Driving Force due to Electron-releasing Groups on the Double Bond in the Solvolytic Ring Closure of Unsaturated Arenesulphonates

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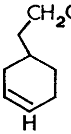
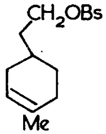
AN interesting, but largely unexplored, aspect of solvolytic ring closures involving double bonds[1] is the effect of varying, by suitable substitution, the nucleophilic reactivity of the double bond. Here we report the extra driving force which results from the presence of methyl (+ *I* effect) and methoxyl (+ *E* effect) groups on the double bond in the cyclohexenylethyl *p*-bromobenzenesulphonates (II), (III), and (V), and the first solvolytic cyclisation of a Δ^3-cyclohexenylcarbinyl compound (IX).

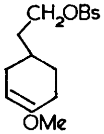
Our rate data are summarised in the Table. The two enol ethers (III and V)† were "solvolysed" in acetonitrile (containing excess triethylamine);[2] the reactions showed good first-order rate constants (zero-order in triethylamine), and gave (after hydrolysis) the bicyclic ketones (VI;R = H and Me)† in good yield.[3] The other *p*-bromobenzenesulphonates [(I),[4] (II),† and (IV)[5]] were solvolysed both in acetic acid and in acetonitrile.



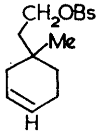
(I)



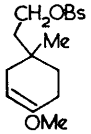
(II)



(III)



(IV)



(V)

Bs = *p*-bromobenzenesulphonyl

The first-order rates in acetonitrile–triethylamine differ by less than an order of magnitude from those in acetic acid, and the effects of different kinds of structural variations are almost

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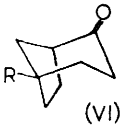
† All the compounds mentioned were prepared by unambiguous routes, and their i.r. and n.m.r. spectra were consistent with the structures assigned to them.

TABLE

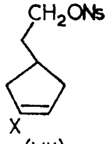
First-order rate constants[a] *and, in parentheses, free energy increments*[b]

	(I)	(II)	(III)	(IV)	(V)
0·01M AcOH–AcO⁻, 79·9°	11·0	75(1·35)	—	—	—
0·01M MeCN–Et$_3$N, 79·9°	1·35	10·5(1·44)	131(3·21)	32·1	—
0·01M MeCN–Et$_3$N, 39·9°	—	—	2·11	0·466	89·3(3·27)

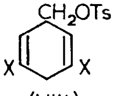
[a] 10^6k, sec.$^{-1}$.
[b] $\Delta\Delta G^{\ddagger}_{X}$, kcal. mol.$^{-1}$ [$=2{\cdot}3RT\log(k_X/k_H).10^{-3}$].



(VI)



(VII)



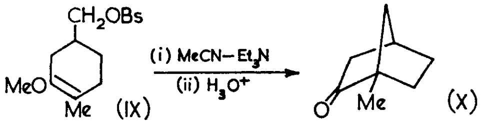
(VIII)

identical in both solvent systems: k_{II}/k_{I} = 6·8 in acetic acid and 7·8 in acetonitrile, and k_{IV}/k_{I} = 25[5] and 24, respectively. Acetonitrile–triethylamine[2] is therefore a very useful solvent system for examining the "solvolytic" behaviour of compounds which give side reactions in acetic acid.

The extra driving force due to the presence of an electron-releasing group on the double bond appears to be not only solvent-independent but also system-independent. In the case of a methoxyl group, it is the same ($\Delta\Delta G^{\ddagger}_{OMe} \simeq$ 3·2 kcal. mol.$^{-1}$) in the cyclohexenylethyl system (III), in which the original double bond provides little driving force (k_{I}/k_{sat} = 4 at 75°),[4] as it is in the 1-methylcyclohexenylethyl system (V), in which the effect of the original double bond is considerable ($k_{IV}/_{sat}$ = 100 at 80°).[5] Similarly, the effect of a methyl group in the cyclohex-ylethyl system (II) is the same ($\Delta\Delta G^{\ddagger}_{Me} \simeq$ 1·3—1·4 kcal. mol.$^{-1}$) as it is in the cyclopentenylethyl system (VII; X = Me),[6] in which again the effect of the original double bond is considerable ($k_{VII;\,X=H}/k_{sat}$ = 95 at 60°).[7]

A plot of these free energy increments (3 points) against Brown's σ^+ constants[8] yields a straight line with a slope of −4·2, corresponding to a ρ-value of −3·0 at 30°. This correlation should have predictive value for other substituents and other systems. A similar Hammett treatment of Chapman and Fitton's acetolysis data on the homoallylic compounds (VIII; X = H, Me, OMe)[9] leads to a larger ρ-value (−4·9 at 30°), suggesting that the degree of bond-formation in the transition state is considerably greater when the double bond is homoallylic than when it is further removed from the electrophilic centre.

We have found that the combined effects of a methyl and a methoxyl group ($\Delta\Delta G^{\ddagger} \simeq$ 4·5 kcal. mol.$^{-1}$ if they are additive) are sufficient to bring about the solvolytic cyclisation of the *p*-bromobenzene-sulphonate (IX).† This compound, when heated (110 hr. at 120°) in 0·03M-acetonitrile–triethylamine, gave (after hydrolysis) the bicyclic ketone (X) (12% yield).[10] All previous attempts



(IX) (X)

to form a bicycloheptane ring system by solvolysis of Δ^3-cyclohexenylcarbinyl (*i.e.*, potentially isoprenoid) precursors have failed.[11]

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[1] For reviews of early work in this field, see P. D. Bartlett, *Annalen*, 1962, **653**, 45; B. Capon, *Quart. Rev.*, 1964, **18**, 45.

[2] H. M. R. Hoffmann and E. D. Hughes, *J. Chem. Soc.*, 1964, 1252.

[3] A similar solvolytic cyclisation involving an enol ether double bond has already been observed (F. C. Uhle, *Tetrahedron Letters*, 1964, 3099; *J. Org. Chem.*, 1966, **31**, 4913), but no rate data have been reported.

[4] S. Winstein and P. Carter, *J. Amer. Chem. Soc.*, 1961, **83**, 4485.

[5] C. Chuit, C. Colard, and H. Felkin, *Chem. Comm.*, 1966, 118.

[6] $k_{VII;\,X=Me}/k_{VII;\,X=H}$ = 7 at 60°: P. D. Bartlett and G. D. Sargent, *J. Amer. Chem. Soc.*, 1965, **87**, 1297. We are indebted to Professor Bartlett for prior communication (1962) of this result.

[7] R. G. Lawton, *J. Amer. Chem. Soc.*, 1961, **83**, 2399; P. D. Bartlett and S. Bank, *ibid.*, p. 2591.

[8] H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, 1958, **80**, 4979.

[9] O. L. Chapman and P. Fitton, *J. Amer. Chem. Soc.*, 1963, **85**, 41.

[10] Semicarbazone, m.p. and mixed m.p. 208—209° (R. Schaber and S. Beckmann, *Annalen*, 1954, **585**, 154). We are indebted to Professor A. Rassat for an authentic sample of (X).

[11] G. Le Ny, *Compt. rend.*, 1960, **251**, 1526; C. F. Wilcox and S. S. Chibber, *J. Org. Chem.*, 1962, **27**, 2332; A. D. Kuh, Ph.D. Thesis, Cornell University, 1965 (quoted by H. Babad, W. Flemon, and J. B. Wood, *J. Org. Chem.*, 1967, **32**, 2871); see also R. S. Bly and H. L. Dryden, *Chem. and Ind.*, 1959, 1287.