559 (1953); (b) R. N. Haszeldine and B. R. Steele, *ibid.*, 1592 (1953).

[7] W. B. Ligett, E. T. McBee, and V. V. Lindgren: (a) U. S. Patent 2,432,997 (1947); (b) U. S. Patent 2,480,080 (1949); (c) U. S. Patent 2,489,969 (1949); (d) U. S. Patent 2,471,831 (1949). (e) E. T. McBee, R. M. Robb, and W. B. Ligett, Canadian Patent 524,610 (1956).

[8] R. P. Ruh and R. A. Davis, U. S. Patent 2,786,738 (1957).

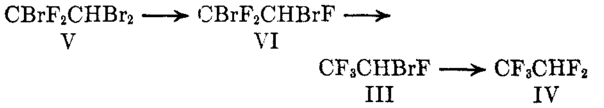
[9] (a) Commercial cylinders of bromine trifluoride normally contain a variable amount of elemental bromine. For the purpose of this work, the moles of BrF_3 used were not corrected for the weight of free bromine. No attempt was made to determine either the amount of unreacted BrF_3 or the loss due to reaction with water or metal salts in the equipment. (b) *Caution!* Bromine trifluoride can react with explosive violence with organic compounds and vigorously with water. Care must be taken to avoid contact of this reagent with organic materials such as rubber, plastics, etc., and to avoid *accidently* allowing water to enter the reactor. Reactions should only be carried out in properly shielded equipment and by personnel wearing proper safety equipment.

to complete the reaction. The reflux temperature of the bromine (59°) tends to set the upper operating limit. When only one bromine atom was to be replaced in a polybrominated compound it was frequently desirable to add the bromine trifluoride–bromine solution to a solution of the alkyl bromide in bromine. The products are separated by either distilling them away from the bromine or by destroying the bromine with aqueous sodium hydroxide[9b] and then separating the organic phase. Product yields were determined by glpc analysis and the products were identified by their physical properties and by infrared and mass spectral analysis.

While the use of liquid bromine as a solvent severely limits the usefulness of this procedure, it is one of the few solvents compatible with bromine trifluoride. Bromine has a dielectric constant[10] ($3.148^{24.70°}$) somewhat higher than benzene[11] (2.28) and tends to solvate large ions. Its Hildebrand solubility parameter[12] (δ 11.8) indicates that it should be mutually soluble with most brominated hydrocarbons (δ 9–12) and with bromine trifluoride (δ 9.1). Liquid bromine does not react with saturated hydrocarbons rapidly enough at temperatures below 60° to cause unwanted by-products.

2,2-Dibromo-1,1,1-trifluoroethane (II) reacts with I to give high yields of 2-bromo-1,1,1,2-tetrafluoroethane (III), along with minor amounts of pentafluoroethane (IV). No evidence of hydrogen substitution, or coupling products, was found with either I, or with I prepared *in situ* from chlorine trifluoride. Attempted fluorination of II in bromine solution with elemental fluorine gave primarily 1,1,1-tribromo-2,2,2-trifluoroethane, resulting from hydrogen replacement, along with small amounts of III. No coupling products were detected.

The other compounds used in this study were substituted in such a manner that the order in which the bromine atoms reacted could be readily determined from the product distribution. In those cases where direct comparisons could not be made, the order could be judged qualitatively from the reaction rate. For example, 1,2,2-tribromo-1,1-difluoroethane (V) reacts with I in a stepwise manner to give good yields of higher fluorinated products (eq B). 2-Bromo-1,1,1-trifluoroethane (VII) reacts with I with difficulty, requiring a large excess (200%) of I in order to obtain reasonable rates below 50°. Attempts to increase the rate of formation of 1,1,1,2-tetrafluoroethane (VIII) by carrying out the reaction at 60° under pressure resulted in the formation of a variety of by-products formed by hydrogen substitution.



$$\underset{\text{V}}{CBrF_2CHBr_2} \longrightarrow \underset{\text{VI}}{CBrF_2CHBrF} \longrightarrow \underset{\text{III}}{CF_3CHBrF} \longrightarrow \underset{\text{IV}}{CF_3CHF_2} \quad (B)$$

In general the relative ease of replacement of a bromine in various groups appears to be $CBr_3 > CBr_2F > CHBr_2 > CF_2Br > CHBrF > CH_2Br$. The presence of fluorine on either the same carbon or the adjacent carbon tends to retard the substitution. This order parallels that reported by Henne[13] for the reaction of the analogous chloroalkanes with antimony and mercuric fluorides. Compound I is, however, more effective than the antimony fluorides since it readily replaces the bromine in CF_2Br and CH_2Br groups.

Chlorine trifluoride is an excellent source of I. Its low boiling point (11°) allows it to be metered as a gas into the bromine where it is rapidly converted to I with the evolution of BrCl which is readily distilled away from the solution. Use of this procedure considerably reduces the hazards associated with the handling of I in its pure form.

Mechanism of Fluorination.—Previous workers[5] have postulated that the reaction of I with perhalogenated compounds is not free radical in nature since coupled products were not found. The absence of coupled products does not, however, exclude a radical mechanism since the bromine produced in the reaction would act as a radical trap and minimize, if not prevent, the formation of coupled products. McBee,[7] however, reported the replacement of hydrogen which indicates that under his conditions radical reactions were occurring to at least a limited extent.

In order to determine the effect of radical reactions under our conditions we passed elemental fluorine into a solution of II in bromine and obtained predominately 1,1,1-tribromo-2,2,2-trifluoroethanes which results from hydrogen substitution. A similar reaction between fluorine and pentachloroethane saturated with chlorine yields hexachloroethane and has been shown to be a radical process.[14] In both of these reactions coupled products were absent.

Since I reacts with polyhalo groups in a manner similar to that found with Lewis acids, *i.e.;* polyhalogenated carbons react more readily than monohalogenated carbons,[15] it is probable that the attacking species in I is likewise a strong Lewis acid.

Bromine trifluoride (I), on the basis of physical evidence of association and ionization, is reported to ionize according to eq C.[16] The introduction of bromine into I is thought to give rise to the following equilibria[17] given in 1–6. On the basis of conductivity

$$2BrF_3 \rightleftharpoons [BrF_2 \cdot BrF_4] \rightleftharpoons BrF_2^+ + BrF_4^- \qquad (C)$$

$$Br_2 + BrF_3 \rightleftharpoons 3BrF \qquad (1)$$

$$Br_2 \rightleftharpoons Br^+ + Br^- \qquad (2)$$

$$2BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^- \qquad (3)$$

$$Br^- + BrF_2^+ \rightleftharpoons 2BrF \qquad (4)$$

$$BrF + BrF_3 \rightleftharpoons Br^+ + BrF_4^- \qquad (5)$$

$$BrF + BrF_3 \rightleftharpoons BrF_2^+ + BrF_2^- \qquad (6)$$

and infrared studies the equilibria represented by 3 and 5 are believed to lead to finite concentrations of several ionic species, *e.g.*, Br^+, BrF_2^+, and BrF_4^-. These equilibria have been shown to exhibit negative temperature coefficients of conductivity, which is be-

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(10) F. Yaron in "Bromine and Its Compounds," Z. E. Jolles, Ed., Ernest Benn Ltd., London, 1966, p 45.

(11) A. Weissberger, *et al.*, "Technique of Organic Chemistry," Vol. VII, 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1955, p 270.

(12) J. H. Hildebrand and R. L. Scott, "Solubility of Non-electrolytes," Reinhold Publishing Corp., New York, N. Y., 1948.

(13) A. L. Henne, *Org. Reactions*, **2**, 51 (1949).

(14) W. T. Miller, Jr., S. D. Koch, Jr., and F. W. McLafferty, *J. Am. Chem. Soc.*, **78**, 4992 (1956).

(15) A. N. Nesmeyanov, R. K. Freidlina, and L. I. Zakharkin, *Quart. Rev.* (London), **10**, 330 (1956).

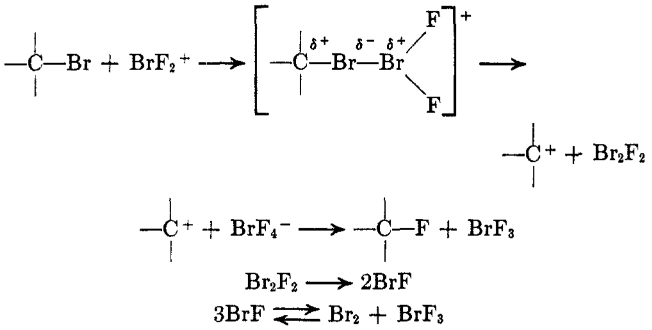
(16) A. A. Banks, H. J. Emeléus, and A. A. Woolf, *J. Chem. Soc.*, 2861 (1949).

(17) L. A. Quarterman, H. H. Hyman, and J. J. Katz, *J. Phys. Chem.*, **61**, 912 (1957).

lieved to indicate that the ionic species are less stable at elevated temperatures.[16,17] The corresponding tendency for hydrogen substitution to become more pronounced with increasing temperature, while bromine replacement dominates at lower temperatures, supports the ionic nature of the fluorination reaction.

One possible mechanism for the reaction of I with alkyl bromides in bromine solution is given in Scheme I. The BrF_2^+ ion (tetrahedral, two unshared electron pairs at two tetrahedron corners) is a strongly electrophilic species[18] and is apparently capable of complexing with an alkyl bromide, in a manner similar to that found with Lewis acids, giving rise to a carbonium ion, and Br_2F_2 (isoelectronic with BrF_3). The carbonium ion formed reacts with BrF_4^- to give the alkyl fluoride and BrF_3. The Br_2F_2 molecule can rapidly decompose to BrF and subsequently to BrF_3.

SCHEME I



The observed decrease in reaction rate brought about by fluorine on the β carbon is in keeping with the fact that only the inductive effect of the fluorine is in operation which decreases the electron density of the adjacent bromine atom. Fluorine substitution on the α carbon likewise tends to retard the reaction by decreasing the electron density of the bromine, but this effect is at least partially offset by back donation of electrons by the fluorine which tends to stabilize the carbonium ion that is in the process of being formed.

No attempt has been made to study the kinetics of the reaction because of inherent difficulties in analyzing bromine trifluoride solutions. The relatively clean orientation observed for the progressive substitution of bromine by fluorine is clearly a rate phenomena, similar to that reported for the substitution of chlorine by fluorine with the metal fluorides.[19]

Experimental Section

The bromine trifluoride,[9a] chlorine trifluoride, and fluorine were used as obtained from the Allied Chemical Co. The bromine was Dow "Purified" grade and was used as received. The fluorobromoalkanes were prepared by literature procedures. Fluorinations were carried out in Monel flasks, fitted with nickel condensers, dropping funnels, and air-driven nickel stirrers. All stoppers were made of Teflon. The needle valve on the dropping funnel was nickel and packed with Teflon valve packing. Copper vent lines from the condenser led to glass traps cooled in Dry Ice–acetone baths. The reaction flasks were surrounded by water baths which could be either heated or cooled to control the reaction.

Bromine trifluoride was added to bromine with stirring and then brought to the desired temperature by adjusting the temperature of the water bath. The organic, either neat or in bromine solution, was added slowly and any low-boiling products were allowed to distill out through the condenser and collected in Dry Ice–acetone cooled traps. Internal reaction temperatures could not be measured directly because of equipment limitation and it was assumed that with slow addition of the reactant and rapid agitation, the internal temperature would be approximately the same as that of the water bath. Products that collected in the cold traps were freed of entrained bromine by passing them through a train consisting of a caustic scrubber (10% aqueous sodium hydroxide), calcium chloride drier, and recollected in cold traps. Bromine was removed from the higher boiling products by slowly pouring the reaction onto crushed ice and then slowly adding cold 10% aqueous sodium hydroxide. The organic product was separated and dried over calcium chloride. The crude organic products were analyzed by glpc and then rectified. The products were identified by their physical properties and by infrared and mass spectral analysis.

Fluorination of 2,2-Dibromo-1,1,1-trifluoroethane (II). A.—With Bromine Trifluoride (I).—Compound II (247 g, 1.0 mole) was added during 15 min to a solution of 54 g (0.4 mole) of I in bromine (75 ml). The temperature of the water bath increased from 25 to 35°. Gaseous products distilled out through the condenser (~10°) during the addition. The reaction mixture was then heated to 50° to complete the reaction and to force out as much product as possible. Gas-liquid partition chromatography showed the crude scrubbed product (156 g) to consist of pentafluoroethane (IV) (<0.5%) and 2-bromo-1,1,1,2-tetrafluoroethane (III) (99.5%). The yield of III, bp 8–9° (lit.[20] bp 8–9°), was 154 g (85%). No organic material was found when the bromine remaining in the reaction flask was worked up.

B. With Chlorine Trifluoride.—To a 1-l. Monel flask containing 350 ml of bromine was added 70 g (0.77 mole) of chlorine trifluoride at a rate of 500 cc of gas per minute. The chlorine trifluoride was added with rapid stirring but without cooling except for water on the condenser. The temperature of the mixture rose to about 50°. When all of the chlorine trifluoride had been added the mixture was heated until bromine distilled from the top of the condenser in order to ensure removal of chlorine and chlorine bromide from the solution. The mixture was cooled to room temperature and 242 g (1.0 mole) of II was added during a space of 45 min. The reaction was held at 20–30° with a water bath. When the addition was complete the temperature was raised to 50° and the product distilled off. The temperature was then raised to 60° until bromine distilled over. The caustic scrubbed product weighed 172 g and was shown by glpc and rectification to consist of 6.2 g (5.1%) of IV (bp −42 to −40° (lit.[21] bp −42°) and 165.8 g (91.7%) of III. The organic recovery was 96.8%.

C. With Fluorine.—Compound II (1000 g, 4.14 moles) and 640 ml of bromine were charged to a 3-l. Monel flask, equipped with a gas sparge pipe, mechanical stirrer, and condenser followed by Dry Ice cooled traps. Fluorine (2.0 moles) was passed gas phase into the flask at a rate of about 200 cc/min. The reaction was maintained at 25–40° with a water bath. Hydrogen fluoride was given off in considerable quantity. The reaction mixture was worked up by carefully adding 10% aqueous sodium bisulfite to the reaction vessel to destroy the bromine. The organic layer was separated and dried over calcium chloride. Rectification of the combined organic (642 g) gave 23 g (5.5%) of III, 440 g (44%) of II (bp 71–74 (lit.[21] bp 71.5–73°)), and 169 g (23.5%) of 1,1,1-tribromo-2,2,2-trifluoroethane (bp 113–114° (lit.[22] bp 113.1°)). Organic recovery was 61%.

Fluorination of 1,2,2-Tribromo-1,1-difluoroethane (V). A. To Prepare 1,2-Dibromo-1,1,2-trifluoroethane (VI).—A solution of 19 g (0.132 mole) of I in 32 ml of bromine was added during a period of 40 min to a stirred solution of 120 g (0.395 mole) of V in 65 ml of bromine. The reaction temperature was maintained at less than 35°. The bromine was destroyed by washing with cold 10% aqueous sodium hydroxide and 71 g of crude organic was recovered. Analysis by glpc and mass spectroscopy showed the product to consist of 42.8 g (44.8%) of 1,2-dibromo-1,1,2-trifluoroethane VI (bp 75–76° (lit.[23] bp 76°)), 28.4 g (23.8%) of V, and a trace (>1%) of III. Organic recovery was 69%.

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B. To Prepare 2-Bromo-1,1,1,2-tetrafluoroethane (III).—Compound V (152 g, 0.5 mole) was added slowly (25 min) to a solution of 55 g (0.4 mole) of I in 75 ml of bromine. The reaction was cooled in an ice-water bath during the addition. (Reaction occurred so rapidly that some product passed through the Dry Ice cooled trap.) The temperature was then raised to about 60° with the condenser cooling water turned off. Product collection was stopped when bromine began to pass through the condenser. Glpc analysis showed the crude, scrubbed product (70.5 g) to consist of III (70 g, 77.1%) along with a trace of IV.

Fluorination of 2-Bromo-1,1,1-trifluoroethane (VII).—Compound VII (60 g, 0.378 mole) was added slowly to a solution of 55 g (0.4 mole) of I in bromine (75 ml). No heat of reaction was observed although product was given off, so the temperature was raised slowly to 50° and finally to 60°. The product that collected in the Dry Ice trap was scrubbed through caustic and analyzed by glpc. The crude product (35.2 g) consisted of 23.8 g (62%) of VIII (bp −26 to −24° (lit.[24] bp −26)) and 11.4 g of VII. The organic recovery was 80.5%. No higher brominated or fluorinated compounds were found.

Fluorination of 1,1,1,2-Tetrabromo-2,2-difluoroethane (IX).—Compound I (15 g, 0.105 mole) in 32 ml of bromine was added slowly (45 min) to a well-stirred solution of 120 g (0.314 mole) of IX in 65 ml of bromine. The reaction was cooled to keep the temperature below 50°. Stirring was continued for 30 min after the addition was complete to finish the reaction. The bromine in the mixture was then neutralized with 10% aqueous sodium hydroxide and the crude product (95 g) separated. The crude product was shown by glpc and mass spectral analysis to contain 2.2 g (2.7%) of 1,2-dibromo-1,1,2,2-tetrafluoroethane (X) (bp 45–47° (lit.[25] bp 46.4°)), 51.7 g (51.3%) of 1,1,2-tribromo-1,2,2-trifluoroethane XI (bp 115–117° (lit.[26] bp 117°)), and 41.5 g of IX.

Fluorination of 1,1,2-Tribromo-1,2-difluoroethane (XII).—Compound XII (61 g, 0.2 mole) was added slowly (20 min) to a solution of 34 g (0.25 mole) of I in 75 ml of bromine. The reaction was cooled in an ice-water bath during the addition. The low-boiling compounds which passed from the top of the reflux condenser were collected in a Dry Ice cooled trap. After all of the organic bromide had been added, the flask was heated slowly to about 60° to distill out as much product as possible. Glpc analysis showed the crude scrubbed product (25.0 g) to consist of III (23.5 g, 65.2%) and IV (1.4 g, 5.7%).

Registry No.—Bromine trifluoride I, 7787-71-5; II, 1894-81-1; III, 124-72-1; IV, 354-33-6; V, 677-34-9; VI, 354-04-1; VII, 421-06-7; VIII, 811-97-2; IX, 3470-67-5; X, 354-49-4; XI, 124-73-2; XII, 353-97-9.

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Evidence for Hyperconjugative Stabilization of Olefins from Tautomeric Equilibria[1a]

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Equilibrium constants have been determined for the alkoxide-catalyzed isomerization of a series of ethyl 4-(*p*-alkylphenyl)-2-methyl-2- and -3-butenoates. The proportion of the β,γ-unsaturated isomer decreases with increasing branching in the *p*-alkyl group. These results are taken as evidence for CH hyperconjugative stabilization of the β,γ double bond in the ground state.

The importance of hyperconjugation has been controversial for a good many years. In particular, there is a lack of experimental observations which indicate that hyperconjugation is significant in the ground states of neutral molecules.[2,3] Over the years, many tautomeric equilibria have been examined in an effort to determine the extent of hyperconjugative stabilization at a given center. However, most of the systems studied were complicated by the fact that the equilibria were affected by both the electronic and steric effects of the substituent. In an effort to find a system insulated from steric effects in which hyperconjugative stabilization of olefins might be observable we have examined the equilibria between ethyl 4-(*p*-alkylphenyl)-2-methyl-2-butenoates and the corresponding β,γ-unsaturated isomers. This choice was prompted by the extensive data available on similar equilibria for aliphatic and alicyclic unsaturated esters. Some pertinent data are presented in Table I.[4]

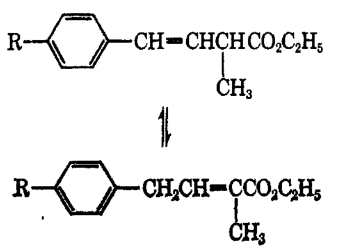
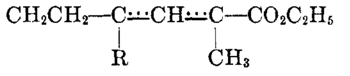


TABLE I

EQUILIBRIUM CONSTANTS AND FREE-ENERGY DIFFERENCES FOR ISOMERIC UNSATURATED ESTERS



$$CH_2CH_2\text{—}\underset{R}{C}\text{⋯}CH\text{⋯}\underset{CH_3}{C}\text{—}CO_2C_2H_5$$

R	Conjugated isomer, %	K_{obsd}[a]	K_{cor}[b]	$-\Delta F$,[c] kcal
CH_3	45	0.82	1.9–2.7	0.60–0.93
C_2H_5	68	2.1	4.2	1.33
i-C_3H_7	78	3.5	4.9–6.1	1.48–1.68
t-C_4H_9	86	6.1	6.1	1.68

[a] $K_{obsd} = (A_1 + A_2)/(B_1 + B_2)$, where A_1 and A_2 are *trans*- and *cis*-α,β-unsaturated isomers, respectively. B_1 and B_2 are *trans*- and *cis*-β,γ-unsaturated isomers, respectively. [b] $K_{cor} = A_1/B_1$. [c] $\Delta F = -RT \ln K_{cor}$; $T = 486°K$.

It is clear that hyperconjugative stabilization does not completely account for these observed equilibria. For example, the equilibrium mixture of 4-neopentyl-2,6-trimethyl-2-heptenoate and the Δ^3 isomer contained 84% of the conjugated isomer whereas the equilibrium mixture of ethyl 2-methyl-4-ethyl-2-hexenoate and the

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