Unrearranged and Other Products from the Solvolysis of Neopentyl Toluene-*p*-sulphonate[1]

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THE solvolysis of neopentyl derivatives has been studied by numerous workers under a variety of conditions. It is generally accepted[2] and quoted in most text-books that these reactions involve complete rearrangement under carbonium-ion conditions.

We have now analysed the products for the solvolysis of neopentyl tosylate in ethanol–water mixtures, to which 2,6-lutidine has been added as a buffer. Under these conditions the product distribution is kinetically controlled, and thus furnishes considerable insight into the mechanism of the rearrangement. From the data in the Table it is obvious that significant amounts of unrearranged products may be formed,† and therefore, two carbonium ions (at least), namely (I) and (III) should be reaction intermediates, as suggested long ago by Ingold and collaborators.[3] As one might expect, the proportion of t-pentyl alcohol increases steadily with increasing water content of the medium. Regarding olefin proportions, the same solvent change produces first a slight increase in Saytzeff olefin (2-ene) at the expense of 1-ene; in media containing 40 mole % and more water the percentage of Saytzeff olefin (of the total olefin) is similar to that obtained for the solvolysis of t-pentyl derivatives,‡ which must involve the classical t-pentyl cation (III).

On the other hand, as the activation barrier to formation of (I) is raised with *decreasing* water content, the proportion of 1-ene and of dimethylcyclopropane can be seen to increase in striking parallel. The formation of both products is mechanistically similar, inasmuch as it requires loss of a proton from any of three unshifted (or partly shifted) methyl groups. While (V) must always arise from a route which by-passes the t-pentyl cation (III), appreciable amounts of 1-ene cannot result from (III) in solvent mixtures containing predominantly ethanol. Thus, (II) is a transition state§ (or an intermediate), which not only rearranges to (III), but may also under favourable conditions collapse to 1-ene and to dimethylcyclopropane *via* (IV). Interestingly, (V) never actually vanishes as a product, not even in pure water.

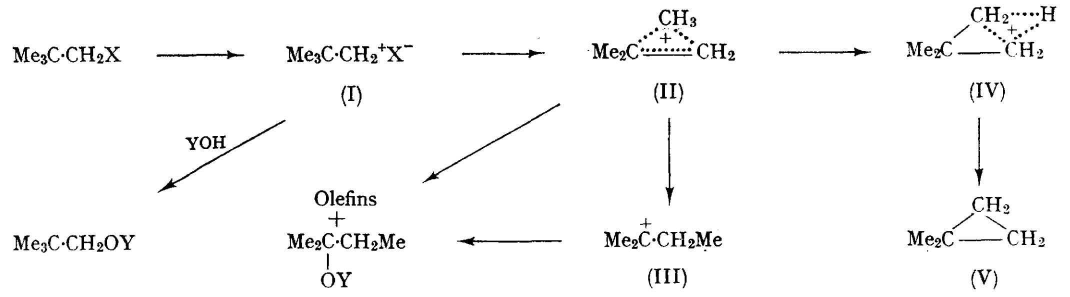
Summarising, it seems clear that the balance of the competing reactions is solvent dependent, and

TABLE

Product distribution[a] *(mole %) for the solvolysis of neopentyl tosylate in ethanol–water mixtures*[b] *at* 129°

Solvent[b]	1-ene	2-ene	Dimethyl-cyclopropane	Neopen OEt	t-Pen OEt	t-Pen OH	Neopen OH
0[c]	25 ± 1	25 ± 1	0·28 ± 0·06	7·3 ± 0·3	43 ± 1	0	0
0[d]	22 ± 1	26 ± 1	0·12 ± 0·05	6·1 ± 0·2	46 ± 1	0	0
3[e]	25 ± 1	28 ± 0·6	0·11 ± 0·04	6·0 ± 0·3	38 ± 1	2 ± 1	0
15[c]	21 ± 2	26 ± 1	0·20 ± 0·05	4·2 ± 0·2	39 ± 1	8 ± 1	~1
20[c]	18 ± 0·5	26 ± 0·5	0·15 ± 0·03	3·7 ± 0·1	34 ± 0·5	17 ± 0·4	~1
27[c]	16 ± 1	26 ± 1	0·21 ± 0·08	1·8 ± 0·2	32 ± 1	23 ± 0·5	~1
40[c]	9·2 ± 0·2	39 ± 1	0·11 ± 0·05	1·0 ± 0·2	22 ± 1·2	27 ± 1·4	1·3 ± 0·3
44[e]	11 ± 0·5	36 ± 1	0·07 ± 0·02	1·0 ± 0·1	18 ± 0·5	31 ± 0·8	—
60[c]	6·0 ± 0·5	34 ± 0·6	0·11 ± 0·05	0·4 ± 0·04	15 ± 0·5	41 ± 0·5	3·6 ± 0·2
70[e]	5·7 ± 0·4	33 ± 0·8	0·08 ± 0·02	0·4 ± 0·1	14 ± 0·5	47 ± 1	—
80[c]	4·2 ± 0·2	26 ± 0·4	0·03 ± 0·02	0·1 ± 0·05	8·0 ± 0·4	57 ± 1	4·1 ± 0·3
100[c]	5·1 ± 0·3	15 ± 0·8	0·03 ± 0·02	0	0	70 ± 2	10·4 ± 0·4

[a] Products were analysed on a 10 ft. column packed with 10% Carbowax 400 on 80—100 mesh G-Cel. Quoted errors refer to measurement of v.p.c. peak area. Errors in conversion into molar proportions are omitted; these will not affect comparisons down the Table or between isomers. [b] Mole % water tabulated; footnotes c, d, and e specify initial concentrations and reaction times. [c] [Neopen OTs] = 0·07 M, [2,6-lutidine] = 0·08; 24 hr. [d] [ROTs] = 0·07, [base] = 0·16; 54 hr.; some equilibration of dimethylcyclopropane is evident in the longer runs. [e] [ROTs] = 0·50, [base] = 0·55; 40 hr.



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† Neopentyl bromide forms at least 9% neopentyl ethyl ether on solvolysis in absolute ethanol (G. M. Fraser, unpublished work).

‡ Typical olefin distributions are 85% 2-ene and 15% 1-ene; see ref. 3b, pp. 442, 445. Acetolysis of t-pentyl chloride yields 75% 2-ene and 25% 1-ene (H. M. R. Hoffmann, unpublished).

§ For simplicity, ion (II) is formulated as a *symmetrically* bridged species.

the greater the energy release in the (I) → (III) cascade, the more pronounced the tendency for leakage into products which are not derived from the classical t-pentyl cation (III). The present study stresses the desirability of testing the presumed classical or nonclassical behaviour of carbonium ions in a variety of solvents and emphasises that the carbonium ion at equilibrium does not necessarily provide the best model for fleeting intermediates in solvolyses.

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[1] For previous Papers in this series, see: G. M. Fraser and H. M. R. Hoffmann, *J. Chem. Soc.* (*B*), 1967, 265, 425.

[2] J. E. Nordlander, S. P. Jindal, P. von R. Schleyer, R. C. Fort, jun., J. J. Harper, and R. D. Nicholas, *J. Amer. Chem. Soc.*, 1966, **88**, 4475, and references cited therein.

[3] (a) F. Brown, E. D. Hughes, C. K. Ingold, and J. F. Smith, *Nature*, 1951, **168**, 65; (b) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, New York, 1953, p. 520; the intermediacy of ion (I) has also been inferred recently from kinetic studies by Schleyer and collaborators (ref. 2).