METHOXONIUM IONS IN SOLVOLYSIS; THE ACETOLYSIS OF

CIS- AND TRANS-5-METHOXY-3-PENTEN-1-YL ARENESULFONATES*

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Neighboring methoxyl group (MeO-) participation in solvolytic substitution reactions

is well documented, and it is generally accepted that these reactions proceed via inter-

mediate cyclic methoxonium ions (1,2). It has been shown (3,4) that the tertiary oxonium

ion I does not open to either a primary or secondary carbonium ion; however, it has been

suggested (4,5) that the oxonium ion has significant resonance contributions from the hybrid

structures depicted below.

I
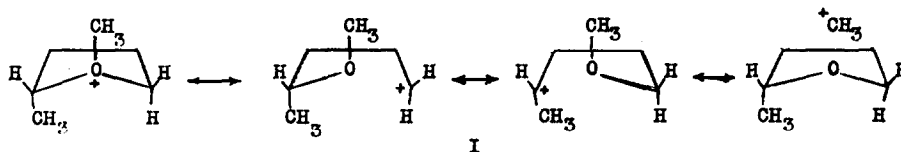
We wish to report evidence that the solvolysis of the cis-5-methoxy-3-penten-1-yl

arenesulfonates II constitutes an example of a case proceeding via MeO-6 participation to

give a 6-membered ring methoxonium ion which does "leak" to a carbonium ion prior to

solvent capture.
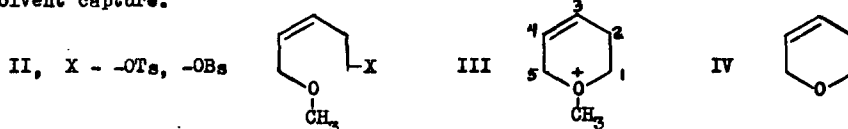
II, X - -OTs, -OBs

III

IV

A kinetic analysis of the acetolysis of II, prepared by straightfoward syntheses (6), showed that the reaction was completely dominated (>99%) by methoxyl participation, the magnitude of the rate acceleration being ca. 1.13×10^2. This estimate was calculated from the solvolysis rate of the corresponding trans brosylate, in which methoxyl participation is geometrically prohibited, after applying a small correction for the difference in solvolytic reactivity of cis and trans homoallylic arenesulfonates (7). The data are summarized in the accompanying Table. Also, the cis brosylate solvolyzes at very nearly the same rate as

Table. Acetolysis of cis- and trans-5-Methoxy-3-penten-1-yl Brosylates

| Compound	Temp., $^\circ$C	ROBs , M	NaOAc , M	k, sec.$^{-1}$
cis	75	0.0788	0	1.17×10^{-4}
	75	0.0797	0.0831	1.33×10^{-4}
	75	0.0850	0.0995	1.40×10^{-4}
trans	75	0.0787	0.0796	5.61×10^{-6}
	75	0.0807	0.0034[a]	5.54×10^{-6}

[a]lithium perchlorate

5-methoxy-1-pentyl brosylate, for which MeO-6 participation has been demonstrated (8). Furthermore, the solvolysis also exhibited some of the characteristic behavior of ion pair reactions (see below).

In addition to the kinetic evidence that the initially formed intermediate is the O-methyl-Δ^3-dihydropyranium ion III is the fact that the major solvolysis product is the cyclized material, Δ^3-dihydropyran IV, formed in ca. 75% yield. Significantly, among the remaining products was found the rearranged allylic acetate, 5-methoxy-1-penten-3-yl acetate V.

That V was formed during the acetolysis was demonstrated by the fact that all of the acetolysis products were stable to the reaction conditions, workup, and gas chromatography analysis. Hence, the formation of the acetate V requires that the allylic cation VI be a solvolysis intermediate (10).

In order to conclude that the intermediate VI arises directly from the oxonium ion III, it must be shown that the formation by ion pair return of the allylic tosylate VII, also a potential source of VI, does not occur under the reaction conditions. A study of the effects of added salts implicated the external ion pair IIIa as a discrete solvolytic intermediate (9). Thus when the acetolysis was conducted in the absence of added salts, rearrangement to methyl tosylate occurred as shown by a low kinetic infinity titer of liberated sulfonic acid and by detection of the tosylate by nmr and thin layer chromatography. In the presence of NaOAc or

V ... VI ... VII ... IIIa ...
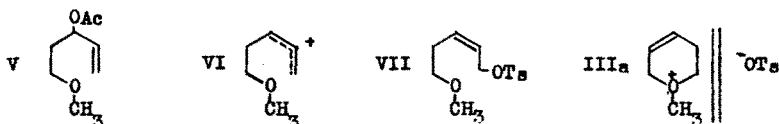
$LiClO_4$ this rearrangement was completely eliminated, the theoretical amount of sulfonic acid being liberated. Clearly, the addition of inert salts diverts IIIa and thus prevents its collapse to the internal ion pair IIIb in which the tosylate anion is situated in the vicinity of the O-methyl group. No methyl tosylate is formed by subsequent internal return from IIIb, since the added salts inhibit the formation of IIIb. It should be emphasized that IIIb can only arise via a chemically interceptible intermediate (IIIa) and not, e.g., by direct inter-conversion of the various internal ion pair species. If the latter were even partially occurring, it would have been impossible to completely suppress MeOTs formation, since it has been generally shown that internal ion pairs are not diverted by added salts (9).

Similarly, it may be reasonably assumed that the formation of internal ion IIIc (and therefore VII), in which the tosylate anion is situated at the back side of C-5, is also prevented due to complete scavenging of IIIa. In short, the scavenging of IIIa precludes ion pair return with rearrangement, a well documented phenomenon in both MeO-5 and MeO-6 reactions (1,4,8). Since VII is not formed in the presence of added salts, carbonium ion VI must arise from the cyclic oxonium ion directly.

IIIb ...   IIIc ...
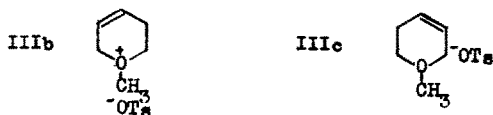
Furthermore, the percent reaction involving ion pair return to the O-methylene carbons of six-membered ring oxonium ions is very small if not totally negligible. Thus, although IIIa is a required intermediate in the solvolysis of II, no lithium perchlorate special salt effect (which is usually diagnostic of the external ion pair) was detected. Since the scavenging of the external ion pair does not manifest itself as a special salt effect, the implication is that the initial ionization step is essentially irreversible, i.e., that there is virtually no internal return to yield starting tosylate. This phenomenon is similar to that observed for the analogous O-methyl tetrahydropyranium ion, and has logically been interpreted as being due primarily to steric hindrance to approach at the methylene carbons by the sulfonate anion (8). Therefore, since internal return occurs at the O-methyl group to the virtual exclusion of O-methylene attack, the formation of VII seems very unlikely indeed.

The reaction may therefore be represented as follows (omitting ion pair species):
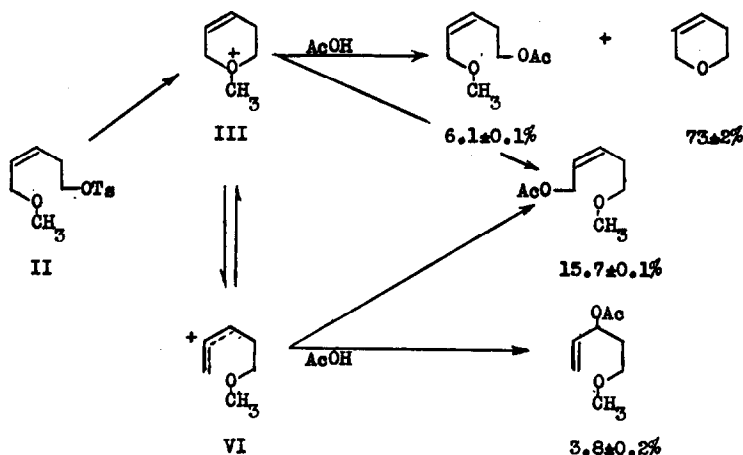
It may be estimated that at least 10% of the products arise via the allylic cation VI, calculated from the known yield of V and the known product spread between primary and secondary allylic isomers under limiting (S_N1) solvolysis conditions (11). The fact that allylic cation formation can compete successfully with product formation by direct solvent capture of the oxonium ion serves to indicate qualitatively that the energy difference between the two ions is quite small.

REFERENCES AND FOOTNOTES

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3. E. R. Novak and D. S. Tarbell, _J. Am. Chem. Soc._, _89_, 73 (1967); A. W. Friederang and D. S. Tarbell, _J. Org. Chem._, in press.

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5. S. Winstein and E. Grunwald, _ibid._, _70_, 828 (1948).

6. All new compounds gave satisfactory elemental analyses and spectral data consistent with their expected structures.

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8. S. Winstein and E. Allred, _ibid._, _89_, 4012 (1967).

9. S. Winstein, B. Appel, R. Baker, and A. Diaz, Special Publication No. 19, The Chemical Society, London, 1965, p. 109, and references therein.

10. An S_N2' attack on III to give V is considered unlikely under the reaction conditions; cf. J. Hine, "Physical Organic Chemistry," McGraw-Hill, 1962, pp. 152-154.

11. R. H. Wolfe and W. G. Young, _Chem. Revs._, _56_, 753 (1956).