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Propellanes. IX. The Nature of Norcaradienylcarbinyl Cations[1]

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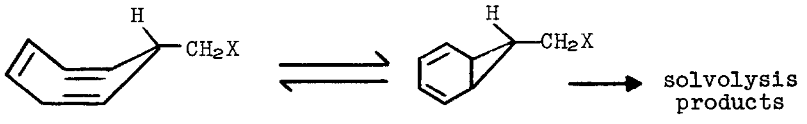
We have recently established that the norcaradiene-cycloheptatriene energy gap is in the neighborhood of 4.5 kcal/mole.[2] We, and Paquette,[3] have concommitantly concluded that 7-cycloheptatrienylcarbinyl systems solvolyze[4] preferentially through the anti configuration (II). Stohrer and Daub[5] have recently provided a partial electronic explanation for this phenomenon.[6] We

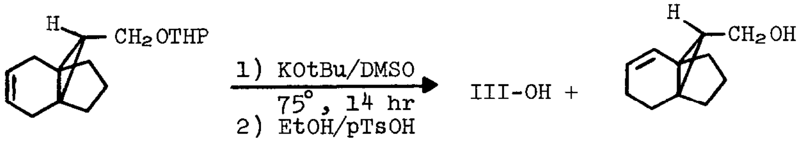


(1)

I II

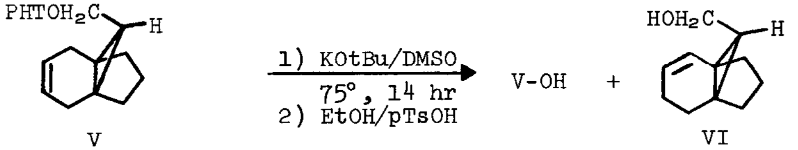
now report additional solvolytic data which afford a clearer picture of the nature of norcaradienylcarbinyl cations.

The requisite compounds were synthesized according to equations (2) and (3). Thus base-catalyzed rearrangement of the symmetrical olefins III and V



(2)

III IV

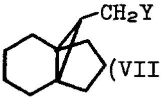
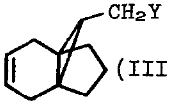
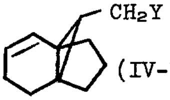
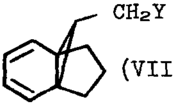
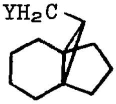
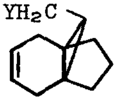
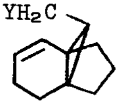
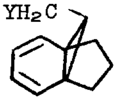


(3)

V VI

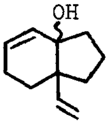
led to a mixture (~1:1) of unrearranged (III and V) and rearranged ethers (IV-OTHP and VI-OTHP). The unsymmetrical olefins were separated from their symmetrical counterparts via chromatography on silver nitrate impregnated (12%) silica gel. Ethanolysis then gave ca. 30% yields of IV and VI from III and V, respectively. The solvolysis rates for the corresponding 3,5-dinitrobenzoates are given in Table I, along with some previously reported.[2]

Table I. Solvolysis Data for 3,5-Dinitrobenzoates in 70:30 Acetone-Water (70.0 + 0.1°)

Compound (Y = ODNB)	k x 10^6, sec^{-1}	Rel rate
 (VII)	21.7	8.58
 (III-Y)	5.18	2.05
 (IV-Y)	8.49	3.36
 (VIII)	203	80.2
 (IX)	10.4	4.11
 (V-Y)	3.04	1.20
 (VI-Y)	3.78	1.49
 (X)	2.53	(1.00)

Several instructive comparisons may be drawn from the kinetic data. First of all, it can be seen that, with the exception of the dienes, the compounds of the *anti* series (III-Y, IV-Y, VII) solvolyze *ca*. twice as fast as those of the *syn* series (V-Y, VI-Y, IX). There is no discernible through-space (field) effect of the double bond of V-Y or VI-Y. The factor of 2 must be attributable to steric acceleration in the *anti* series.

Secondly, one may evaluate the conjugative effect of a vinyl group in the β-position of a cyclopropylcarbinyl cation. This is of interest vis a vis the recently reported[7] chrysanthemyl solvolyses, in which a *trans* β-vinyl (actually *iso*-butenyl) substituent is five times more accelerative than a *cis* β-vinyl substituent. At least in our case, the idea[7] that *trans* β-vinyl groups can conjugate better than *cis* ones is illusory; the relative rate for the *trans* case (*i.e.*, IV-Y/VII = 0.39) is the same as for the *cis* (VI-Y/IX = 0.36). The absolute rate difference between *cis* and *trans* is due to steric factors. Indeed, the *cis/trans* ratios found by Sasaki, *et al*.[7] are most likely also due to steric effects. Furthermore, with respect to the ability of the cyclopropane ring to transmit the conjugative effect of a vinyl group,[8] it can be seen that our data indicate a very small, but real, effect. This is best noted by comparing the unsymmetrical to symmetrical olefins (*i.e.*, (IV-Y/III-Y) = 1.64 and (VI-Y/V-Y) = 1.24). The blend of inductive and resonance effects are such that *both* need be stronger in the unsymmetrical cases. In any event, we do not feel the finding of allylcarbinyl-type products requires the postulation of distorted cyclopropylcarbinyl-type ions.[7] We find only allylcarbinyl type products, with *ca*. 1/3 of the "product" being that of internal return for III-Y, V-Y, VII and IX. However, we find no internal return for IV-Y or VI-Y, whereby we surmise that the product is the allylic alcohol only (XI).

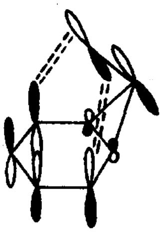


XI

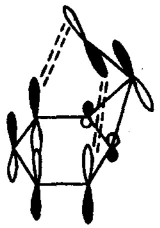
Thirdly, it is most interesting to compare the data for the unsymmetrical olefins (IV-Y, VI-Y) with that for the dienes (VIII, X). If the effect of the double bonds in the dienes is similar to that of the double bonds in the unsymmetrical monoenes, then the predicted relative solvolysis rates are 1.31 for VIII [(IV-Y/VII)(IV-Y)] and 0.54 for X [(VI-Y/IX)(VI-Y)]. The actual relative rates are 80.2 and 1.00, corresponding to an "unexpected" acceleration of 61.1 and 1.85. This serves to reemphasize[2] the *syn*-*anti* difference, where the conjugative acceleration is offset by through-space *antibonding* in the *syn* case.[9] Although the "unexpected" acceleration of the *anti* case is not great, it may be due to a slight change in the appropriate orbital coefficients[8a] of the β cyclopropyl carbons.

References

1. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.
2. P. Warner and S. Lu, *J. Amer. Chem. Soc.*, *95*, 5099 (1973).
3. G. L. Thompson, W. E. Heyd and L. A. Paquette, *ibid.*, *96*, 3177 (1974).
4. For the original solvolytic work on such compounds, see G. D. Sargent, N. Lowry and S. D. Reich, *ibid.*, *89*, 5985 (1967).
5. W. D. Stohrer and J. Daub, *Ang. Chem. Int. Ed.*, *13*, 86 (1974).
6. For other relevant studies, see: (a) J. Daub and W. Betz, *Tetrahedron Lett.*, 3451 (1972); (b) S. Kohen and S. J. Weininger, *ibid.*, 4403 (1972).
7. T. Sasaki, S. Eguchi, M. Ohno and T. Umemura, *Chem. Lett.*, 503 (1972).
8. (a) For a theoretical discussion, see C. F. Wilcox, L. M. Loew and R. Hoffmann, *J. Amer. Chem. Soc.*, *95*, 8192 (1973); see, also, (b) R. S. Brown and T. G. Traylor, *ibid.*, *95*, 8025 (1973).
9. Stohrer and Daub[5] have explained this by considering the antibonding combination of the diene and cyclopropylcarbinyl units (i). We point out[10,11] that a higher energy, occupied orbital, involving the bonding combination of the diene and antibonded cyclopropylcarbinyl units, (ii), is also important.



i



ii

In any event, we may calculate a minimum energy difference between the *syn* and *anti* cations (actually the energy difference between the transition states for their formation), as follows: $\Delta F = -RT \ln (k^s/k^a) = 2.5$ kcal/mole, where $k_s = (X/IX)$ and $k_a = (VIII/VII)$. This compares with a ΔF_{calc} (EH method) = 5.1 kcal/mole.[5]

10. We thank Profs. C. F. Wilcox[11] and Warren Hehre for pointing this out to us.
11. Cf. L. M. Loew, Ph.D. Dissertation, Cornell University, 1974.