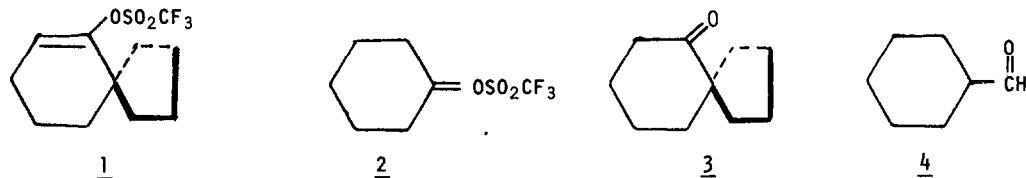


PREPARATION AND SOLVOLYSIS OF VINYL TRIFLATES. XIV.  
FURTHER REARRANGEMENTS IN VINYL CATIONS<sup>1</sup>

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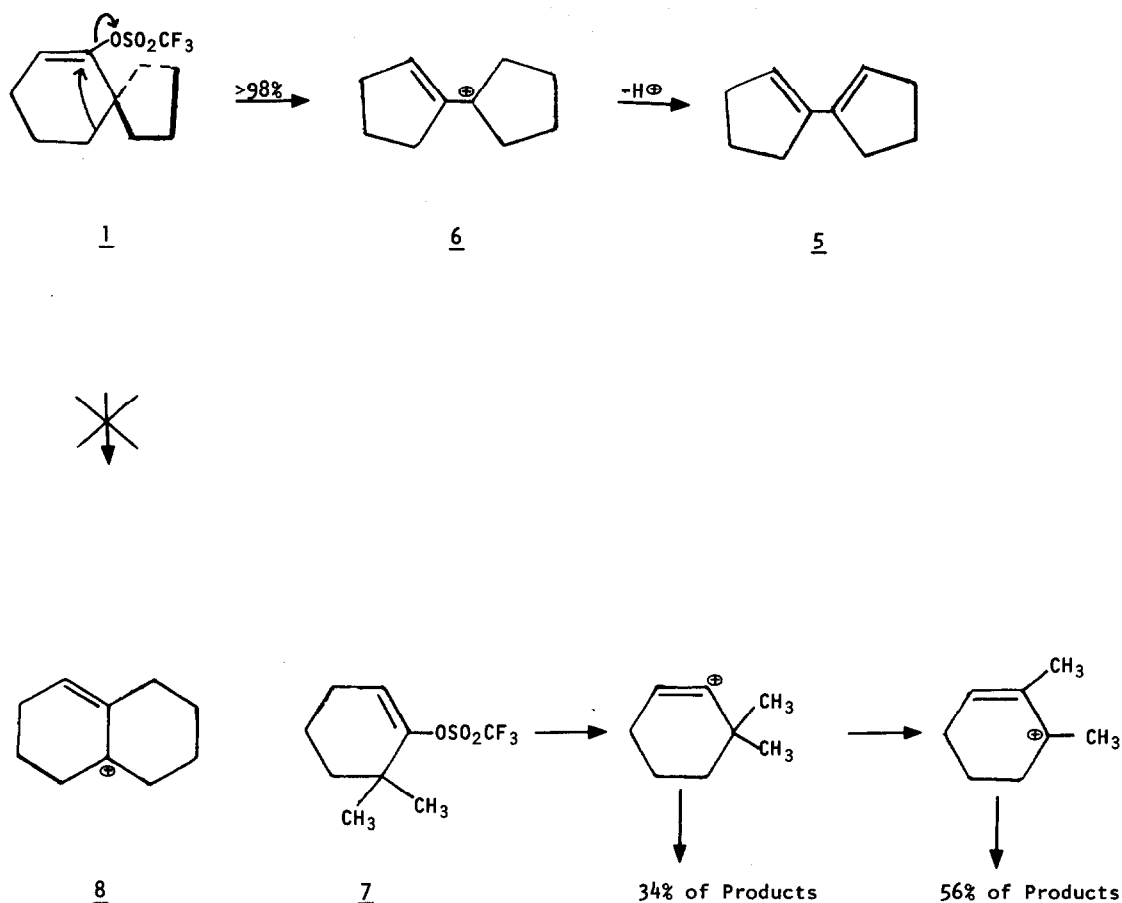
Similar to carbonium ions vinyl cations<sup>2</sup> readily undergo rearrangements. Such vinyl cation rearrangements have been classified into two broad categories; a) rearrangements to the double bond and b) rearrangements across the double bond and examples of both are known.<sup>3</sup> In this paper we wish to report two additional novel instances of possible vinyl cation rearrangements involving a spirovinyl triflate 1 and a primary vinyl substrate 2. Spirovinyl triflate 1 was obtained from spiro ketone 3 according to literature procedures<sup>4</sup> and triflate 2 was prepared via the



silyl enol ether<sup>5</sup> of commercially available cyclohexanecarboxaldehyde 4. Spiro ketone 3 was synthesized from cyclopentanone according to Zelinskii and Elagina.<sup>6</sup>

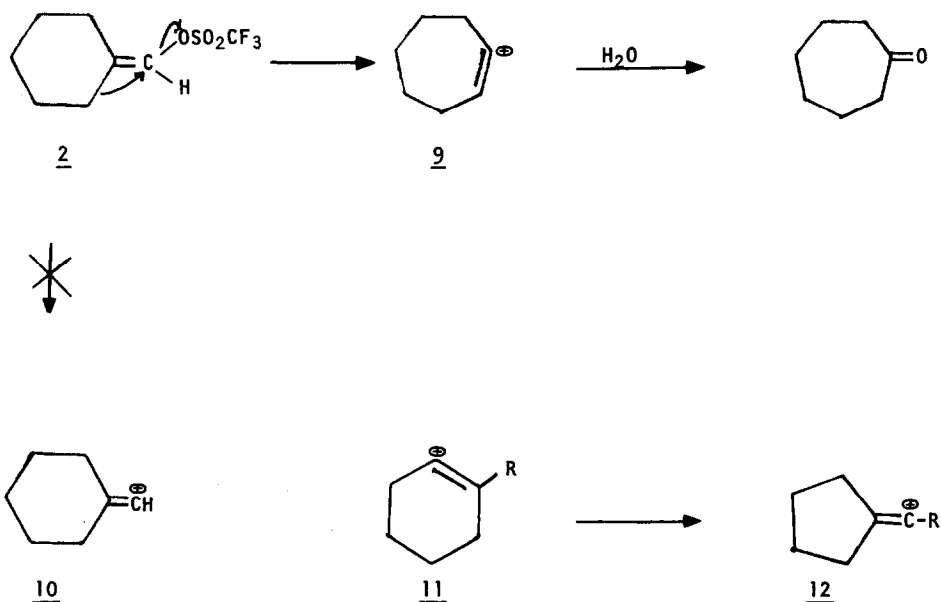
Reaction of 1 at 130° in 60% aqueous EtOH buffered with pyridine gave 90% of diene 5, 4.5% of spiro ketone 3 and 4.5% of an unknown product. Solvolysis in 50% (w/w) aqueous trifluoroethanol (TFE) also at 130° and buffered with pyridine, gave >98% diene 5 and ~2% of the same unknown product but no ketone 3. Diene 5 was isolated by preparative gc and characterized by spectral means, which were identical to literature<sup>7</sup> values. Diene 5 arises via migration of the adjacent cyclohexyl bond to the vinyl cation center, formation of carbonium ion 6 and loss of a proton from 6. Interestingly, in contrast to the behavior of cyclic vinyl triflate 7 where the majority of products arise, via neighboring alkyl (methyl) migration,<sup>8</sup> no analogous spiro alkyl migration

and formation of ion 8 was observed in the solvolysis of 1. This strongly suggests a concerted ionization and migration in the solvolysis of 1 with probable anchimeric assistance by the favorably located cyclohexyl bond. The small amount of unrearranged product ketone 3 in 60% EtOH and no ketone 3 at all in the less nucleophilic aqueous TFE is in accord with this hypothesis.



Solvolysis of 2 in 50% (w/w) aqueous TFE buffered with pyridine for 8 days at  $130^\circ$  (about 70% reaction) gave as products; 95% cycloheptanone and 2.5% of cyclohexanecarboxaldehyde identified by gc-coinjection as well as isolation and spectral comparison with authentic samples, along with 2.5% of an unidentified component.<sup>9</sup> Formation of the large amount of cycloheptanone once again strongly suggests a concerted ionization and alkyl migration to the double bond with concomitant formation of the rearranged cyclic vinyl cation 9. This is perhaps not surprising as direct ionization would result in an energetically unfavorable primary vinyl cation 10.<sup>10</sup> This rearrangement further suggests that a bent secondary vinyl cation of type 9 is more stable

than a linear<sup>12</sup> but primary vinyl cation like 10. Indeed only cycloheptanone and no cyclohexanecarboxaldehyde is observed in the solvolysis of cycloheptenyl triflate.<sup>8</sup> It has been previously established<sup>8,13</sup> that a linear secondary vinyl cation like 12 is more stable than a bent



secondary vinyl cation such as 11, although products derived from both ions are observed in the solvolysis of 2-methylcyclohexenyl triflate.<sup>8</sup>

Hence, we have presented evidence for two concerted presumably anchimerically assisted alkyl migrations, in one case to the double bond in the other across the double bond, in the solvolysis of simple alkyl vinyl triflates.

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#### References and Notes

- (1) a) Paper XIII, P.J. Stang, R.J. Hargrove, and T.E. Dueber, *J. Chem. Soc. Perkin II*, in press; b) Abstracted in part from the Ph.D. Thesis of T.E. Dueber, The University of Utah, 1974.
- (2) For reviews and leading references see: a) L.R. Subramanian and M. Hanack, *J. Chem. Ed.*, **52**, 80 (1975); b) P.J. Stang, *Prog. Phys. Org. Chem.*, **10**, 205 (1973); c) G. Modena and U. Tonellato, *Adv. Phys. Org. Chem.*, **9**, 185 (1971); d) M. Hanack, *Accounts Chem. Res.*, **3**, 209 (1970).

- (3) Inter alia: A.G. Martinez, M. Hanack, R.H. Summerville, P.v.R. Schleyer and P.J. Stang Angew. Chem. Int. Ed. Engl., 9, 302 (1970); M.A. Imhoff, R.H. Summerville, P.v.R. Schleyer, A.G. Martinez, M. Hanack, T.E. Dueber, and P.J. Stang, J. Amer. Chem. Soc., 92, 3802 (1970); P.J. Stang and T.E. Dueber, ibid., 95, 2683, 2686 (1973).
- (4) P.J. Stang and T.E. Dueber, Org. Syn., 54, 79 (1974); T.E. Dueber, et. al., Angew. Chem. Int. Ed. Engl., 9, 521 (1970).
- (5) P.J. Stang, M.G. Mangum, D.P. Fox and P. Haak, J. Am. Chem. Soc., 96, 4562 (1974).
- (6) N.D. Zelinskii and N.V. Elagina, Compt. Rend. Acad. Soc., 49, 568 (1945); CA, 40, 6058 (1946).
- (7) J.W. Rowe, A. Melero, D. Arigoni, O. Jeger, and L. Ruzicka, Helv. Chim. Acta., 40, 1 (1957); T.A. Mannel, Inorg. Chem., 3, 510 (1964).
- (8) W.D. Pfeifer, C.A. Bahn, P.v.R. Schleyer, S. Bocher, C.E. Harding, K. Hummel, M. Hanack, and P.J. Stang, J. Am. Chem. Soc., 93, 1513 (1971).
- (9) Control experiments established that all products in the solvolysis of both 1 and 2 were stable to the reaction conditions.
- (10) We do not know if the small amount of 4 observed in the solvolysis of 2 was via direct ionization to 10 and solvent capture or by S-O cleavage of the triflate. Such nucleophilic attack on S and the attendant S-O cleavage is well known.<sup>11</sup>
- (11) R.H. Summerville, C.A. Sankler, P.v.R. Schleyer, T.E. Dueber, and P.J. Stang, J. Am. Chem. Soc., 96, 1100 (1974); S. Oae and R. Kiritani, Bull. Chem. Soc. Japan, 38, 765 (1965); S. Oae, T. Fukumoto, and R. Kiritani, ibid., 36, 346 (1963); A. Bunton and Y.F. Frei, J. Chem. Soc., 1872 (1951).
- (12) Energetically vinyl cations prefer to be linear; R. Sustmann, J.E. Williams, M.J.S. Dewar, L.C. Alenn, and P.v. R. Schleyer, J. Am. Chem. Soc., 91, 5350 (1969); W.A. Lathan, W.J. Hehre, and J.A. Pople, ibid., 93, 808 (1971).
- (13) P.E. Peterson and R.J. Kamat, J. Am. Chem. Soc., 91, 4521 (1969).