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The Elimination Orientation in the Fluoride-promoted Olefin Formation. A Comparison with the Alkoxide-promoted Eliminations[1]

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When the 2-butyl and 2-pentyl derivatives were treated with tetraethylammonium fluoride in acetonitrile, an olefin-forming elimination took place and an overwhelming Saytzeff orientation was observed. The relative yield of 1-olefin was little affected by changes in the leaving group and β-alkyl group. These results were compared with the results of the eliminations with the conventional base-solvent systems (EtO^- in EtOH, t-BuO^- in t-BuOH, and t-BuO^- in DMSO).

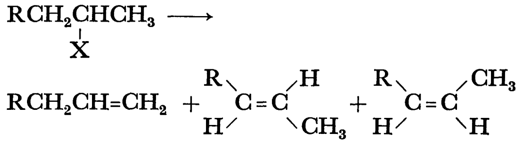
Directive effects in elimination reactions have been well documented.[2] Recently, the transition state of the E2 reaction has attracted the interest of many workers. Brown[3] has shown that the Hoffmann-rule product increases with an increase in the steric requirements of the attacking base, of the alkyl group in the incipient double bond, or of the leaving group. Some results contradicting Brown's explanation have also been presented.[4-8] Bunnett[4-6] has explained the orientation rule by the variable-transition-state theory. According to this theory, a positional orientation correlates with the relative degree of the breaking of the C_β-H and C_α-X bonds in the transition state.

Nearly all of the results cited above have been obtained in studies where alkoxides were used as the base. A thorough investigation of other base-solvent effects is worthwhile in order to elucidate the fine aspects of the mechanism of the olefin-forming elimination reaction.

In previous papers,[9-12] it has been reported that tetraethylammonium fluoride behaves as a strong base in dipolar aprotic solvents, and that styrene and substituted styrenes were produced in high yields in the E2 reaction of 2-arylethyl halides. The fluoride-induced eliminations were considered to proceed through a very tight transition state where the β-proton is less than half transferred to the base.[11] This fact indicates that the fluoride ion plays an interesting role in the β-eliminations from 2-alkyl derivatives. In the present paper, the orientation of the fluoride-induced eliminations from 2-alkyl derivatives will be determined, and the results will be compared with those of alkoxide-induced reactions.

Results and Discussion

The reactions were carried out at 50°C with a base that has a molar ratio to the substrate of two to one. To prevent the isomerization of the olefinic products during the eliminations, a constant stream of dry nitrogen was bubbled through the reaction mixture and the products were collected at −76°C in a cold trap containing a few milliliters of dimethylformamide. Using gas-liquid partition chromatography (glpc), the relative proportions of the isomeric olefins obtained in the eliminations from 2-alkyl derivatives (Eq. (1)) have been determined.



$$\mathrm{RCH_2\underset{X}{C}HCH_3} \longrightarrow$$

$$\mathrm{RCH_2CH{=}CH_2} + \begin{matrix}\mathrm{R} & & \mathrm{H}\\ & \mathrm{C{=}C} & \\ \mathrm{H} & & \mathrm{CH_3}\end{matrix} + \begin{matrix}\mathrm{R} & & \mathrm{CH_3}\\ & \mathrm{C{=}C} & \\ \mathrm{H} & & \mathrm{H}\end{matrix} \qquad (1)$$

R=Me, Et X=Cl, Br, I, OTs

The results, together with the results for the reactions with ethoxide in ethanol, t-butoxide in t-butanol, and t-butoxide in dimethylsulfoxide (DMSO), are summarized in Table 1. Most of the data with alkoxide ions are taken from earlier papers. For convenience in comparing these results, these data are presented graphically in Figs. 1—4. The changes in the 1-olefin/2-olefin ratio in the eliminations from 2-butyl and 2-pentyl derivatives are plotted *versus* the change in the leaving group (X) in Figs. 1 and 2. Similar plots for 2-alkyl bromides and tosylates *versus* the change in the alkyl group (R) attached to the β-position to the leaving group are shown in Figs. 3 and 4. The scales of the abscissae are arbitrary, but are chosen so that the straight line is obtained for the reaction with ethoxide in ethanol.

A previous report[11] from this laboratory showed that the 2-arylethyl derivatives underwent fluoride-induced E2 reaction in the acetonitrile solvent. For example, the reaction of 2-arylethyl chloride followed second-order kinetics, first-order in tetraethylammonium fluoride and first-order in the substrate. The Hammett $\sigma\ \rho$ relation was established with ρ equal to 2.033, k_0

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1) Presented at the 23rd Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1970.

2) a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry 2nd Edition," Cornell Univ. Press, Ithaca, New York (1969), p. 649. b) D. V. Banthorpe, "Elimination Reaction," Elsevier Publishing Co., London (1963).

3) H. C. Brown and R. L. Kilimisch, *J. Amer. Chem. Soc.*, **88**, 1425 (1966), and preceding papers.

4) R. A. Bartsch and J. F. Bunnett, *ibid.*, **90**, 408 (1968).

5) R. A. Bartsch and J. F. Bunnett, *ibid.*, **91**, 1376 (1969).

6) R. A. Bartsch and J. F. Bunnett, *ibid.*, **91**, 1382 (1969).

7) D. H. Froemsdorf and M. E. McCain, *ibid.*, **87**, 3983 (1965).

8) D. H. Froemsdorf, M. E. McCain, and W. W. Wilkison, *ibid.*, **87**, 3984 (1965).

9) J. Hayami, N. Ono and A. Kaji, *Tetrahedron Lett.*, **1968**, 1385.

10) J. Hayami, N. Ono, and A. Kaji, *ibid.*, **1970**, 2727.

11) J. Hayami, N. Ono, and A. Kaji, This Bulletin, 44 (1971) in Press.

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being 3.89×10^{-3} l/mol sec at 25°C. The kinetic isotope effect was also determined, k_H/k_D being 3.99. In the present instances, no butene was obtained in the reaction of 2-butyl iodide in the acetonitrile solvent, even in the presence of tetraethylammonium perchlorate. There is little possibility that the E1 mechanism is operative in the present instances of the olefin-forming eliminations.

The outstanding features of the fluoride-induced elimination reaction are clearly shown in Figs. 1—4. The changes in the leaving groups and alkyl groups had essentially no effect upon the orientation of elimination from 2-alkyl derivatives. These is a definite predominance of the Saytzeff orientation, the ratio of the 1-olefin to 2-olefin ranging from 0.10 to 0.16. Bartsch[16] has reported the orientation in the elimination from 2-alkyl halides induced with halide ions in demethylformamide and DMSO. He has reported the Saytzeff orientation in the reaction of 2-butyl halides with fluoride, but his fluoride is not free of water, and, therefore, there may be trouble in discussing the nature of the base-solvent system. As has been reported earlier,[9,12] the presence of two molar equivalents of water in the fluoride-acetonitrile system reduced the reactivity drastically.

The explanations that have been postulated for the base-solvent effect upon the orientation of the elimination reaction fall into two categories. One is that the size of the attacking bases affects the orientation of

Table 1. Products from the eliminations of RCH_2CHXCH_3

R	X	Base	Solvent	Temp. C°	Olefin composition % 1-olefin	*trans*-2	*cis*-2
CH_3	I	F^-	CH_3CN	50	10.3	71.2	18.5
CH_3	Br	F^-	CH_3CN	50	11.6	68.9	19.5
CH_3	Cl	F^-	CH_3CN	50	11.6	67.7	20.7
CH_3	OTs	F^-	CH_3CN	50	13.7	55.4	30.9
CH_3	I	EtO^-	EtOH	reflux	9.9	65.3	24.8
CH_3	Br	EtO^-	EtOH	reflux	18.0	61.1	20.9[a]
CH_3	Cl	EtO^-	EtOH	reflux	23.8	58.5	17.7
CH_3	OTs	EtO^-	EtOH	55	35	43	22[b]
CH_3	I	*t*-BuO^-	DMSO	25	19.6	62.4	18.0[c]
CH_3	Br	*t*-BuO^-	DMSO	25	31.5	54.1	14.4[c]
CH_3	Cl	*t*-BuO^-	DMSO	25	41.2	47.2	11.6[c]
CH_3	OTs	*t*-BuO^-	DMSO	55	61	28	11[b]
CH_3	I	*t*-BuO^-	*t*-BuOH	50	33.8	44.3	21.9[d]
CH_3	Br	*t*-BuO^-	*t*-BuOH	50	53.4	27.7	18.9[d]
CH_3	Cl	*t*-BuO^-	*t*-BuOH	50	68.3	17.7	13.8[d]
C_2H_5	I	F^-	CH_3CN	50	10.3	76.5	13.2
C_2H_5	Br	F^-	CH_3CN	50	12.4	74.1	13.5
C_2H_5	Cl	F^-	CH_3CN	50	12.8	70.8	16.4
C_2H_5	OTs	F^-	CH_3CN	50	14.2	55.6	30.2
C_2H_5	I	EtO^-	EtOH	reflux	19.3	65.2	15.5[e]
C_2H_5	Br	EtO^-	EtOH	reflux	24.2	58.9	16.9[f]
C_2H_5	Cl	EtO^-	EtOH	reflux	36.2	51.6	13.6[e]
C_2H_5	OTs	EtO^-	EtOH	55	42	38	20[b]
C_2H_5	I	*t*-BuO^-	DMSO	50	23.6	60.7	15.7
C_2H_5	Br	*t*-BuO^-	DMSO	50	43.5	46.8	9.7[g]
C_2H_5	OTs	*t*-BuO^-	DMSO	50	70.1	22.9	7.0[h]
C_2H_5	I	*t*-BuO^-	*t*-BuOH	50	55.0	33.8	9.2
C_2H_5	Br	*t*-BuO^-	*t*-BuOH	50	81.2	12.0	6.8[g]

a) Ref. 8 gives 19%, 62%, 19%.
b) Data from Ref. 7.
c) Data from Ref. 13.
d) Data from Ref. 3.
e) Data from Ref. 14.
f) Ref. 14 gives 24.6%, 59.0%, 16.4%.
g) Data from Ref. 15.
h) Ref. 7 gives 72%, 21.4%, 6.6%.

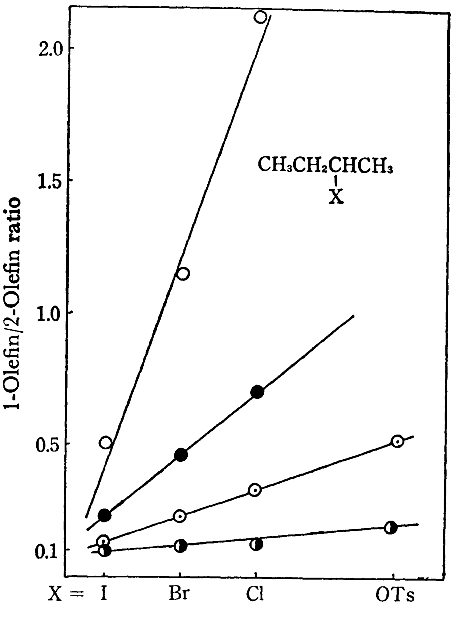

Fig. 1. 1-Olefin/2-Olefin ratio in the eliminations from 2-butyl derivatives.
○ *t*-BuO^- in *t*-BuOH, ● *t*-BuO^- in DMSO, ⊙ EtO^- in EtOH ◑, F^- in CH_3CN

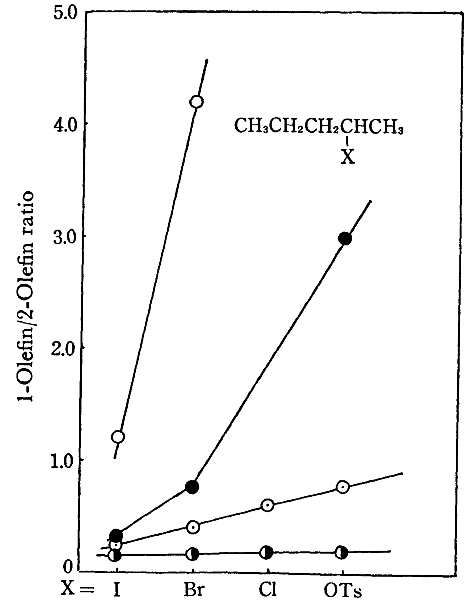

Fig. 2. 1-Olefin/2-Olefin ratio in the eliminations from 2-pentyl derivatives.
○ *t*-BuO^- in *t*-BuOH, ● *t*-BuO^- in DMSO, ⊙ EtO^- in EtOH, ◑ F^- in CH_3CN

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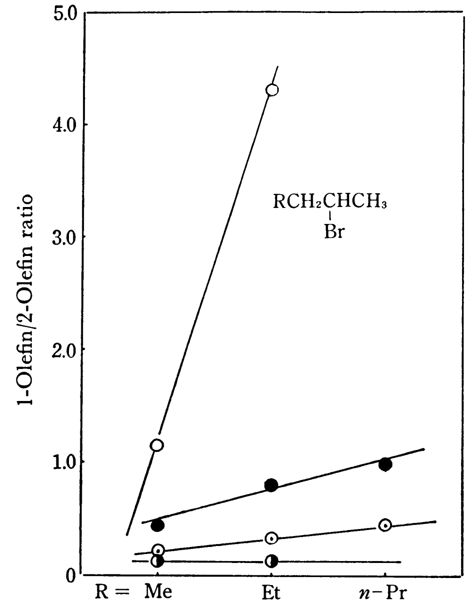

Fig. 3. 1-Olefin/2-Oelefin ratio in the eliminations from 2-alkyl bromides.
○ t-BuO$^-$ in t-BuOH, ● t-BuO$^-$ in DMSO, ⊙ EtO$^-$ in EtOH, ◑ F$^-$ in CH_3CN
R=n-Pr: from Refs. 5 and 6

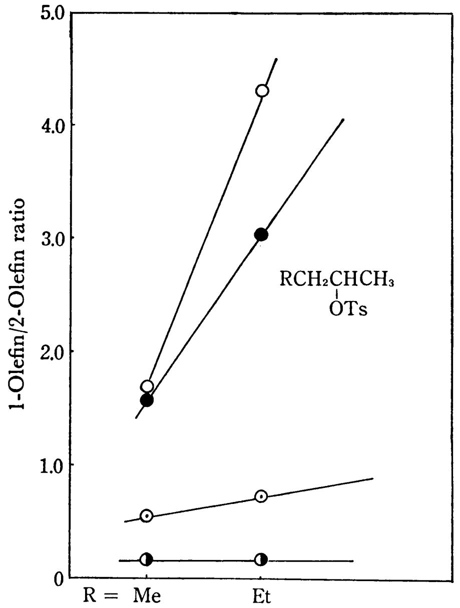

Fig. 4. 1-Olefin/2-Olefin ratio in the eliminations from 2-alkyl tosylates.
○ t-BuO$^-$ in t-BuOH, ● t-BuO$^-$ in DMSO, ⊙ EtO$^-$ in EtOH ◑ F$^-$ in CH_3CN

the elimination, and the other is that the base strength affects the orientation of the elimination. Brown[3] has proposed that, in the absence of significant steric interaction, the reaction proceeds to form the more stable of the two possible olefins; however, an increase in the steric requirement of the attacking base and the environment should tend to shift the course of the reaction from the Saytzeff toward the Hoffmann elimination. On the other hand, Bunnett[5] and also, Froemsdorf[7,8] have proposed that an increase in the Hoffmann elimination is attributable to the carbanion character in the transition state induced by an increase in the base strength, the "poorer" leaving group also assisting the carbanion character.

The explanation based on the base strength is not adequate to explain the present results in the light of the following facts. First, the variations in the olefin proportion in each of the figures (Figs. 1—4) are smallest for the elimination with the fluoride ion in acetonitrile and are intermediate for the reactions with ethoxide in ethanol, and with t-butoxide in DMSO, and are largest for the reaction with t-butoxide in t-butanol. These orders scarcely correlate at all with the reactivity of the base.[17] Second, in the eliminations from 2-alkyl derivatives with t-butoxide in t-butanol, more 1-olefin is produced than in the same reactions with the stronger base, t-butoxide in DMSO. Third, as Saunders[19] has pointed out, in a reaction of 2-arylethyl-ammonium bromides, the kinetic isotope effect and the substituent effect indicate a distinctly less carbanion character for the reaction with t-butoxide in t-butanol than for that with ethoxide in ethanol, although the relative yield of 1-olefin increases on the change from ethoxide in ethanol to t-butoxide in t-butanol for the reactions of 2-alkyl derivatives. It may be concluded, therefore, that the change in the apparent base strength does not play any major role in altering the olefin proportion in the present reactions.

In explaining the present results, the role of the steric requirements of the entities attacking the substrate should be taken into account. As Brown[3] has pointed out, solvation, both of the attacking base and of the leaving group, must be considered in estimating their steric requirements and their influence on the direction of elimination. Considering the anion solvation, it is quite plausible that the fluoride ion in acetonitrile has the smallest steric requirement, and that the t-butoxide ion in t-butanol has the largest steric requirement, among the four base-solvent systems.[20] The largest change in the 1-olefin/2-olefin ratio is observed in the reactions induced by t-butoxide in t-butanol, because this base-solvent system has the largest steric requirement. When the steric requirements of the attacking entities become smaller, the attacking entities should become less sensitive to smaller changes in the steric requirements of the environment (the leaving group the alkyl group, and solvation), and *vice versa*. As a result of this steric interrelation, the more stable Saytzeff-type product definitely predominates and the changes

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[17] The relative reactivity of the base increases from the alkoxide ion in alcohol to the fluoride ion in acetonitrile to the alkoxide ion in DMSO. Tetraethylammonium fluoride in acetonitrile is about 800 times as effective as sodium ethoxide in ethanol in promoting the E2 reaction from 2-phenylethyl chloride at 25°C,[10,11] and t-butoxide in DMSO is several times stronger than fluoride in acetonitrile.[18]

[18] A. F. Cockerill, S. Rottschaefer, and W. H. Saunders, Jr., *J. Amer. Chem. Soc.*, **89**, 901 (1967).

[19] W. H. Saunders, Jr., D. G. Bushman, and A. F. Cockerill, *ibid.*, **90**, 1775 (1968).

[20] It is uncertain which has the larger steric requirement, the ethoxide ion in ethanol or the t-butoxide ion in DMSO; however, the results in Figs. 1—4 are suggestive and can be correlated with steric requirements better than with the reactivities of the attacking entities.

in the leaving groups and alkyl groups have little effect on the orientation in the fluoride-induced eliminations.

The data in Table 1 also reveal interesting changes in the *trans*-2-olefin/*cis*-2-olefin ratios with the solvents. High *trans/cis* ratios of about 4—5 are observed in dipolar aprotic solvents; on the contrary, smaller *trans/cis* ratios of about 1—2 are observed in *t*-butanol. Bartsch and Bunnett have reported similar results.[6] A high *trans/cis* ratio of about 5 was observed in the reaction of 2-hexyl halides with *t*-butoxide in DMSO, and a *syn*-elimination stereochemistry was postulated. However, the possibility of the intervention of *syn*-elimination has been ruled out recently by an experiment with erythro-3-deutero-2-bromobutane.[21] The *trans/cis* ratios have been interpreted as indicating the extent of the double-bond character in the transition states.[5,6]. However, at present no direct relationship between the 1-olefin/2-olefin ratio and the *tran/cis* ratio has been found for the reactions discussed above.[6,22] The reason for the high *trans/cis* ratio in dipolar aprotic solvents is hard to find and needs to be studied further.

Experimental

Materials. *2-Alkyl Halides*: The 2-butyl halides were either commercial samples or were prepared from alcohols by the usual method. 2-Pentyl iodide was prepared analogously to the procedure used for Coe[23]: 2-pentanol (25 g) was added, drop by drop, to triphenylphosphite diiodide (from 76 g of iodine and 100 g of triphenyl phosphite); the mixture was then kept at room temperature for 30 min. Two distillations gave 2-pentyl iodide (11 g, 20%); bp 55°C/50mmHg (lit,[24] 139—142°C). 2-Pentyl bromide was prepared by a procedure similar to that used for 2-pentyl iodide except that bromine was used instead of iodine. 2-Pentyl chloride was prepared by the method of Whitmore and Karnatz[25] from 2-pentanol, pyridine, and thionyl chloride. Two distillations gave a material with a bp of 94—96°C (lit,[14] 96°C). These 2-pentyl halides were shown to be free of isomers by glpc.

2-Alkyl Tosylates: The tosylates were prepared in the usual fashion[26] by treating the alcohols with freshly-recrystallized *p*-tolueneuslfonyl chloride in dry pyridine. After having been stored in a refrigerator for one day, the mixture was poured onto ice and dilute sulfuric acid, and extracted with methylene chloride. After washing and drying, the solvent was replaced by hexane and the solution was treated with charcoal. The hexane was then removed at reduced pressure, leaving a pale yellow liquid.

Base and Solvent. The solvents were purified by the usual method. The tetraethylammonium fluoride was prepared by a method reported previously.[12]

Elimination Products from Reactions of 2-Alkyl Derivatives. The reactions of 2-alkyl derivatives with Et_4NF in acetonitrile were performed as follows. In a typical case, 2-butyl iodide (1.8 g, 0.01 mol) was treated with 3 g (0.02 mol) of Et_4NF in 30 m*l* of acetonitrile at 50.0°C. Volatile products were bubbled out of the reaction vessel with a slow nitrogen stream in order to minimize the isomerization of the olefins. The products were then collected at −76°C in a cold trap containing a few milliliters of dimethylformamide and were then analyzed by glpc. Gas-liquid partition chromatographic analyses were performed with a Yanagimoto GCG-5DH instrument. Activated alumina was used as the solid support; the three isomers of butene or pentene were thus successfully separated at an ambient temperature on a 6 m × 3 mm dimethylformamide column (40%).

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22) Bartsch has recently found the same trend in several dipolar aprotic solvents, high *trans/cis* ratios of 3.0—4.0, which are independent of the percentage of 1-olefin, but no reasonable explanation of it has been found (R. A. Bartsch, private communication).

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