

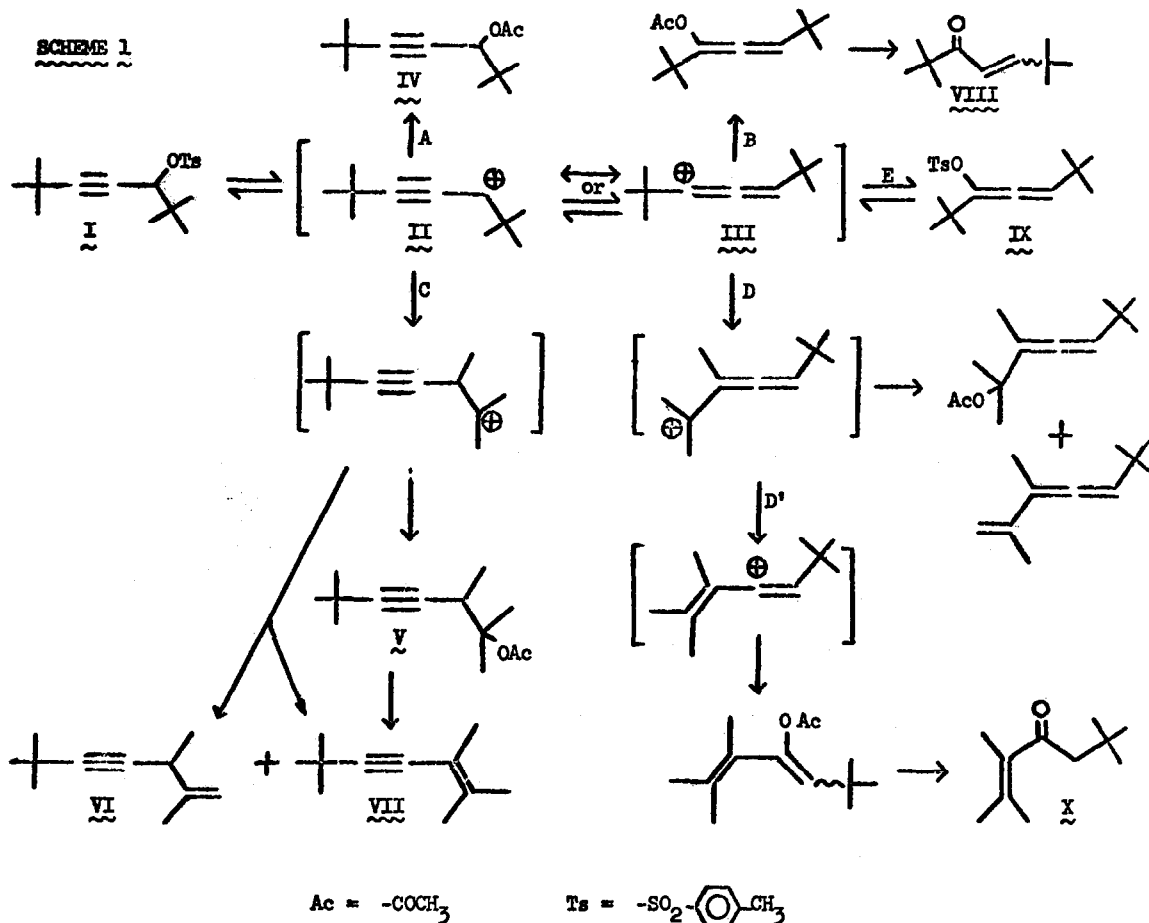
ACETOLYSIS OF 1,3-DI-*t*-BUTYLPROPARGYL TOSYLATE

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A common example of allylic-type interaction, often encountered at the undergraduate level, is the resonance between propargyl and allenic structures (e.g. Scheme 1, $\text{II} \leftrightarrow \text{III}$). A search of the literature reveals, however, that relatively little recent work has been done on the formation and reactions of substituted propargyl (\leftrightarrow allenic) cations. Burawoy and Spinner investigated ⁽¹⁾ the solvolysis of a series of tertiary halides $\text{RC}\equiv\text{C}-\text{C}(\text{CH}_3)_2-\text{X}$ in 80% aqueous ethanol, and found that the triple bond "efficiently transmitted polar effects," as inferred from relative solvolytic rates. The products from these reactions were not identified. More recently the pmr spectra of several tertiary propargyl carbonium ions in "super acid" have been obtained,^(2,3) and it was concluded,⁽²⁾ "allenyl cation resonance forms play an important part in alkynyl carbonium ions." Recovered products from these experiments generally contained less than 10% of compounds which would have arisen from allenic precursors. The renewed interest in vinyl cations⁽⁴⁾ (of which III is an example) prompts this report.

The acetolysis of 1,3-di-*t*-butylpropargyl tosylate (I) might be expected to yield some or all of the products shown in Scheme 1.⁽⁵⁾ Direct trapping by solvent of cation(s) $\text{II} \leftrightarrow \text{III}$ (paths A and B) would lead to propargyl and allenic acetates, respectively. To the extent that positive charge resides at C_1 or C_3 , methyl migrations (paths C and D) could be expected by analogy with the behavior of neopentyl-like carbonium ions. Finally, ion-pair return to allenic tosylate IX (path E) might be anticipated. With our attention focused on these intriguing possibilities, and the information they might yield concerning charge densities in propargyl cations, and the energetics of methyl migrations and ion-pair return in these systems, we prepared tosylate I by the method of Corey and Borden.⁽⁶⁾



The acetolysis of I was carried out in dry acetic acid containing one equivalent of sodium acetate, and the rates of the solvolyses were monitored titrimetrically.⁽⁷⁾ The reactions were uniformly first-order through two to three half-lives; rates and activation parameters are given in Table I. Following the work of Shiner and coworkers,⁽⁸⁾ we feel a suitable model compound for I would be 3,3-dimethyl-2-butyl (pinacoly) tosylate, for which the acetolysis rate constant at 50° is 6.35×10^{-6} .⁽⁹⁾ Comparison of this value with the one for I (Table I) indicates a significant eight-fold enhancement for the latter due to α -triple-bond participation.

Preparative acetolysis under the same conditions led to a product mixture (Table II) comprising three major products (totalling 99%) and seven minor components (totalling ca. 1%) which could be efficiently separated by glpc on a Carbowax 20M column. Of the major products, one was immediately

TABLE I
Apparent First-Order Acetolysis Rate Constants for I^(a)

T ± 0.05 °C	k, sec ⁻¹	ΔH [‡] kcal/mole	ΔS [‡] eu ^(b)
40.0	(1.34 ± 0.006) × 10 ⁻⁵	26.47	3.59
50.0	(5.01 ± 0.04) × 10 ⁻⁵	26.45	3.48
65.0	(3.27 ± 0.02) × 10 ⁻⁴	26.42	3.43

(a) $E_a = 27.09 \pm 0.16 \frac{\text{kcal}}{\text{mole}}$. (b) In solvolyses positive ΔS^\ddagger is uncommon, but suggestive of an ionization process involving a highly stable cation. Identified as IV by comparison with a sample⁽¹⁰⁾ prepared directly from the alcohol.⁽⁶⁾ Ester IV was found to be completely stable to the reaction and separations conditions. Structural assignments for the other two major products, isolated via preparative glpc, were made on the following basis: a) both had glpc retention characteristics of hydrocarbons, b) the first-eluted product showed the following spectral absorptions—ir:⁽¹¹⁾ 1730 cm⁻¹ (w), 1640 (w), 1265 (m), 1210 (m), 905 (s), 800 (vs); pmr (in CCl₄/TMS): δ 1.20 (s) + 1.28 (d) totalling 12H, 1.79 (sharp m, 3H), 3.0 (m, 1H), 4.65-5.2 (m, 2H); assignment: VI. The third eluted product showed ir: 2210 (vw), 1720 (m), 1305 (s), 1255 (s), 1210 (s), 1140 (s), 800 (vs); pmr: δ 1.25 (s, 9H), 1.71 (s, 6H), 1.87 (broadened s, 3H); uv (MeOH): λ_{max} 227 nm (log ϵ 4.13); assignment: VII. Of the minor product apparently none is allenic (ir), and at least four are esters (ir and retention characteristics).

TABLE II
Products from the Acetolysis of I at 65° C (a)

Product	Relative GLPC Peak Areas ^(b)		
	1 \mathcal{Y} ^(c)	5 \mathcal{Y} ^(c)	6 \mathcal{Y} ^(c,d)
<u>IV</u>	82.3	84.4	82.5
<u>VI</u>	5.3	4.7	5.3
<u>VII</u>	11.4	9.9	9.2
Other ^(e)	< 1	< 1	~ 3

- (a) Tosylate I (4.60 g, 14.2 mmole) yielded 2.81 g crude acetolysate. Using above percentages, this corresponds to 11.1 mmole IV, 0.9 mmole VI, and 2.0 mmole VII for an absolute yield of (14.0/14.2) × 100 = 99%.
- (b) Disk-integrated glpc peak areas using Carbowax 20M column.
- (c) \mathcal{Y} (half-life) = 2100 sec. (d) Two equivalents of sodium acetate.
- (e) Seven other components.

Undoubtedly V is among these, but being a tertiary acetate it was unstable with respect to VI and VII.⁽⁷⁾ An absorption at 1685 cm^{-1} in the ir spectrum of a mixture of three trace components suggested that VIII or X might have been present. The fact that the product ratios (Table II) were virtually unaffected by reaction time and added acetate ion suggests that at least the three major components are primary products, stable to the reaction conditions. Finally, a sample of I isolated without recrystallization after one acetolysis half-life was identical in all respects to starting material.

These data indicate that paths A (~83%) and C (~16%) are predominant during the acetolysis of I.⁽⁵⁾ Paths B, D, and E cannot account for more than 1% of the products. Similarly, the lack of evidence for IX rules out any significant ion-pair return with rearrangement. It can be inferred from these results that positive charge density resides mostly at C_1 in the propargyl cation, and that vinyl cation (resonance form) III, although "allylic," is considerably less stable than II.

We are presently engaged in the synthesis of optically active IX in order to determine whether the cation formed by its solvolysis (III ?) in fact enters the same manifold as that from I.⁽¹²⁾

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- (4) M. Hanack, Accounts Chem. Res., 3, 209 (1970).
- (5) Direct displacement by solvent of the tosylate group is sterically unfavorable in neopentyl-type systems. See also Table I, footnote b.
- (6) W. T. Borden and E. J. Corey, Tet. Lett., 315 (1969). These authors report that optically pure I had mp $87.5\text{--}88.0^\circ$; for analytically pure racemic I (recrystallized from hexane) we found mp $80.0\text{--}81.3^\circ$. Similarly for optically pure 1,3-di-*t*-butylpropargyl alcohol they gave mp $58.8\text{--}60.3$; for racemic alcohol we found, after recrystallization from hexane, mp $38.5\text{--}40^\circ$.
- (7) For a typical procedure, see T. L. Jacobs and R. S. Macomber, J. Am. Chem. Soc., 91, 4824 (1969).
- (8) V. J. Shiner, Jr., R. D. Fisher, and W. Dowd, ibid., 7748 (1969).
- (9) A. H. Fainberg and S. Winstein, ibid., 78, 2780 (1956).
- (10) bp $81\text{--}82^\circ$ (13 mm); ir: 2270 cm^{-1} (s), 1735 (vs), 1240 (vs); pmr: δ 0.95 (s, 9H), 1.22 (s, 9H), 2.01 (s, 3H), 5.07 (s, 1H). Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.55. Found: C, 74.06; H, 10.59.
- (11) In the ir spectrum of VI the absorption attributable to $\text{--C}\equiv\text{C--}$ stretch was not intense enough to be assigned. This is not an uncommon situation for relatively symmetrical acetylenes (K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco 1962).
- (12) Acknowledgement is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this work.