

Kinetics of Olefin-Forming Elimination from Benzyldimethylcarbinyl Halides Induced by Halide Ions in Acetone^{1,2}

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Rates and product ratios of reactions of benzyldimethylcarbinyl chloride (Ia) and bromide (Ib) with tetra-butylammonium chloride, bromide, and iodide in dry acetone, to form β,β -dimethylstyrene (II) and 2-methyl-3-phenyl-1-propene (III), are determined. Alkyl bromide Ib is about 1000-fold more reactive than alkyl chloride Ia, chloride ion is about 10-fold more reactive than bromide ion, and iodide ion is still less reactive. From either substrate, about 86% II is formed with Cl⁻ and about 78% with Br⁻. Differences in reactivity between the alkyl halides stem largely from changes in ΔH^\ddagger , but differences between chloride and bromide ions arise mainly from changes in ΔS^\ddagger . The pattern of kinetic effects is quite similar to that observed by other workers for reactions of 2-halo-2-benzyl-4,4-dimethyl-1-tetralones with halide ions in acetonitrile. Various types of evidence concerning eliminations of this type seem best accommodated by a more or less conventional E2 transition state with a large degree of C=C double-bond character and considerable synchronization of C α -X and C β -H rupture.

Part A

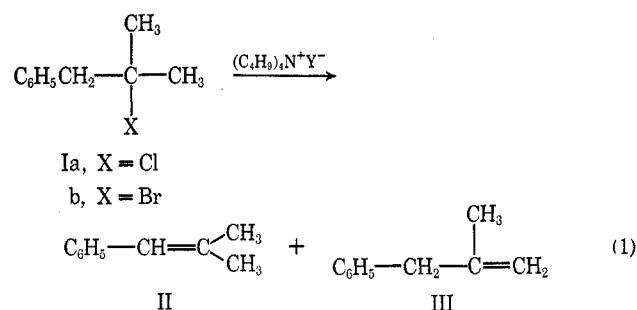
Halide ions in acetone solution are surprisingly effective in bringing about olefin-forming elimination from secondary and tertiary alkyl halides and arene-sulfonates. This was discovered by Winstein and coworkers.⁴ Eliminations of this type have been studied extensively in Winstein's laboratory,⁵ but only a summary⁶ and two communications^{4,7} have been published. Some reports have appeared from other sources.^{8,9} Halide ion induced eliminations in other dipolar, aprotic solvents have also received some attention.^{10,11}

It is a challenge to understand why and how reagents of such low basicity as halide ions are so effective. An early hypothesis took account of the known reactivity of halide ions toward carbon in substitution reactions and postulated that E2 and S_N2 mechanisms may merge, so as to have a common intermediate.⁴ Subsequent stereochemical studies^{5,6} required rejection of this hypothesis. A more recent suggestion, the "E2C" mechanism, also postulates covalent interaction of the base (nucleophile) with C α , as well as with H β , in the transition state.^{7,8} However, it implies that halide ion induced eliminations should be very sensitive to

steric hindrance of C α ; they are not; and it is therefore also dismissed.⁹

Although eliminations from the benzyldimethylcarbinyl system have been studied with other base-solvent combinations,^{12,13} no studies have yet been reported of reactions with halide ions in acetone.

The reactions summarized in Table I were carried out with tetra-*n*-butylammonium halide salts in dry acetone, the salt being in 3- to 12-fold molar excess over the alkyl halide. Excess 2,6-lutidine was present in all runs for the purpose of neutralizing hydrogen halide by-products; it does not affect either rates or olefinic product ratios.⁶ Runs were followed by acid-base titration.



(1) EDITOR'S NOTE.—This article was prepared in two parts as an illustration of a possible division of papers into short and full versions. Part A contains the background, main results, and conclusions which the author considers suitable for a short version. Part B contains experimental details, supplemental data, and discussion; combination of the two parts comprises the full paper. J. A. M.

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

(5) S. Winstein, P. Beltrame, G. Biale, R. Cetina, D. Darwish, S. Smith, I. D. R. Stevens, and J. Takahashi, 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1963, Abstracts, p 8M.

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

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

(8) D. J. Lloyd and A. J. Parker, *ibid.*, 5183 (1968); D. Cook, A. J. Parker, and M. Ruane, *ibid.*, 5715 (1968); D. Cook and A. J. Parker, *J. Chem. Soc., B*, 142 (1968); R. Alexander, E. C. F. Ko, A. J. Parker, and T. J. Broxton, *J. Amer. Chem. Soc.*, **90**, 5049 (1968).

(9) D. Eck and J. F. Bunnett, *ibid.*, **91**, 3099 (1969).

(10) D. N. Kevill, G. A. Coppens, and N. H. Cromwell, *ibid.*, **86**, 1553 (1964), and earlier papers.

(11) D. N. Kevill and J. E. Dorsey, *J. Org. Chem.*, **34**, 1985 (1969); R. A. Bartsch, submitted for publication.

Salient features of the data in Table I are (a) that the alkyl bromide, Ib, is enormously more reactive than the alkyl chloride, Ia, by factors of 2370 with chloride ion reagent and 1320 with bromide ion; (b) that chloride ion is more effective than bromide ion in inducing elimination, by factors of 7.7 with Ia and 12.7 with Ib, which are rather high for this type of reaction; (c) that appreciable amounts of terminal olefin III are formed in all cases, the fraction of III being dependent on the halide ion reagent (ca. 14% with Cl⁻, 22% with Br⁻) but practically independent of the leaving group; and (d) that differences in reactivity between alkyl halides arise mainly from differences in ΔH^\ddagger , while differences in reactivity between halide ions arise mainly from differences in ΔS^\ddagger . Let us now discuss some of these features individually.

(12) J. F. Bunnett, G. T. Davis, and H. Tanida, *J. Amer. Chem. Soc.*, **84**, 1606 (1962).

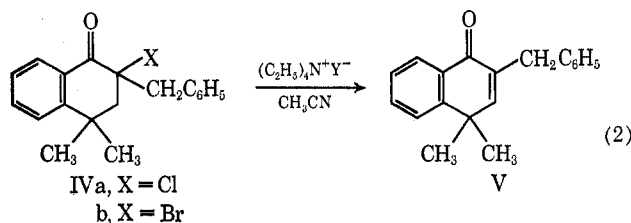
(13) J. F. Bunnett and E. Baciocchi, *J. Org. Chem.*, **32**, 11 (1967); L. F. Blackwell, A. Fischer, and J. Vaughan, *J. Chem. Soc., B*, 1084 (1967).

TABLE I
 REACTIONS OF BENZYLDIMETHYLCARBINYL HALIDES WITH TETRABUTYLAMMONIUM HALIDES IN ACETONE^a

Halide ion of (C ₄ H ₉) ₄ N ⁺ Y ⁻	Temp, °C	k, M ⁻¹ sec ⁻¹	Olefin yields ^b		ΔH [‡] , kcal/mol	ΔS [‡] , gibbs/mol
			II, %	III, %		
Reactions with C ₆ H ₅ CH ₂ C(CH ₃) ₂ Br						
Cl ⁻	29.68	6.86 × 10 ⁻⁴	87.7	12.3	19.8	-7.6
	59.55	1.44 × 10 ⁻²	86.4	13.6		
Br ⁻	29.68	5.44 × 10 ⁻⁵	78.0	22.0	20.4	-11.0
	59.55	1.24 × 10 ⁻³				
I ⁻	29.68	6.79 × 10 ⁻⁶				
Reactions with C ₆ H ₅ CH ₂ C(CH ₃) ₂ Cl						
Cl ⁻	29.68	(2.89 × 10 ⁻⁷) ^b	85.1	14.9	24.9	-6.3
	73.7	6.23 × 10 ⁻⁵				
	100.7	9.00 × 10 ⁻⁴				
Br ⁻	29.68	(4.11 × 10 ⁻⁸) ^b	77.7	22.3	25.0	-9.9
	73.7	9.01 × 10 ⁻⁶				
	100.7	1.30 × 10 ⁻⁴				

^a Initial concentrations were typically alkyl halide, 0.02 M; (C₄H₉)₄NX, 0.1 M; 2,6-lutidine, 0.07 M; see expanded version of this communication for details. ^b Extrapolated from higher temperatures.

(a) In E2 and S_N2 reactions, alkyl bromides commonly react faster than chlorides by 30- to 80-fold, although higher RBr/RCl rate ratios have been reported.¹⁴ The RBr/RCl ratios observed in this work are extraordinarily high, and are approached only by those for reactions of 2-halo-2-benzyl-4,4-dimethyl-1-tetralones IVa and IVb with halide ions in acetonitrile (eq 2), for which the ratios are 1500 with Cl⁻ and 1160 with Br⁻.¹⁰ A high RBr/RCl rate ratio implies a large degree of scission of the C—X bond at the transition state.

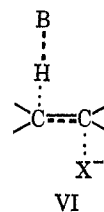


(c) Experiments summarized by Winstein⁶ show halide ion induced eliminations to obey the Saytzeff rule of orientation to an exceptional degree. For example, 3-methyl-2-butyl bromide and tosylate afforded more than 99% 2-methyl-2-butene on reaction with halide ions in acetone. Winstein has tentatively suggested a large degree of C=C double-bond character at the transition state to be responsible for the strong Saytzeff orientation.⁶ In our experiments, the predominance of Saytzeff orientation is less strong. The percentages of II formed in the present work (78% with Br⁻, 86% with Cl⁻, in acetone) are lower than the apparent percentage of II in the equilibrium between II and III (ca. 93%, in methanol¹²).

Our results are remarkably similar to those reported by Kevill, Coppens, and Cromwell¹⁰ for the reactions of eq 2. As mentioned, they also found the alkyl bromide to be enormously more reactive than the alkyl chloride. Moreover, the difference also stemmed largely from differences in ΔH[‡]. Even subtle trends in en-

tropies of activation, some of them scarcely greater than the experimental error, are similar in direction in the two studies, although absolute differences are not the same. These striking resemblances imply a similarity in mechanism, which is remarkable in view of structural differences in the substrates. Ia and Ib have two α-alkyl substituents and a β-phenyl substituent, while IVa and IVb have an α-keto, an α-benzyl, and a β-alkyl substituent. Since these sets of substituents have rather different electronic effects, the similarities in kinetic behavior between the two series imply that C_α and C_β have developed very little electrical charge at the transition state.

Thus various types of evidence suggest a transition state which has (i) a large degree of C—X rupture, (ii) a large degree of C=C double-bond character, (iii) little electrical charge on C_α, and (iv) no close interaction of the base (nucleophile) with C_α. These various specifications seem best met by a more or less conventional E2 transition state, in which C_α—X and C_β—H scission are both quite far advanced and nearly synchronous, and there is a large degree of C=C double-bond character. Such a transition state might be sketched as VI.¹⁵



Certainly one wishes further experimental evidence for this postulate. Also, it remains somewhat obscure why halide ions in acetone are so efficacious as elimination reagents.

We also made a few measurements of the rate of solvolysis of Ia and Ib in 90% acetone-10% methanol; these are reported in Part B.

(14) D. J. McLennan, *J. Chem. Soc., B*, 705 (1966); B. O. Coniglio, D. E. Giles, W. R. McDonald, and A. J. Parker, *ibid.*, 152 (1966).

(15) E. Baciocchi and A. Schioli [*ibid.*, 554 (1969)] have come to a similar conclusion regarding the transition state for iodide ion-induced dehalogenations of 1,2-dibromo-1,2-diarylethanes and related substrates.

Part B
Experimental Section

Materials. Benzylidimethylcarbinyl chloride (Ia) was prepared as previously described.¹² Benzylidimethylcarbinyl bromide (Ib) was prepared from the corresponding carbinol and HBr by the method of Wilt;¹⁶ it had bp 108–109° (14 Torr), n_D^{20} 1.5353, and the expected nmr spectrum. *t*-Butyl bromide was a commercial sample redistilled. Tetrabutylammonium iodide was an Eastman Kodak sample purified by recrystallization from ethyl acetate containing 5% of ethanol: mp 146–147°. Tetrabutylammonium bromide was an Eastman Kodak sample purified by recrystallization from a benzene-petroleum ether mixture: mp 117–118°. *Anal.* Calcd for $C_{16}H_{36}NBr$: Br, 24.79. Found: Br, 24.81. Tetrabutylammonium chloride was obtained by stirring an aqueous suspension of tetrabutylammonium iodide with a 10% excess of AgCl; the mixture was filtered; and the filtrate evaporated to dryness under reduced pressure and ultimately in a vacuum desiccator over Anhydron. *Anal.* Calcd for $C_{16}H_{36}NCl$: Cl, 12.76. Found: Cl, 12.76. 2,6-Lutidine was a commercial sample redistilled. Reagent grade acetone was dried over anhydrous Na_2SO_4 , refluxed over Drierite, and distilled therefrom. "90% acetone-10% methanol" was prepared by diluting 1 vol. of methanol with acetone to a total of 10 vol.

Rate Determinations.—Runs at 59.5° and higher temperatures were performed by the ampoule technique, 5.0-ml aliquots of the

29.5°, the experimental V_∞ always coincided, within experimental error, with the theoretical V_∞ . However, for runs at higher temperatures the amount of titratable acid formed was found to level off with time and eventually to decrease. This peculiarity was a minor perturbation for runs at 59.5°, where the experimental V_∞ was often about 90% of the theoretical, but was severe for runs at 73.7 and 100.7°, in which cases titratable acid sometimes began to diminish after the first half-life. Increasing the concentration of 2,6-lutidine reduced but did not eliminate the phenomenon. We suspect that addition of HCl or HBr to condensation products from the acetone solvent, such as mesityl oxide or phorone, is responsible for the disturbance.¹⁷ In these cases, the theoretical V_∞ value was used to construct kinetic plots, and the k_p was based on the linear early segment of the plot which in the most severe cases corresponded to the first 30–50% of reaction.

Product Analysis.—Glpc procedure B of Bunnett, Davis, and Tanida¹² was employed; a silicone fluid column, 91 cm long, was used at about 90°.

Results and Discussion

We amplify and extend the presentation and discussion in Part A.

Reactions in Dry Acetone.—Kinetic data on all runs are set forth in Table II. It is to be noted that, for sev-

TABLE II
KINETIC DATA FOR RUNS IN DRY ACETONE

Substrate	Salt ^a	Temp, °C	[Substrate], M	[Salt], M	[2,6-Lutidine], M	k_p , sec ⁻¹	k_2 , M ⁻¹ sec ⁻¹
Ib	None	59.55	0.020		0.062	3.97×10^{-6}	
		29.68	0.024	0.0792	0.065	5.42×10^{-5}	6.85×10^{-4}
	R ₄ NCl	59.55	0.021	0.126	0.040	8.60×10^{-5}	6.85×10^{-4}
			0.022	0.0700	0.065	1.02×10^{-3}	1.46×10^{-2}
			0.020	0.106	0.040	1.50×10^{-3}	1.42×10^{-2}
		29.68	0.025	0.144	0.074	7.77×10^{-6}	5.40×10^{-5}
			0.021	0.216	0.050	1.18×10^{-5}	5.48×10^{-5}
			0.021	0.102	0.045	1.27×10^{-4}	1.25×10^{-3}
	R ₄ NBr	59.55	0.023	0.130	0.067	1.70×10^{-4}	1.30×10^{-3}
			0.020	0.201	0.057	2.35×10^{-4}	1.17×10^{-3}
			0.017	0.126	0.025	8.51×10^{-7}	6.80×10^{-6}
		29.68	0.023	0.200	0.040	1.35×10^{-6}	6.78×10^{-6}
0.020				0.064	<i>b</i>		
0.013			0.0572	0.071	3.62×10^{-6}	6.32×10^{-5}	
Ia	None	100.7	0.020		0.064	<i>b</i>	
		73.7	0.013	0.0572	0.071	3.62×10^{-6}	6.32×10^{-5}
	R ₄ NCl	100.7	0.018	0.0832	0.032	5.11×10^{-6}	6.14×10^{-5}
			0.021	0.0771	0.060	7.00×10^{-5}	9.05×10^{-4}
			0.020	0.116	0.043	1.04×10^{-4}	8.96×10^{-4}
		73.7	0.024	0.169	0.069	1.53×10^{-6}	9.04×10^{-6}
			0.020	0.256	0.040	2.30×10^{-6}	8.99×10^{-6}
			0.015	0.184	0.050	2.32×10^{-5}	1.26×10^{-4}
	R ₄ NBr	100.7	0.021	0.195	0.070	2.43×10^{-5}	1.24×10^{-4}
			0.019	0.202	0.066	2.78×10^{-5}	1.38×10^{-4}
			0.021	0.204	0.050	2.67×10^{-5}	1.31×10^{-4}
		73.7	0.020	0.0906	0.058	2.05×10^{-4}	2.26×10^{-3}
0.020			0.0863	0.052	1.14×10^{-5}	1.32×10^{-4}	
0.020				0.052			
(CH ₃) ₃ CBr	R ₄ NCl	59.55	0.020	0.0906	0.058	2.05×10^{-4}	2.26×10^{-3}
	R ₄ NI	59.55	0.020	0.0863	0.052	1.14×10^{-5}	1.32×10^{-4}

^a R = *n*-butyl. ^b Negligible change in 18 hr.

reaction solution being used. Individual ampoules were removed at recorded times and plunged into ice-cold water. The contents were rinsed into a separatory funnel containing dry ether, the ether solution was extracted with about 20 ml of chilled water, and hydrogen ion was determined by potentiometric acid-base titration of the aqueous extract. For runs at 29.5°, the reaction solution was contained in a volumetric flask in the thermostat; samples (5.0 ml) were removed by pipet and released into dry ether in a separatory funnel, the time of release being recorded; thereafter the procedure was the same as for higher temperatures.

Pseudo-first-order rate coefficients, k_p , were reckoned as -2.30 times the slopes of plots of $\log(V_\infty - V_t)$ against time, where V_t is the volume of NaOH solution required for any sample and V_∞ is the volume required at completion of reaction. For runs at

eral combinations of substrate and tetrabutylammonium salt, the salt concentration was varied as much as twofold without discernible effect on k_2 . This substantiates that the elimination reaction is first order in halide ion, as well as first order in substrate. It is also to be noted that variations in lutidine concentration by 50% or more had no effect on reaction rate; this is consistent with other reports^{6,9,17} that lutidine does not affect either rates or products in this type of reaction.

For both Ia and Ib, solvolysis rates were studied. The solvolytic reactivity of Ia was so low that a rate

(16) J. W. Wilt, *J. Amer. Chem. Soc.*, **77**, 6397 (1955).

(17) Cf. S. Winstein, S. G. Smith, and D. Darwish, *Tetrahedron Lett.*, No. 16, 24 (1959).

TABLE III
 KINETIC DATA FOR RUNS IN 90% ACETONE-10% METHANOL

Substrate	Solvent	Temp, °C	Salt ^a	[Substrate], <i>M</i>	[Salt], <i>M</i>	[2,6-Lutidine], <i>M</i>	<i>k_ψ</i> , sec ⁻¹
Ib	90% acetone- 10% methanol	29.68	None	0.022		0.062	5.50 × 10 ⁻⁷
			R ₄ NCl	0.022	0.0806	0.066	1.85 × 10 ⁻⁸
			R ₄ NBr	0.022	0.166	0.062	2.69 × 10 ⁻⁸
			R ₄ NI	0.021	0.179	0.065	2.78 × 10 ⁻⁸
Ia	90% acetone- 10% methanol	59.55	None	0.019		0.064	1.72 × 10 ⁻⁷
		100.7	None	0.019		0.064	9.83 × 10 ⁻⁸

^a R = *n*-butyl.

coefficient could not conveniently be determined. The *k_ψ* value for solvolysis of Ib at 59.55° is only 1/32 the lowest *k_ψ* measured for reaction of Ib with any salt. Thus solvolysis makes a negligible contribution to reaction rate when halide ions are present.

Rates of reaction of *t*-butyl bromide with tetrabutylammonium chloride and iodide are also reported in Table II. The rate of the former reaction has been determined by other workers at other temperatures;^{6,8,9} on an Arrhenius plot constructed from the several reports, the present datum is in reasonable harmony with the rest; we note in passing that some discrepancies exist among "the rest."

Our data for reactions of Ib and *t*-butyl bromide with tetrabutylammonium chloride enable estimates to be made of the kinetic effect of the β-phenyl substituent in Ib. From the data at 59.55°, the *k₂* contribution for elimination into the benzyl "branch" of Ib is 86% of 14.4 × 10⁻³ M⁻¹ sec⁻¹, or 12.4 × 10⁻³ M⁻¹ sec⁻¹, and for elimination into each methyl branch 1.01 × 10⁻³ M⁻¹ sec⁻¹. From these figures, and taking account of the availability of two β hydrogens per benzyl branch and three per methyl branch, the acceleration due to β-phenyl is 18.4-fold. The *k₂* contribution for elimination into a single methyl branch of *t*-butyl bromide is 0.75 × 10⁻³ M⁻¹ sec⁻¹. From comparison of the rate per benzyl branch in Ib with this value, the acceleration due to β-phenyl is 24.8-fold. Comparison of the rates of elimination per methyl branch of the two substrates reveals that the phenyl substituent in Ib accelerates elimination into a methyl branch by 33%; this is possibly due to steric acceleration; in Ib the phenyl group is unavoidably *gauche* to two rather large groups (CH₃ and Br), and compressions between the phenyl group and methyl groups are probably somewhat relaxed in the transition state leading to III.

A striking and puzzling feature of our results is the considerable effect of the halide ion reagent on orientation (86% of II with Cl⁻, 78% of II with Br⁻) in contrast to the miniscule effect of the halogen leaving group. Because of the incompleteness of our understanding of the transition states for eliminations of this type, we withhold further comment on this phenomenon.

It is also noteworthy that differences in Δ*H*[‡] for reactions of Cl⁻ and Br⁻ with a given substrate are relatively small and that differences in reactivity stem mainly from differences in Δ*S*[‡]. If the differences in Δ*S*[‡] should happen to arise mainly from differences in the solvation or degree of ion-pair association¹⁸ of the halide ions, a conceivable possibility, it would then be especially remarkable that the halide ion has so much influence on orientation.

Reactions in 90% Acetone-10% Methanol.—We made only a few determinations, which are summarized in Table III. In the data concerning Ib, it is plain that all three of the tetrabutylammonium halides somewhat accelerate production of hydrogen bromide. However, the kinetic effects of all three salts are very nearly proportional to salt concentration without much dependence on the anion involved. It is therefore probable that the acceleration represents a general salt effect on ionization of Ib, rather than reaction induced by halide ions acting as nucleophiles or bases.

The products formed in 90% acetone-10% methanol were not determined.

Registry No.—Ia, 1754-74-1; Ib, 23264-13-3; (CH₃)₃CBr, 507-19-7; tetrabutylammonium chloride, 75-57-0; tetrabutylammonium bromide, 64-20-0; tetrabutylammonium iodide, 75-58-1.

(18) From the ion-pair dissociation constants listed by Winstein,⁸ we reckon that 0.1 *M* (C₄H₉)₄NCl is 12% dissociated and the bromide salt 16% dissociated.