

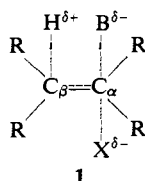
nine-atom class is being studied with substituted polyhedral boranes.

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 Received January 18, 1969

Evidence against the Putative E2C Mechanism of Olefin-Forming Elimination

Sir:

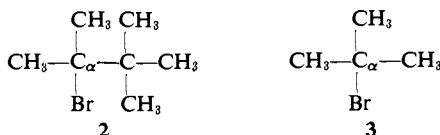
It has been known since 1956 that certain anions which are comparatively weak as bases toward hydrogen are quite effective in provoking elimination from alkyl halides and arenesulfonates.^{1,2} Examples are mercaptide ions in alcohols and chloride ion in acetone. These are strong nucleophiles toward carbon, and some authors have attributed their surprising efficacy as elimination reagents to partial covalent interaction of the base (nucleophile) with C_α in the transition state.²⁻⁵ Transition states such as **1** have been suggested, and this



sort of mechanism has been dubbed "E2C."⁴

However, other workers have argued from experimental evidence against such explanations.^{7,8}

Any mechanism which required covalent interaction of the base (nucleophile) with C_α in order to make the transition state energetically accessible should be sensitive to steric hindrance of C_α. In 2-bromo-2,3,3-trimethylbutane (**2**), C_α is both tertiary and neopentyl, and thus exceptionally shielded from nucleophilic attack.



We have studied the kinetics of chloride ion induced olefin-forming elimination from **2** and from *t*-butyl bromide (**3**), in acetone and in 1,4-dioxane. Structurally, the difference between **2** and **3** is analogous to the difference between ethyl and neopentyl bromides. Ethyl bromide is 240,000 times more reactive than neopentyl bromide in S_N2 reactions with NaOC₂H₅ in ethanol,⁹ and 38,000 times more reactive with lithium chloride in acetone;¹⁰ these data suggest the extent to

(1) P. B. D. de la Mare and C. A. Vernon, *J. Chem. Soc.*, 41 (1956).

(2) S. Winstein, D. Darwish, and N. J. Holness, *J. Amer. Chem. Soc.*, **78**, 2915 (1956).

(3) D. N. Kevill, G. A. Coppens, and N. H. Cromwell, *J. Org. Chem.*, **28**, 567 (1963).

(4) A. J. Parker, M. Ruane, G. Biale, and S. Winstein, *Tetrahedron Lett.*, 2113 (1968).

(5) The early hypothesis of "merged substitution and elimination"² is abandoned in recent publications of Winstein.^{4,6}

(6) S. Winstein, "Chimica Teorica," Accademia Nazionale dei Lincei, Rome, Italy, 1965, p 327.

(7) D. J. McLennan, *J. Chem. Soc., B*, 705, 709 (1966).

(8) J. F. Bunnett and E. Baciocchi, *J. Org. Chem.*, **32**, 11 (1967).

(9) I. Dostrovsky and E. D. Hughes, *J. Chem. Soc.*, 157 (1946).

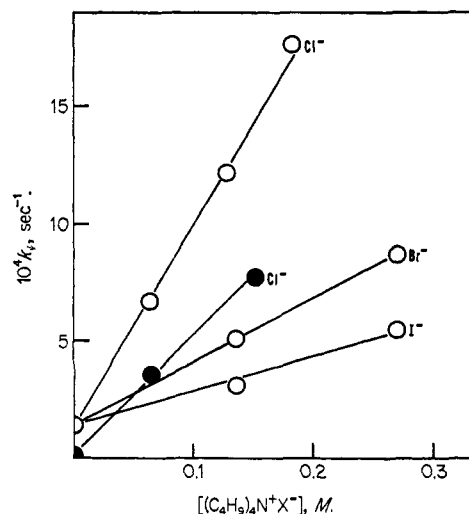


Figure 1. Pseudo-first-order rate coefficients for elimination from **2** (open circles) and from **3** (filled circles), in acetone solution at 69.9°, as functions of tetrabutylammonium halide concentration. The halide ions involved are indicated.

which **2** should undergo elimination more slowly than **3** if the E2C mechanism prevailed.

In our rate studies, **2** or **3** (*ca.* 0.02 M) was allowed to react with excess tetrabutylammonium chloride, bromide, or iodide in dry acetone or dioxane in the presence of sufficient 2,6-lutidine to neutralize the hydrogen halide generated in the elimination reaction.^{4,6} The progress of reaction was followed by acid-base titration. Good linear kinetic plots were obtained. The olefin from **2** was in all cases 2,3,3-trimethyl-1-butene.

The results for acetone solvent at 69.9° are presented in Figure 1. Rates of reaction of both substrates with chloride ion increase linearly with R₄N⁺Cl⁻ concentration; the slopes represent second-order rate coefficients and are 8.8 × 10⁻³ M⁻¹ sec⁻¹ for **2** and 5.20 × 10⁻³ M⁻¹ sec⁻¹ for **3**.¹¹ Thus the highly hindered substrate is actually more reactive than the less hindered one, by a factor of nearly two. Also, it is noteworthy that the halide ions stand in the reactivity order: Cl⁻ > Br⁻ > I⁻.¹²

The results for dioxane solvent at 69.9° are shown in Figure 2. The picture is substantially the same as in acetone. The second-order rate coefficients (for reaction with (C₄H₉)₄N⁺Cl⁻) are 3.92 × 10⁻³ M⁻¹ sec⁻¹ for **2** and 2.44 × 10⁻³ M⁻¹ sec⁻¹ for **3**. Again, the highly hindered **2** reacts nearly twice as fast as *t*-butyl bromide.

Solvolysis rates (which are independent of 2,6-lutidine concentration) are low in acetone and particularly low in dioxane. In both solvents, solvolysis of **2** is about tenfold faster than of **3**; rate coefficients are 1.42 × 10⁻⁴ sec⁻¹ for **2** and 0.16 × 10⁻⁴ sec⁻¹ for **3** in acetone; in dioxane, they are 6.5 × 10⁻⁶ sec⁻¹ for **2** and 0.61 × 10⁻⁶ sec⁻¹ for **3**. The greater solvolytic reactivity of **2** in both solvents is attributed to steric acceleration, arising from compressions in **2** between the bromine atom and methyl groups.

(10) E. D. Hughes, C. K. Ingold, and J. D. H. Mackie, *ibid.*, 3173 (1955).

(11) Winstein⁶ reports that reaction of **3** with chloride ion at 50° gives *ca.* 3% *t*-butyl chloride.

(12) Ion pairing for tetrabutylammonium halides in acetone is much less than for alkali metal halides: S. Winstein, L. G. Savedoff, S. Smith, I. D. R. Stevens, and J. S. Gall, *Tetrahedron Lett.*, No. 9, 24 (1960).

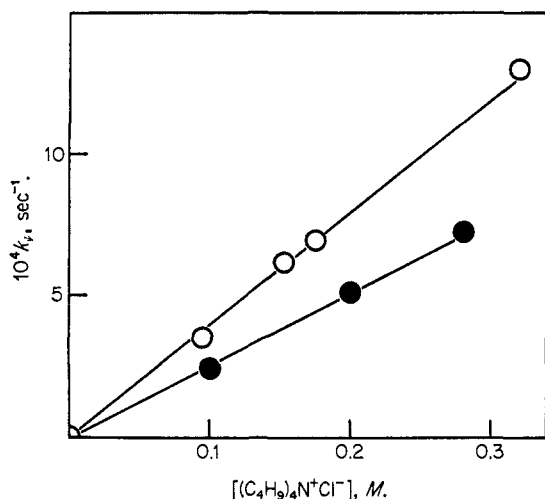


Figure 2. Pseudo-first-order rate coefficients for elimination from **2** (open circles) and from **3** (filled circles), in 1,4-dioxane at 69.9°, as functions of tetrabutylammonium chloride concentration.

The fact that rates of chloride ion induced elimination are greater for the more hindered substrate is probably also to be ascribed to steric acceleration. If the transition-state geometries for solvolysis and bimolecular elimination were the same in the vicinity of bromine (which they probably are not), and if there were no steric hindrance of chloride ion attack, **2** ought to have reacted about ten times faster than **3** in bimolecular elimination. Inasmuch as it actually reacted only about twice as fast, the extent of steric retardation caused by changing from **3** to **2** is crudely estimated as fivefold. This is reasonable if the chloride ion attacks β -H in the elimination transition state, but steric retardation should have depressed the rate by several powers of ten if covalent interaction of chloride ion with C_α were requisite.

Thus, a specific prediction of the "E2C" mechanism fails to be fulfilled. We conclude that chloride ion, as an elimination-inducing base, does not need closely to approach C_α in the transition state. Inasmuch as the "E2C" mechanism fails to meet this crucial test, and in view of the absence of compelling evidence in support of it, we feel that the notion should be discarded.

Acknowledgment. This research was supported in part by a grant from the Petroleum Research Fund, administered by the American Chemical Society.

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Received February 24, 1969

Identification of an Intermediate Common to Mechanisms S_N2 and E2¹

Sir:

Historically mechanisms [S_N2 and E2, bimolecular nucleophilic substitution and elimination, although often observed concurrently, have been interpreted separately as distinct modes of reaction, the one initiated by nucleophilic attack on carbon and the other by attack on hydrogen. We herein report evidence that

(1) Supported in part by the National Science Foundation.

these mechanisms, as operative in the reactions of α -phenylethyl bromide with sodium ethoxide in solvent ethanol, share a common ion-pair intermediate.

Before the theory is developed it is desirable to establish that, in fact, the kinetic behavior of α -phenylethyl bromide under these conditions is extraordinary. It will later be established that the data are consistent with an ion-pair mechanism.

In particular, as is evident from Table I, the second-order rate "constant" for the reaction of α -phenylethyl bromide with ethoxide² decreases by a factor of greater than two on passing from 0.114 M to 0.533 M base. On the other hand the model substrate, ethyl bromide, under these conditions shows a modest decrease of only 17% over approximately the same concentration range, and this latter behavior appears to be fairly typical.³ Thus there would appear to be something unique about the α -phenylethyl bromide system.

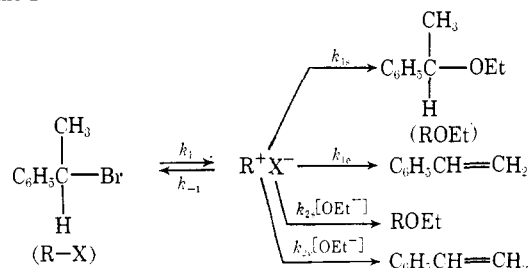
Table I. Comparison of Observed and Predicted Rate Constants in Ethanol at 50°

[NaOEt], M	k _{obsd} , ^a sec ⁻¹ × 10 ⁵	k ₂ , ^b l. mole ⁻¹ sec ⁻¹ × 10 ⁴	k _{ip} , ^c sec ⁻¹ × 10 ⁶	k _{SN2} , ^d sec ⁻¹ × 10 ⁵
	11.3 ± 0.3			
0.114	35.4 ± 1.0	21.1	28.8	36.2
0.121	35.7 ± 1.1	20.2	29.6	36.7
0.533	65.7 ± 1.9	10.2	59.6	123
0.686	74.8 ± 0.7	9.2	65.0	150
1.07 ^e	98 ± 7	8.2	75.6	236
∞			106	∞

^a Experimentally observed pseudo-first-order rate constant. ^b Calculated from the equation $k_{\text{obsd}} = k_1 + k_2[\text{OEt}^-]$. ^c Calculated from eq 10 with $a = 0.018$, $b = 0.500$, $y = 12.5$, and $x = 8.5$. ^d Calculated from eq 10 with $a = 0.018$, $b = 0.500$, $y = 12.5$, and $x = \infty$. ^e Average of three separate runs.

The experimental approach chosen to implicate such a common ion-pair intermediate recognizes that certain quantitative relations between rates of reaction and product distributions as a function of sodium ethoxide concentration, assuming such a mechanism, must necessarily exist. Scheme I is consistent with our experimental observations.

Scheme I



According to this scheme the ratio, R , of styrene to α -phenylethyl ethyl ether is given by eq 1.

$$\frac{[\text{styrene}]}{[\alpha\text{-phenylethyl ethyl ether}]} = R = \frac{k_{1e} + k_{2e}[\text{OEt}^-]}{k_{1s} + k_{2s}[\text{OEt}^-]} \quad (1)$$

(2) Calculated from the equation $k_{\text{obsd}} = k_1 + k_3[\text{OEt}^-]$.

(3) See for example, D. J. Cram, F. D. Greene, and C. H. Depuy, *J. Am. Chem. Soc.*, **78**, 790 (1956).