Concerted and Non-concerted Fragmentation Reactions in the Solvolysis of *endo*-3,4-Benzobicyclo[4,2,1,$0^{2,5}$]non-9-on-7-yl Toluene-*p*-sulphonates

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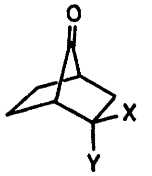
Summary A synchronous fragmentation reaction, with acceleration, has been observed in the acetolysis of the *endo*-toluene-*p*-sulphonate of the title compound: for the *exo*-toluene-*p*-sulphonate, although some fragmentation occurs, no rate acceleration was observed.

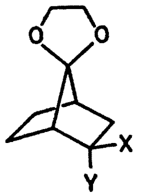
GASSMAN and his co-workers have reported extensive data on the solvolysis of norbornyl systems bearing electron-withdrawing substituents.[1-3] In particular, the acetolysis of *exo*- and *endo*-2-tosyloxybicyclo[2,2,1]heptan-7-one (**1** and **2**)[2] and the corresponding ethylene glycol acetals (**3** and **4**)[1] have been studied in detail. A number of products were obtained from the solvolysis of (**3**) and (**4**); one of them (**5**), produced in 57% yield from (**4**) and 19% from (**3**), was the result of a fragmentation reaction. Although Gassman postulated that for (**4**) this fragmentation was concerted, no rate enhancement was observed in the rate of solvolysis compared to that of the parent *endo*-2-norbornyl toluene-*p*-sulphonate (in fact a slower rate was observed). No fragmentation was observed in the solvolysis of (**1**) and (**2**). As part of our studies on the relationship between structure and reactivity we have examined the acetolysis of (**6**) and (**7**) and report details of novel fragmentation reactions in these systems.

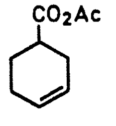
(**6**) was prepared by the reaction of dimethylfulvene and di-iodobenzocyclobutane, followed by selective hydroboration, ozonolysis, and formation of the toluene-*p*-sulphonate, m.p. 132—134°, ν_{max} 1762 cm^{-1}. Oxidation of the *exo*-alcohol from hydroboration of the Diels–Alder adduct, followed by reduction, ozonolysis, and treatment with toluene-*p*-sulphonyl chloride gave (**7**), m.p. 144—146°, ν_{max} 1770 cm^{-1}. Rates of acetolysis are summarised in the Table compared to those of the parent unsubstituted systems (**9** and **10**) previously reported.[4] The high rate of solvolysis of (**7**) compared to (**10**) is immediately evident and product studies revealed the exclusive formation of (**8**) resulting from fragmentation subsequent to addition of acetic acid to the carbonyl function. The structure of (**8**) (ν_{max} 1804, 1734 cm^{-1}) was further confirmed by conversion into the methyl ester (**11**) (ν_{max} 1729 cm^{-1}) of the corresponding acid by treatment with MeOH and HCl. The solvolysis of (**7**) provides a novel example of the one-step Grob fragmentation process occurring with "frangomeric acceleration."[5] Orientation of the lone pair of electrons of the hydroxyl oxygen atom at C-9, the –C-7–O– and the –C-9–C-6, –C-6–C-7– bonds in the acetic acid adduct of (7) are ideally disposed for this mechanism.

Toluene-*p*-sulphonate	10^7k (sec^{-1})^b		$\Delta H^{\ddagger}$ (kcal)	$\Delta S^{\ddagger}$(e.u.)
	75·0°	100·0°		
6	22·3	360	29·0	−1·7
7	198	2550	26·8	−3·5
9^a	305	3340	24·0	−10·6
10^a	1·20	25·0	30·6	−2·5

[a] Ref. 4.
[b] Average of two runs, ±3%; 0·005M-tolylate; acetic acid containing 0·01M-sodium acetate.

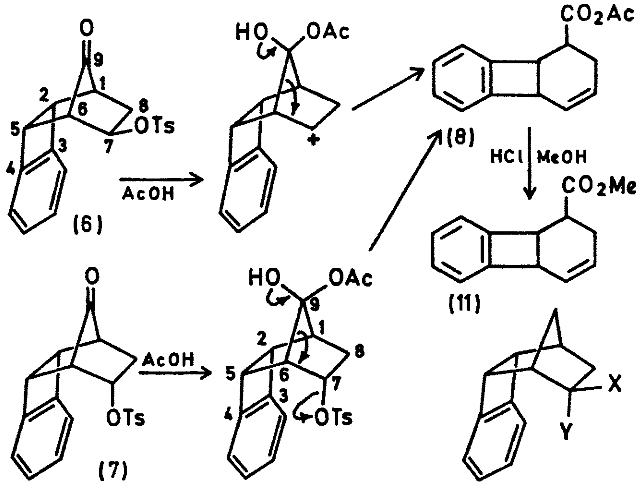






(**5**)

(**1**) X = OTs, Y = H (**3**) X = OTs, Y = H
(**2**) X = H, Y = OTs (**4**) X = H, Y = OTs



(**9**) X = OTs, Y = H
(**10**) X = H, Y = OTs

In contrast, no comparable rate increase is observed for (**6**); in fact a slower rate is observed compared to the parent system due, in part, to the electron-withdrawing property of the carbonyl group. Nevertheless, a substantial amount of the fragmentation product, (**8**) (70%) is produced. A clear example is therefore provided of the second type of fragmentation process suggested by Grob; a two-step process which involves an initial ionisation to the carbonium ion, followed by fragmentation.[5] This type of non-concerted mechanism, observed when the arrangement for fragmentation with acceleration is unfavourable, is usually characterised by the formation of other products together with that resulting from fragmentation. Together with (**8**), eleven other minor products in varying amounts have been detected by g.l.c.

Comparison of the rate of solvolysis of (**6**) with that of (**9**) is complicated by the rearrangement observed in the solvolysis of (**9**) due to Wagner–Meerwein –C-5–C-6– bond shift.[4,6] The introduction of the carbonyl function appears to prevent –C-5–C-6– bond migration indicating that the ion produced from the solvolysis of (**9**) has some non-classical character, and part of the rate decrease of (**6**) compared to

(**9**) arises from the absence of any σ-bond participation in the solvolysis of (**6**).

It is interesting to consider the origin of the marked differences in behaviour of (**6**) and (**7**) in solvolysis, compared to the systems previously studied by Gassman. The observation of fragmentation in the solvolysis of (**7**) but not of (**2**) must result from the substantial steric interactions present in (**7**). The slow solvolysis rate of (**10**) has previously been ascribed to steric inhibition to ionisation resulting from interactions of the leaving group and *endo*-2,5-substituent.[4,7] As a result of similar interactions in (**7**) the fragmentation process probably becomes the more favoured pathway for the solvolysis; rate acceleration results when the stereoelectronic conditions are satisfied for the *endo*-toluene-*p*-sulphonate (**7**) but not for the *exo*-derivative (**6**). Even for the latter, fragmentation of the carbonium ion is evidently still a favoured process.

Although only some spectral details are reported, n.m.r. and other analytical data are fully consistent with all suggested structures.

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