

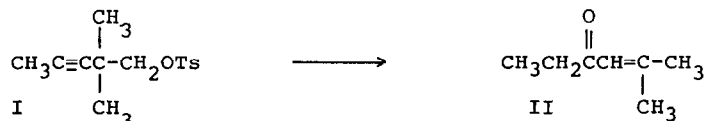
THE SOLVOLYSIS OF A HOMOPROPARGYL COMPOUND, 2,2-DIMETHYL-3-PENTYN-1-YL TOSYLATE

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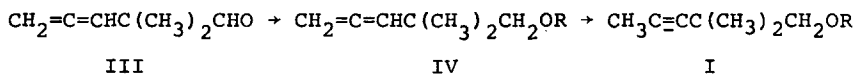
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The question of neighboring group participation by the carbon-carbon triple bond during solvolysis reactions has been examined recently by a number of investigators (1-4), including ourselves. The present contribution concerns the formolysis of 2,2-dimethyl-3-pentyn-1-yl tosylate, I, from which was isolated 5-methyl-4-hexen-3-one, II, in nearly quantitative yield. This product is of a different type than those reported by the other groups and sheds new light on the mechanisms of these solvolyses.



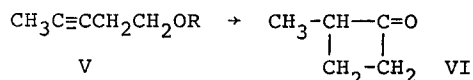
The synthesis of I employed the allenic aldehyde III as the starting point (5). Sodium borohydride reduction provided the alcohol IV (R = H), which was handled more easily as the tetrahydropyranyl ether IV (R = THP). The ether was isomerized to the acetylenic ether at 60° by potassium *t*-butoxide in *t*-butanol. The protecting group was removed in acidic benzyl alcohol. The n.m.r. spectrum of the



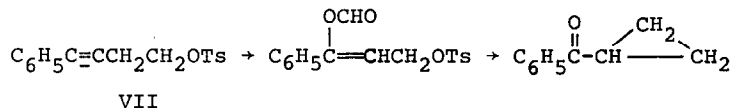
acetylenic alcohol, I (R = H), showed the expected four singlets at δ 1.10 [(CH₃)₂], δ 1.82 [CH₃C≡], δ 2.63 [O-H] and δ 3.23 [-CH₂O]. The structure of II was established by the identity of its infrared and n.m.r. spectra with those of an authentic sample (6). Compound II took up one equivalent of hydrogen to form 5-methyl-3-hexanone, the semicarbazone of which melts at 152° [lit 152° (7)]. Specifically excluded as a structure of II was 4-methyl-3-hexen-2-one. An authentic sample of its hydrogenation product, 4-methyl-2-hexone, has different

physical properties from the ketone we obtained. Another isomer of II, 4-methyl-4-hexen-3-one, was also excluded by the fact that the semicarbazone of its hydrogenation product, 4-methyl-3-hexanone, melts at 137° (7). When the formolysis was carried out at 75°, at about 0.6 M in the presence of 0.6 M sodium formate, tosylate I had nearly disappeared at the end of three hours as determined by n.m.r. spectroscopy.

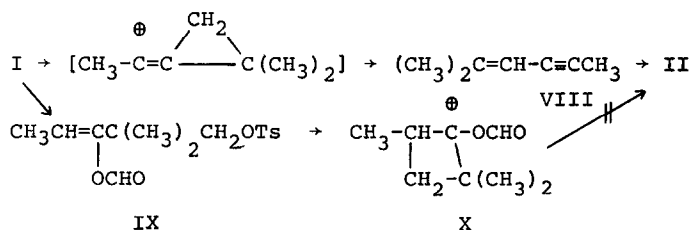
While the synthesis of I was underway, Hanack and co-workers (1) reported the slow (17 days at 60° in formic acid) conversion of V (R = Ts) to VI (20% yield). Very recently Ward and Sherman (4) have reported the solvolysis of



another homopropargyl system, VII, which was shown to undergo addition of formic acid prior to solvolysis and cyclization.



In the present case a mechanism involving triple bond migration followed by solvent addition seems secure. The addition of formic acid to VIII is expected (8) to yield II. It is unlikely that solvent addition to I would be so specific



as to form only IX (9). Even if IX were formed in high yield, it would very probably cyclize to X, which cannot yield II.

A sequence of rapid migration followed by a slow cyclization step may apply in the conversion (1) of V (R = Ts) to VI, for acetylene migration yields the same system back again, V (R = CHO). Thus, the present case represents the first clear example of neighboring group participation by the carbon-carbon triple bond in a homopropargyl system (10).

FOOTNOTES and REFERENCES

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5. The aldehyde was supplied by the Tennessee Eastman Company, to whom we are grateful.
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10. Special thanks are due to F. Marshall van Meter for preliminary work on this problem. Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support.