THE NOVEL ORIENTATION IN THE FLUORIDE PROMOTED ELIMINATION REACTIONS.
THE EFFECT OF THE VARIOUS BASE SYSTEMS UPON THE ORIENTATION OF THE BASE-CATALYZED
OLEFIN FORMATION.

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The recent publication by Bartsch (1) on the base-catalyzed elimination from 2-alkyl bromides prompts the authors to report at this time the results of their investigation on the elimination reaction promoted by the varieties of bases.

The previous communication from this laboratory (2) upon the quarternary ammonium fluoride capable of promoting the stable carbanion formation, α-elimination, and β-elimination had clearly shown that the fluoride anion in the dipolar aprotic solvents furnishes a strong base system which had a potential utility in the study of organic reaction mechanism.

In fact, tetraethylammonium fluoride (I) is about 800 times as effective as sodium ethoxide in ethanol in promoting the E2 reaction from β-phenylethyl chloride, the second order rate constants being 3.89×10^{-3} and 4.5×10^{-6} 1/mole.sec. at 25°C respectively (3). The very interesting features of the fluoride promoted elimination were shown by the small kinetic isotope effect (k_H/k_D = 3.99 for β-phenylethyl chloride) and also by the very low k_{OTs}/k_{Br} ratio of 0.027 for β-p-tolylethyl derivatives (3),(4).

These features strongly suggest that the very tight transition state should be taken in the E2 reaction promoted by I in the dipolar aprotic solvents and also may promise an interesting role in the E2 reaction from 2-alkyl systems. The results presented in the present communication vindicated the outstanding features of the new base system.

The treatment of the 2-butyl derivatives (IIa--d, a; X = I, b; X = Br, c; X = Cl, d; X = OTs) and of the 2-pentyl derivatives (IIIa--d, a; X = I, b; X = Br, c; X = Cl, d; X = OTs) with I in acetonitrile gave rise to the mixture of olefins where Saytzeff products predominate.

In the typical experiment, 1.8g. (0.01 mole) of IIa was treated with 3g. (0.02 mole) of I in 30ml. of acetonitrile at 50.0°C. Volatile products were bubbled out of the reaction vessel with the slow nitrogen stream to minimize the isomerization of the olefins. The products were collected at -76°C in a cold trap containing few ml. of DMF and were analyzed by glc (5). The results are summarized in the Tables.

Similar experiments were undertaken with sodium ethoxide in ethanol and the 1-butene to 2-butene ratios obtained are plotted in Figure 1., some points are taken from the relevant reports by Saunders (6) and by Brown (7). Figure 2 shows similar results from IIIa--d.

The general trends for the base system t-BuOK--t-BuOH, t-BuOK--DMSO, and EtONa--EtOH are in accord with the reported results, the 1-olefin/ 2-olefin ratios increase steadily for the change of the leaving group from iodide, through bromide and chloride, to tosylate (8). In contrary, the outstanding feature of the fluoride promoted elimination reaction is clearly

shown in these figures. The change of the leaving groups gave essentially no effect upon the orientation of elimination from the 2-alkyl derivatives. There is a definite predominance of the Saytzeff orientation, the ratios of the 1-olefin to 2-olefin are in the range of 0.10 to 0.16.

The present results suggest that the change of the 1-olefin to 2-olefin ratio with the change in the base system may be rationalized in terms of the steric requirement of the attacking entities upon the substrate rather than in terms of the relative reactivities of the base (9). The detailed discussion of the role of the base system upon the change of the orientation rule will be given in the forthcoming paper.

<div align="center">References</div>

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3) Abstracts of Papers, III-1649, 22nd Annual Meeting of the Chemical Society of Japan, Tokyo, April 1969. The values for EtONa was calculated by extraporation from other temperatures.

4) G. M. Fraser and H. M. R. Hoffmann, J.Chem. Soc.,(B) 265 (1967).

5) 3mm$\times$6m column of 40% DMF--activated alumina at room temperature.

6) W. H. Saunders, S. R. Fahrenholtz, E. A. Caress, J. P. Lowe and M. Schreiber, J. Amer. Chem. Soc., 87, 3401 (1965).

7) a) H. C. Brown and R. L. Klimisch, ibid., 88,1425 (1966).

   b) D. L. Griffith, D. L. Meges and H. C. Brown, Chem. Commun., 90 (1968).

8) R. A. Bartsch and J. F. Bunnett, J. Amer. Chem.Soc., 90, 408 (1968); 91, 1376, 1382 (1969).

9) The order of the relative reactivities of these bases are t-BuOK--DMSO > I--acetonitrile > EtONa--EtOH ≧ t-BuOK--t-BuOH. C.f. H. C. Brown et al., J. Amer. Chem. Soc., 78, 2196 (1956).

Elimination from 2-BuX

$2\text{-BuX}+\text{F}^{-} \xrightarrow[50.0°]{CH_3CN}$ Butenes

X	1-Butene (%)	2-Butene trans(%)	cis(%)
I	10.3	71.2	18.5
Br	11.6	68.9	19.5
Cl	11.6	67.7	20.7
OTs	13.7	55.4	30.9

Elimination from 2-Pent.X

$2\text{-Pent X}+\text{F}^{-} \xrightarrow[50.0°]{CH_3CN}$ Pentenes

X	1-Pentene(%)	2-Pentene trans(%)	cis(%)
I	10.3	76.5	13.2
Br	12.4	74.1	13.5
Cl	12.8	70.8	16.4
OTs	14.2	55.6	30.2