Effect of the Leaving Group on Product Proportions in the Ethanolysis of 2-Pentyl and t-Pentyl Derivatives

By IRVING N. FEIT* and DONALD G. WRIGHT
(*Department of Chemistry, C. W. Post College, Greenvale, New York* 11548)

Summary The nature of the leaving group can affect olefin proportions as well as the ratio of substitution to elimination in ethanolysis reactions.

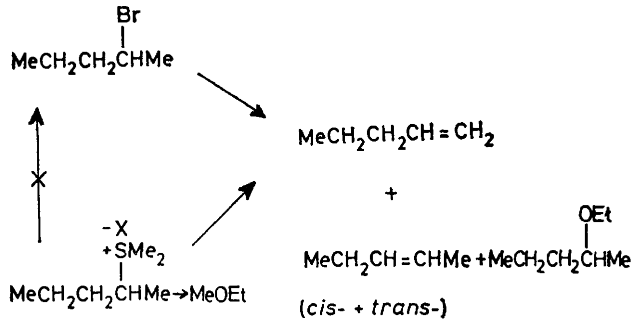
STUDIES of the effect of the leaving group on solvolysis products have played an important role in elucidating the mechanism of carbonium ion reactions. To date, the relative proportions of possible carbonium ion processes: substitution, elimination, rearrangement, and ion-pair return have been shown to depend on the leaving group in solvolysis reactions.[1]

We have extended these leaving group effect studies to the ethanolysis of 2-pentyl derivatives. This system has the advantage of giving three different elimination products; pent-1-ene, *trans*-pent-2-ene, and *cis* pent-2-ene, in addition to the substitution product, 2-pentyl ethyl ether (Scheme 1). We were able to examine, therefore, whether the relative proportions of the isomeric olefins formed in an *E*1 reaction could also be a function of the leaving group.[2]

When the leaving group was $-SMe_2^+$ or $-NMe_3^+$, methyl ethyl ether was also found in the product mixture. We attribute this to a bimolecular displacement process. The product proportions are given in the Table. Analyses were by gas chromatography. All products were shown to be stable to the reaction conditions.

A change in the leaving group from $-Br$ to $-SMe_2Br$, $-SMe_2I$, $-NMe_3Br$, or $-NMe_3I$ led to a substantial decrease in the ratio of 2-pentyl ethyl ether: olefin. The composition of the olefin mixture, on the other hand, was virtually unchanged.

A further change in the leaving group to $-SMe_2ClO_4$ produced no further change in the ratio of ether to olefin, but did produce a substantial change in the composition of the olefins. It appears, therefore, that ratios of ether to olefin depend on the charge type of the leaving group while the proportions of the isomeric pentenes depend on the counterion of the carbonium ion.



Scheme 1

We can dismiss two possible explanations that are based on an active role of the halide ions either present initially or generated in our reactions. If substitution by a halide ion preceeded carbonium ion formation from the onium salts, the product proportions would be the same for 2-pentyl bromide and 2-pentyldimethylsulphonium bromide or 2-pentyltrimethylammonium bromide. In fact, the ratio of 2-pentyl ethyl ether to olefin differed by a factor of five.

If the halide ions could abstract protons, on the other hand, the ratio of ether to olefin would increase when 2-pentyl bromide or one of the onium halides was changed to the corresponding dimethylsulphonium perchlorate. In fact, the ratio either decreased or stayed the same. We conclude that the leaving group can affect product proportions without taking part in the reaction directly.

We were surprised that the ratio of ether to olefin decreased when the substrate was changed from 2-pentyl bromide to the corresponding onium ions. This trend is opposite to that observed by Cocivera and Winstein in the t-butyl series.[1c] We therefore measured the product proportions from the solvolysis of three t-pentyl derivatives (Scheme 2).

The change from t-pentyl bromide to t-pentyldimethyl sulphonium iodide resulted in a decrease in the ratio of ether to olefin, consistent with the trend in the 2-pentyl series. The change from t-pentyl bromide to t-pentyldimethylsulphonium perchlorate, however, resulted in an increase in the ratio of ether to olefin, consistent with the trend reported by Cocivera and Winstein[1c] in the t-butyl series.

Thus, the change from a leaving group that is initially uncharged to one that is charged generally causes an increase in elimination at the expense of substitution. The increase in substitution on changing from a tertiary alkyl bromide to the corresponding dimethylsulphonium perchlorate appears to be an exception.

The olefin proportions from secondary and tertiary alkyl derivatives respond differently to changes in the leaving group. In the 2-pentyl series, the change in leaving group from –Br to any of the onium halides caused no variation in olefin proportions while the change from Br to –SMe$_2$ClO$_4$ did cause a variation (see Table).

In the t-pentyl series, on the other hand, the change in leaving group from –Br to –SMe$_2$I caused a variation in the olefin proportions while the change from Br to –SMe$_2$ClO$_4$ caused no variation.

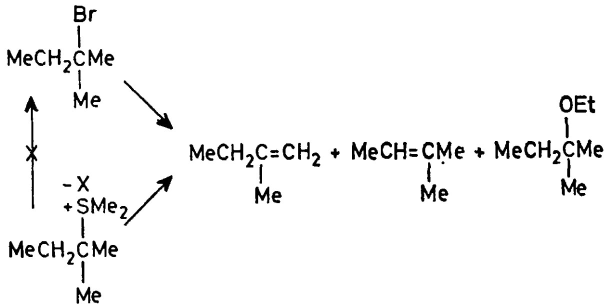
Table

Products of ethanolysis of 2-pentyl[a] (2Pe) and t-pentyl[b] (t-Pe) derivatives

Substrate	%2-ene / %1-ene	*trans/cis* pent-2-ene	Ether[c] / Olefin
2PeBr[d,e1]	16	2·8	2·6
2PeSMe$_2$Br[d,e2]	13	2·5	0·5
2PeSMe$_2$I[d,e3]	16	3·0	0·6
2PeNMe$_3$Br[e4]	16	3·0	0·6
2PeNMe$_3$I[e5]	16	3·1	0·4
2PeSMe$_2$ClO$_4$[d,e6] ..	7	1·6	0·7
t-PeBr[d,e7]	28	—	0·57
t-PeSMe$_2$I[d,e8]	19	—	0·36
t-PeSMe$_2$ClO$_4$[d,e9] ..	28	—	2·32
t-BuBr	—	—	1·8[f]
t-BuSMe$_2$ClO$_4$	—	—	4·6[f]

[a] 135 °C. [b] 85 °C. [c] 2-PeOEt or t-PeOEt. [d] 2,6-Lutidine was added as a buffer. [e] Total % yield/reaction time (h): 1. 96/24; 2. 25/48; 3. 12/48; 4. 3·6/165; 5. 4·6/165; 6. 92/90; 7. 100/42; 8. 90/33; 9. 83/24. [f] ref. 1c.

The discovery that the counterion of an alkyldimethylsulphonium salt can affect product proportions cannot be explained simply by invoking a series of ion-pairs. The details of solvolysis must be more complex than originally envisaged by Winstein and his co-workers.[1b] It is becoming increasingly apparent that solvent structure can play an important role in product distribution.[3]



Scheme 2

A recent suggestion by Kwart and his co-workers[4] is useful in explaining our data. They proposed that an ion-pair formed in a solvolysis reaction is born into the solvation environment left behind by its precursor. Thus, even subtle changes in the leaving group can influence the distribution of products from an incipient carbonium ion by influencing the solvent structure surrounding the parent substrate.

We thank the Research Corporation and the C. W. Post College Research Committee for financial assistance.

(*Received, 24th June* 1975; *Com.* 717.)

---

[1] (a) C. K. Ingold, 'Structure and Mechanism in Organic Chemistry,' Cornell University Press, Ithaca, N.Y., **1953**, p. **426**; (b) S. Winstein, B. Appel, R. Baker, and A. Diaz, *Chem. Soc. Special Publ.*, 1965, No. 19, 124; (c) M. Cocivera and S. Winstein, *J. Amer. Chem. Soc.*, 1963, **85**, 1702; (d) A. F. Diaz and S. Winstein, *ibid.*, 1966, **88**, 1318; (e) R. L. Buckson and S. G. Smith, *J. Org. Chem.*, 1967, **32**, 634; (f) M. L. Sinnot and M. C. Whiting, *J. Chem. Soc.* (*B*), 1967, 965; (g) V. J. Shiner, Jr., and W. Dowd, *J. Amer. Chem. Soc.*, 1971, **93**, 1029; (h) J. F. Bunnett and D. L. Eck, *J. Org. Chem.*, 1971, **36**, 897.

[2] Cram has shown that the olefin proportions from the 2-phenyl-2-butyl cation generated from various derivatives in glacial acetic acid depend on the leaving group. In these reactions, the departed leaving group is a much stronger nucleophile than the solvent and is probably removing the proton in the elimination step. Thus, the nucleophile changes at the same time the leaving group changes. We have minimized this possibility by using the more nucleophilic solvent, ethanol; D. J. Cram and M. R. V. Sahyun, *J. Amer. Chem. Soc.*, 1965, **85**, 1257.

[3] *e.g.* C. A. Bunton and S. K. Huang, *J. Amer. Chem. Soc.*, 1972, **94**, 3536; C. A. Bunton, T. W. DelPesco, A. N. Dunlop, and K-U. Yang, *J. Org. Chem.*, 1971, **36**, 887; F. G. Bordwell and G. A. Pagani, *J. Amer. Chem. Soc.*, 1975, **97**, 123; F. G. Bordwell, P. F. Wiley, and T. G. Mecca, *ibid.*, p. 132; R. E. Robertson, *Progr. Phys. Org. Chem.*, 1967, **4**, 213; C. D. Ritchie, G. A. Skinner, and V. G. Badding, *J. Amer. Chem. Soc.*, 1967, **89**, 2063.

[4] H. Kwart, R. W. Body, and D. M. Hoffman, *Chem. Comm.*, 1967, 765.