Eliminations from 2-Butyl Halides Induced by Halide Ions in Dimethylformamide and Dimethyl Sulfoxide

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Olefinic products from reactions of 2-butyl halides with lithium halides and tetraalkylammonium fluorides in dimethylformamide and dimethyl sulfoxide are reported. For the iodide, bromide, and chloride ion induced eliminations, overwhelming Saytzeff orientation, high *trans-*:*cis*-2-butene ratios, and low olefin yields are observed. Tetra-*n*-butylammonium fluoride is shown to be an effective agent for dehydrohalogenation of 2-butyl iodide and bromide under mild conditions. In fluoride ion promoted eliminations, the percentage of 1-butene is dependent upon the halogen leaving group of the 2-butyl halide, increasing in the order iodide < bromide < chloride. The effects of the nature of the halide ion base and the halogen leaving group upon orientation are discussed.

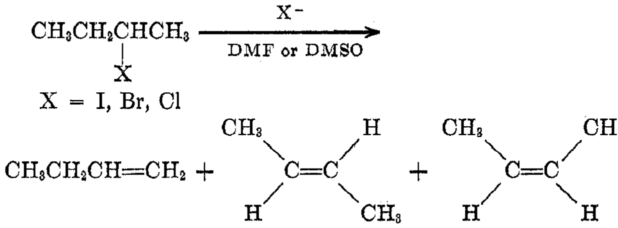
Recent investigations of positional and geometrical orientation[1] in base-catalyzed dehydrohalogenations from 2-halo alkanes have given considerable insight into the nature of the olefin-forming transition states.[2] Although a number of base-solvent systems have been employed, no information is available concerning halide ion-promoted β eliminations from 2-alkyl halides. We report a study of, orientation in and synthetic utility of, eliminations from 2-butyl halides induced by halide ions in dimethylformamide and dimethyl sulfoxide with special emphasis upon the relatively unexplored fluoride ion bases.

Dehydrohalogenations induced by halide ions in dipolar aprotic solvents have been reported for cyclohexyl halides,[3] tertiary alkyl halides,[3b,4] α-halocyclohexanone[5] and cyclopentanone[6] derivatives, β-phenethyl bromide,[7] and *t*-amyl bromide.[3b]

Results

Using gas-liquid partition chromatography (glpc), the relative proportions of the three isomeric olefins formed in reactions of 2-butyl iodide, bromide, and chloride with halide ions in dimethylformamide and dimethyl sulfoxide have been measured (Scheme I). In several cases, the yields of butenes were determined by a standard bromimetric method.

SCHEME I



Reactions of 2-Butyl Halides with Lithium Halides.—The relative amounts of isomeric olefins and olefin yields found in reactions of 2-butyl halides with lithium halides in dimethylformamide and dimethyl sulfoxide at 50° are listed in Table I. The absence of entries for other 2-butyl halides and lithium halides denotes insufficient elimination. For the reported reactions a negligible contribution from E1 processes was demonstrated.

Comparison of the relative olefinic proportions obtained from reactions in dimethylformamide and in dimethyl sulfoxide reveals little change in the per cent of 1-butene. However, consistently lower *trans-*:*cis*-2-butene ratios are observed in dimethyl sulfoxide. Similar variations have been reported for reactions of 2-butyl bromide with potassium *t*-butoxide in dimethylformamide and dimethyl sulfoxide.[2a]

The relative amounts of isomeric butenes obtained from reactions of lithium chloride with 2-butyl iodide in dimethylformamide were unaffected by small amounts (2%) of water in the solvent. However, a solvent mixture of 90% dimethylformamide-10% water produced noticeable change.

The per cent of 1-butene from a given 2-butyl halide is much larger with lithium fluoride than with the other lithium halides. For the chloride-, bromide-, and iodide-promoted eliminations from a given substrate, the per cent of 1-butene is constant within experimental error. The overwhelming Saytzeff orientation observed in reactions of 2-butyl iodide with lithium chloride, bromide, and iodide is the most complete favoring of internal olefin formation reported for an E2 reaction of a 2-substituted alkane.[8]

In all cases, the *trans-*:*cis*-2-butene ratios are very high and are similar to those observed in eliminations from 2-butyl bromide induced by alkoxide ions in dimethylformamide and dimethyl sulfoxide.[2a,f]

The synthetic utility of these reactions is severely limited by the low olefin yields. Longer reaction times produced no yield enhancement.

Reactions of 2-Butyl Halides with Tetraalkylammonium Fluorides.—Table II lists the relative amounts

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[1] Positional orientation refers to the relative proportions of 1- and 2-alkenes formed, whereas geometrical orientation compares the relative amounts of *trans-* and *cis*-2-alkene produced.

[2] (a) R. A. Bartsch, *J. Org. Chem.*, accepted for publication; (b–d) R. A. Bartsch and J. F. Bunnett, *J. Amer. Chem. Soc.*, **90**, 408 (1968); **91**, 1376, 1382 (1969); (e) H. C. Brown and R. L. Klimisch, *ibid.*, **88**, 1425 (1966); (f) D. H. Froemsdorf, M. E. McCain, and W. W. Wilkison, *ibid.*, **87**, 3984 (1965); (g) D. L. Griffith, D. L. Meges, and H. C. Brown, *Chem. Commun.*, 90 (1968); (h) W. H. Saunders, Jr., S. R. Fahrenholtz, E. A. Caress, J. P. Lowe, and M. Schreiber, *J. Amer. Chem. Soc.*, **87**, 3401 (1965).

[3] (a) D. J. Lloyd and A. J. Parker, *Tetrahedron Lett.*, 5183 (1968); (b) S. Winstein, "Chemica Teorica", Accademia Nazionale dei Lincei Chimica Teorica, Rome, Italy, 1965, p 327.

[4] D. Eck and J. F. Bunnett, *J. Amer. Chem. Soc.*, **91**, 3099 (1969).

[5] (a) R. P. Holysz, *ibid.*, **75**, 4432 (1953); (b) R. Joly, J. Warnant, G. Nomine, and D. Bertin, *Bull. Soc. Chim. Fr.*, 366 (1958); D. N. Kevill and N. H. Cromwell, *J. Amer. Chem. Soc.*, **83**, 3812 (1961); (d) C. Coppens, D. N. Kevill, and N. Cromwell, *J. Org. Chem.*, **27**, 3299 (1962); (e) E. W. Warnhoff, D. G. Martin, and W. S. Johnson, "Organic Syntheses," Coll. Vol. IV, 1963, p 162; (f) V. Delaroff, R. Smolik, M. Bolla, and M. Legrand, *Bull. Soc. Chim. Fr.*, 966 (1963); (g) E. J. Corey and A. G. Hortmann, *J. Amer. Chem. Soc.*, **87**, 5736 (1965).

[6] N. L. Wender, D. Taub, and H. Kuo, *ibid.*, **82**, 5701 (1960).

[7] J. Hayami, N. Ono, and A. Kaji, *Tetrahedron Lett.*, 1385 (1968).

[8] Reference 3b reports that the olefin mixture produced from reaction of *t*-amyl bromide with tetra-*n*-butylammonium chloride in acetone is 99.9% Saytzeff product, 3-methyl-2-butene.

TABLE I

OLEFINIC PRODUCTS FROM REACTIONS OF 2-BUTYL HALIDES[a] WITH LITHIUM HALIDES IN DMF AND DMSO AT 50.2°

X of 2-BuX	LiX	Solvent	Total butenes, yield, %	Per cent of total butenes			*trans*-2-Butene: *cis*-2-butene
				1-Butene	*trans*-2-Butene	*cis*-2-Butene	
I	LiF^{b,c}	DMF	2.0^{d}	18.9 ± 0.3^{e}	63.1 ± 0.3	18.0 ± 0.2	3.51 ± 0.03
	LiF^{c}	DMSO	*f*	19.4 ± 0.2	61.5 ± 0.5	19.1 ± 0.3	3.23 ± 0.08
	LiCl^{b,g}	DMF	7.9^{d}	2.4 ± 0.1	78.0 ± 0.4	19.6 ± 0.4	3.95 ± 0.12
	LiCl^{b,g}	DMF^{h}	*f*	2.4 ± 0.1	77.9 ± 0.6	19.7 ± 0.7	3.95 ± 0.17
	LiCl^{b,g}	DMF^{i}	*f*	2.2 ± 0.1	75.6 ± 0.1	22.2 ± 0.1	3.40 ± 0.01
	LiCl^{g}	DMSO	*f*	2.6 ± 0.1	75.8 ± 0.3	21.7 ± 0.3	3.50 ± 0.07
	LiBr^{b,g}	DMF	*f*	2.1 ± 0.1	77.6 ± 0.4	20.3 ± 0.5	3.83 ± 0.11
	LiBr^{g}	DMSO	*f*	3.3 ± 0.1	74.4 ± 0.4	22.3 ± 0.4	3.33 ± 0.07
	LiI^{b,g}	DMF	*f*	1.5 ± 0.1	76.8 ± 0.4	21.6 ± 0.4	3.55 ± 0.09
	LiI^{g}	DMSO	*f*	2.2	75.2	22.6	3.33
Br	LiF^{c}	DMF	*f*	29.3 ± 0.3	55.0 ± 0.5	15.7 ± 0.4	3.50 ± 0.12
	LiF^{c}	DMSO	*f*	29.5 ± 0.3	54.2 ± 0.4	16.3 ± 0.2	3.32 ± 0.06
	LiCl^{g}	DMF	*f*	9.8 ± 0.1	70.1 ± 0.3	20.1 ± 0.3	3.48 ± 0.10
Cl	LiF^{b,c}	DMF	*f*	39.8 ± 0.2	47.6 ± 0.3	12.6 ± 0.2	3.79 ± 0.05
	LiF^{c}	DMSO	*f*	40.8 ± 0.2	45.6 ± 0.2	13.6 ± 0.1	3.36 ± 0.05

[a] [RX] = 0.3–0.4 *M*. [b] Two runs. [c] Saturated solution. [d] Reaction time, 10 min. [e] Standard deviation. [f] Yield not determined. [g] 1.0 *M*. [h] 98% DMF–2% H_2O. [i] 90% DMF–10% H_2O.

TABLE II

OLEFINIC PRODUCTS FROM REACTIONS OF 2-BUTYL HALIDES[a] WITH TETRAALKYLAMMONIUM FLUORIDES IN DMF AT 50.2°

X of 2-BuX	R of R_4NF	Total butenes, yield, %	Per cent of total butenes			*trans*-2-Butene: *cis*-2-butene
			1-Butene	*trans*-2-Butene	*cis*-2-Butene	
I	Me^{b}	9.5^{c}	9.5 ± 0.1	71.1 ± 0.3	19.4 ± 0.2	3.66 ± 0.06
	n-Bu^{d,e}	77^{c}	10.6 ± 0.2	69.6 ± 0.3	19.7 ± 0.2	3.53 ± 0.06
	n-Bu^{d,f}	*g*	7.6 ± 0.1	72.8 ± 0.3	19.6 ± 0.2	3.73 ± 0.06
Br	Me^{b}	*g*	15.5 ± 0.1	66.5 ± 0.2	18.0 ± 0.2	3.68 ± 0.06
	n-Bu^{d}	37^{c}	16.7 ± 0.1	64.5 ± 0.4	18.7 ± 0.5	3.45 ± 0.11
Cl	Me^{b}	*g*	22.1 ± 0.1	61.3 ± 0.4	16.6 ± 0.2	3.72 ± 0.08
	n-Bu^{d}	2.0^{c}	22.5 ± 0.1	61.1 ± 0.1	16.4 ± 0.1	3.76 ± 0.04

[a] [RX] = 0.3–0.4 *M*. [b] Saturated solution. [c] Reaction time, 10 min. [d] [R_4NF] = 0.7 *M*. [e] Three runs. [f] 90% DMF–10% H_2O. [g] Yield not determined.

of isomeric olefins and olefin yields observed in reactions of 2-butyl halides with tetramethylammonium and tetra-*n*-butylammonium fluorides in dimethylformamide. A control experiment demonstrated the absence of fluoride ion-catalyzed elimination of tetra-*n*-butylammonium fluoride under the reaction conditions.

Comparison of eliminations using lithium fluoride (Table I) with reactions employing the tetraalkylammonium fluorides (Table II) shows that the *trans*-:*cis*-2-butene ratios are independent of the nature of the cation and are nearly the same for the three 2-butyl halides, whereas, for a given 2-butyl halide, the per cent of 1-butene is influenced by the identity of the cation, decreasing in the order lithium > tetra-*n*-butylammonium ≈ tetramethylammonium.

Tetra-*n*-butylammonium fluoride produces reasonable yields of butenes from 2-butyl iodide and bromide under mild reaction conditions.

Discussion

Halide ions in dipolar aprotic solvents are relatively strong bases as well as powerful nucleophiles. In addition, dimethylformamide and dimethyl sulfoxide act as proton acceptors and formation of hydrogen-bonded species such as $(DMF)_2H^+$ and (DMF)HX in dimethylformamide deactivates the proton for back addition to olefinic products.[9]

Eliminations Induced by Chloride, Bromide, and Iodide Ions.—The synthetic use of lithium chloride, bromide, and iodide as dehydrohalogenating agents for 2-butyl halides is precluded by poor olefin yields, resulting from low reactivity and facile substitution reactions.

In E2 reactions of 2-substituted alkanes, the per cent of 1-alkene reflects the relative amounts of C–H and C–X bond rupture in the elimination transition states.[2f,10] The greater the per cent of 1-alkene, the greater is the ratio of C–H to C–X bond cleavage. In the chloride-, bromide-, and iodide-induced eliminations from 2-butyl iodide and bromide, the per cent of 1-butene is very low. Thus, transition states with high degrees of C–X bond scission, but nearly intact C–H bonds (*i.e.*, "paenecarbonium" type[2c]), are indicated. This postulation is consistent with the relatively weak halide ion bases and the good halogen leaving groups involved.

In base-catalyzed eliminations from 2-substituted alkanes, *trans*-:*cis*-2-alkene ratios denote the extent of double-bond formation in the internal olefin transition states.[2b,f,h] The greater the degree of double-bond character, the greater is the eclipsing of *cis*-destined alkyl groups, resulting in a higher *trans*-:*cis*-2-alkene ratio. A paenecarbonium transition state possesses only slight carbon–carbon double-bond character. Therefore, judging from the low per cent of 1-butene observed in reactions of 2-butyl iodide and bromide

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(9) A. J. Parker, *Quart. Rev.* (London), **16**, 163 (1962).

(10) J. F. Bunnett, *Angew. Chem., Int. Ed. Engl.*, **1**, 225 (1962).

with lithium chloride, bromide, and iodide, low[11] *trans*-:*cis*-2-alkene ratios would be predicted. It is immediately apparent that this is not the case for the *trans*-:*cis*-2-alkene ratios are very high (3.40–3.95). These values surpass reported high ratios observed in reactions of 2-butyl bromide with potassium *t*-butoxide in dimethylformamide and dimethyl sulfoxide[2a,f] and are the highest known for base-catalyzed β elimination from a 2-substituted butane at 50°.

The *trans*-:*cis*-2-butene ratios closely approach a value of 4.0, extrapolated from the gas-phase pyrolysis of 2-butyl acetate at 450° (a known *syn* elimination process).[12] However, a *syn* elimination seems unlikely in view of the *anti* elimination stereochemistry observed in fluoride ion promoted elimination from *erythro*-3-deuterio-2-bromobutane in dimethylformamide[13] and in other halide ion induced eliminations.[3b,6]

The present results necessitate further consideration of the factors affecting *trans*-:*cis*-2-alkene ratios in eliminations from 2-substituted alkanes. A conceivable explanation of the observed *trans*-:*cis*-2-butene ratios is that eclipsing of alkyl groups may also be important in paenecarbonium transition states. Although such transition states have little double-bond character, the high degree of C–X bond rupture results in nearly trigonal α-carbon atoms. Thus, in transition states for formation of *cis*-2-butene, the *cis*-destined methyl groups are closer together than in the ground states and steric repulsions could occur. Comparable steric interactions are absent in transition states leading to *trans*-2-butene.

Eliminations Induced by Fluoride Ions.—In spite of the current interest in dehydrohalogenations promoted by halide ions, there are very few reports of the use of fluoride ion bases.[7] As shown in Table II, useful amounts of elimination are produced from reactions of 2-butyl iodide and bromide with tetra-*n*-butylammonium fluoride under mild reaction conditions. The lower reactivities of tetramethylammonium fluoride and especially lithium fluoride are probably due to limited solubility.

With all three fluoride ion bases, the per cent of 1-butene increases as the leaving group becomes poorer (*i.e.*, $I < Br < Cl$) in accord with the predictions of the variable E2 transition state theory.[10] Like trends and similar interpretations may be found in alkoxide ion promoted eliminations.[2b–d,h] The effect of the leaving group upon positional orientation in eliminations from 2-substituted alkanes has previously been demonstrated only with bases having oxygen as the first atom.

The influence of the cation upon the per cent of 1-butene is not a steric effect since, in dimethylformamide, solvated alkali metal and tetraalkylammonium ions are of similar size.[9] Attempts to prepare anhydrous tetra-*n*-butylammonium fluoride have been unsuccessful; therefore both tetraalkylammonium fluorides are hydrates. A small amount of water in the reaction solvent would reduce the reactivity of the fluoride ion by specific hydrogen-bonding solvation. The water-solvated fluoride ion would be a weaker base and a lower per cent of 1-butene would be anticipated.[14] In support of this proposal is a further reduction of the per cent of 1-butene in the reaction of 2-butyl iodide with tetra-*n*-butylammonium fluoride in 90% DMF–10% H_2O.

An *anti* elimination stereochemistry has been demonstrated in reactions of *erythro*-3-deuterio-2-bromobutane with tetra-*n*-butylammonium fluoride in dimethylformamide.[13]

Experimental Section

Reagents.—Anhydrous dimethylformamide (Baker, reagent) was used directly from freshly opened bottles. Dimethyl sulfoxide was purified as before.[2d] Anhydrous lithium fluoride (Alfa Inorganics), anhydrous lithium chloride (Baker, reagent), anhydrous lithium bromide (Mallinkrodt, reagent), lithium iodide monohydrate (Alfa Inorganics), and tetramethylammonium fluoride trihydrate (Eastman) were used directly. Tetra-*n*-butylammonium fluoride hydrate was prepared according to Mohr, Wilk, and Barrow.[15] Commercially available 2-butyl halides (Eastman, Halogen Chemicals) were distilled and shown to be homogeneous by glpc.

Elimination Products from Reactions of 2-Butyl Halides with Halide Ions in Dimethylformamide and Dimethyl Sulfoxide.—Except for the modification of preparing the base–solvent solution directly in the reaction vessel, the previously described[2a] apparatus, procedure, and glpc analysis of olefinic products was employed. A 10-min reaction period was used throughout.

For measurement of olefin yields, 5.0 ml of chloroform was added to the olefins collected in the cold trap. The chloroform solution was treated with an excess of 0.1 *M* bromine in acetic acid and the amount of unreacted bromine was determined in the usual manner.

Control Experiments.—Negligible amounts of butenes (determined by glpc) were formed in reactions of 0.3 *M* 2-butyl iodide with dimethylformamide or of 0.3 *M* 2-butyl iodide with 1.0 *M* lithium perchlorate in dimethylformamide for 10 min at 50°. No butenes could be detected in the reaction of 0.7 *M* tetra-*n*-butylammonium fluoride with dimethylformamide for 15 min at 50°.

Registry No.—2-BuI, 513-48-2; 2-BuBr, 78-76-2; 2-BuCl, 78-86-4; LiF, 7789-24-4; LiCl, 7447-41-8; LiBr, 7550-35-8; LiI, 10377-51-2; Me_4NF, 373-68-2; *n*-Bu_4NF, 429-41-4; dimethylformamide, 68-12-2; dimethyl sulfoxide, 67-68-5.

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[11] E1 reactions of 2-butyl bromide exhibit *trans*-:*cis*-2-butene ratios near unity: W. B. Smith and W. H. Watson, Jr., *J. Amer. Chem. Soc.*, **84**, 3174 (1962).

[12] C. H. DePuy, C. A. Bishop, and C. N. Goeders, *ibid.*, **83**, 2151 (1961).

[13] R. A. Bartsch, *Tetrahedron Lett.*, 297 (1970).

[14] D. H. Froemsdorf and M. D. Robbins, *J. Amer. Chem. Soc.*, **89**, 1737 (1967).

[15] S. C. Mohr, W. D. Wilk, and G. M. Barrow, *ibid.*, **87**, 3048 (1965).