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PARTICIPATION BY CYCLOPROPYL GROUPS AND COMPETITION WITH NORBORNYL PARTICIPATION

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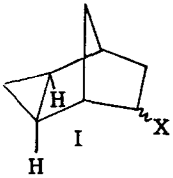
Participation of cyclopropyl groups with carbonium ion centers has been investigated for several orientations of the cyclopropyl group relative to the cationic center, including two substances (1), I and II, where the cyclopropyl group is not bonded to the center, as well as the more common cyclopropyl carbinyl systems (2). The nonadjacent cases studied failed to show major alteration in rate in marked contrast to the bonded cases. We wish to report here on three systems of spiro-cyclopropyl compounds, III, IV, and V, which have a bearing on this difference.



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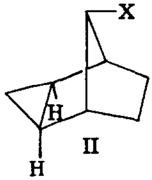

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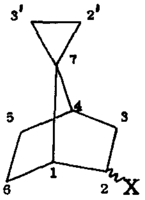

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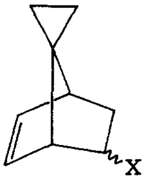

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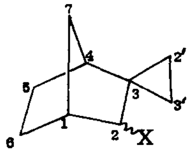

V

It is believed that a cyclopropane ring protonates preferentially edgewise (3) and it

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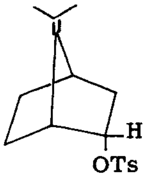
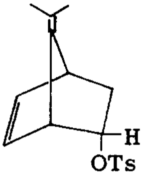
might be argued that I and II, unlike the cyclopropyl carbinyl systems, cannot donate charge in this manner. Systems III and IV more nearly approach this edgewise orientation. System V provides an internal check on the rearrangement process and the accompanying rates. It also provides interesting examples of norbornyl solvolyses in which any participation by the C_1C_6 bonding electrons might be swamped out (4).

For comparison it might be noted that DePuy's olefinic analogs (5), VI and VII, show rate enhancement by factors of 1800 and 270 relative to the molecules without a 7-olefinic group. The corresponding sets of *exo*-tosylates showed virtually no rate enhancements.



VI



VII

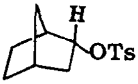
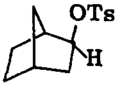
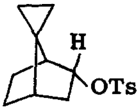
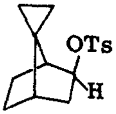
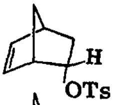
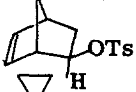
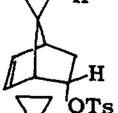
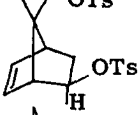
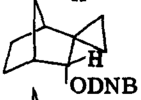
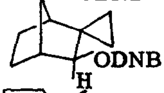
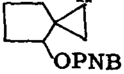
The *exo*- and *endo*-tosylates of III and IV were prepared (6) and solvolyzed in anhydrous acetic acid; the *exo*- and *endo*-3,5-dinitrobenzoates of V were prepared and solvolyzed in 70% acetone-water. The leaving group was altered for V because the tosylates proved to be so unstable that in our hands they could not be purified sufficiently to give meaningful rates (7). The kinetic data are collected in Table I along with pertinent reference rates.

The products isolated from solvolyses of both the *exo* and *endo* isomers of III and V were very largely (89-93%) *exo* acetate (or alcohol) of V. The main product from IV was the corresponding *exo* acetate.

The acetolysis rates of *exo* and *endo* III are similar to those of the apoisobornyl-camphenilyl systems but the product composition is much simpler (8). The rates of solvolysis of *exo* and *endo* V are strikingly similar showing little of the large *exo*/*endo* rate ratio associated with the norbornyl system. Also striking is the *ca*. 10^3 rate enhancement of *exo* V over *exo* norbornyl 3, 5-dinitrobenzoate (9) ($k = 3.4 \times 10^{-8}$ at 100°). The rates and products are consistent with the following picture. The *exo* and *endo* 3-spiro compounds yield a cation highly stabilized by

TABLE I

Solvolysis Rates and Activation Parameters[a]

Compound	Solvent	Rate (sec^{-1})	Temp.	$\Delta H^{\ddagger}$ (kcal/mole)	$\Delta S^{\ddagger}$ (e.u.)
	HOAc[b]	8.28×10^{-8}	25°	25.8	- 4.4
	HOAc[b]	2.33×10^{-5}	25°	21.7	- 6.9
	HOAc	(4.40×10^{-8}) 1.46×10^{-6} 2.91×10^{-5} 3.84×10^{-4}	25° 50° 75° 100°	26.1	- 4.4
	HOAc	7.88×10^{-5} 1.31×10^{-3}	25° 50°	20.9	- 7.3
	HOAc[c]	2.0×10^{-9}	25°	----	-----
	HOAc[c]	1.5×10^{-5}	25°	----	-----
	HOAc	(1.75×10^{-9}) 2.05×10^{-6} 3.47×10^{-5}	25° 75° 100°	28.5	- 3.0
	HOAc	4.05×10^{-5} 7.58×10^{-4}	25° 50°	21.8	- 5.5
	70% acetone-water	1.07×10^{-5} 9.76×10^{-5}	100° 125°	25.1	-14.3
	70% acetone-water	2.78×10^{-5} 3.08×10^{-4}	100° 125°	27.7	- 5.7
	60% acetone-water[d]	5.36×10^{-4}	100°	23.9	- 9.9

[a] OTs = p-toluenesulfonate; ODNB = 3,5-dinitrobenzoate; OPNB = p-nitrobenzoate.

[b] P. von R. Schleyer, M. M. Donaldson, W. E. Watts, J. Am. Chem. Soc., **87**, 375 (1965).

[c] S. Winstein and M. Shatavsky, ibid., **78**, 593 (1956).

[d] Based on data of A. P. Krapcho reported by W. D. Closson and G. T. Kwiatkowski, Tetrahedron, **21**, 2779 (1965). Para nitrobenzoates in 60% acetone have about the same rates as dinitrobenzoates in 70% acetone.

the neighboring cyclopropyl group. This stabilization swamps out the usual stabilization of the _exo_-norbornyl transition state although much of the preference for _exo_ solvent collapse remains. The 7-spiro compounds do not show significant stabilization, however they do yield the rearranged product corresponding to the stabilized 3-spiro cation. The continued preference (attenuated) for _exo_ attack of solvent without a corresponding preference for departure of a 3,5-dinitrobenzoate anion might be related to the difference in their charge states and the consequent difference in resemblance of the respective transition states with the alcohol or ester ground states. The unsaturated 7-spiro compounds IV, like III, show no rate enhancement due to interaction of the cyclopropyl group with the developing carbonium ion center.

One assumption inherent in this analysis is that _exo_ and _endo_ norbornyl 3,5-dinitrobenzoates retain a large difference in solvolysis rate in 70% acetone at 100°. In partial confirmation of this, it can be noted that the _endo_ norbornyl 3,5-dinitrobenzoate solvolyzed at an unmeasurably slow rate. This establishes, because of the very slow _exo_ rate, only a minimum rate ratio of about 10. Another assumption is that the 3-spiro _exo_ and _endo_ esters differ little in stability either between themselves or relative to norbornyl esters. Pertinent here is that equilibration of the alcohols at 120° gives a normal _exo_:_endo_ ratio of about 2:1 (10). _exo_-Camphenilyl brosylate acetolyzes _ca._ 2.7 × _slower_ than _exo_-norbornyl brosylate indicating no significant enhancement in rate due to adjacent bulky groups (8a).

The present investigation demonstrates that significant rate enhancement does not arise from either electrical polarization or delocalization of the electrons of a cyclopropyl group at C_7 despite its favorable geometry, whereas major participation does occur with a cyclopropyl group at C_3. Because the overlap integral between π orbitals at C_7 and C_2 is smaller (0. 06 _vs._ 0. 19) than the integral for orbitals at C_2 and C_3 the present results provide only presumptive evidence for participation at the C_2' and C_3' pseudo π orbitals (11). It is believed that torsional effects (12), while involved, are not sufficiently large to account for the observed rate enhancements. The small _exo_/_endo_ rate ratio of 2. 8 for the 3-spiro esters, V, indicates that the source of the large norbornyl rate ratio can be swamped. This is clearly consistent with an electronic interpretation (such as C_1-C_6 bond delocalization or polarization) but is difficultly reconciled with other data by a single steric factor. Thus it might be argued that the transition states were close to the ground state and little of any special norbornyl steric effect had developed. Such an analysis would seem to be unsatisfactory since introduction of a 2-phenyl or 2-anisyl group into norbornyl gives a large exo/endo ratio even though these compounds solvolyze with rate enhancements comparable to those from a neighboring cyclopropyl group (13). Some combination of steric arguments might rationalize these results (14). However, the electronic picture is tempting since it should be just such a symmetrical group as cyclopropyl that would be expected to show similar exo/endo rates free of steric complications.

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(2) R. Breslow in "Molecular Rearrangements," Vol.1, P. de Mayo, Ed., Interscience Publishers, Inc., 1963, Chap. 4; N. C. Deno, Prog. Phys. Org. Chem., **2**, 129 (1964); M.J.S. Dewar and A. P. Marchand, Ann. Rev. Phys. Chem., **16**, 321 (1965); P. von R. Schleyer and G. W. Van Dine, J. Am. Chem. Soc., **88**, 2321 (1966).

(3) R. L. Baird and A. A. Abodevin, ibid., **86**, 252 (1964); W. A. Bennett, J. Chem. Ed., **44**, 17 (1967).

(4) The acceleration from a neighboring cyclopropyl group has been estimated as ca. 10^9, M. C. Caserio, W. H. Graham, and J. D. Roberts, Tetrahedron, **11**, 171 (1960).

(5) C. H. Depuy, I. A. Ogawa, and J. C. McDaniel, J. Am. Chem. Soc., **83**, 1668 (1961).

(6) All compounds mentioned in this manuscript have been characterized and give satisfactory analyses.

(7) It is estimated from solvolysis of the dinitrobenzoates that the half-lives of both tosylates in acetic acid at 25° were about 10 seconds derived from a rate enhancement for exo of ca. 1000 and for endo of ca. 300, 000.

(8) A. K. Colter, E. C. Friedrick, N. J. Holness, and S. Winstein, J. Am. Chem. Soc., **87**, 378 (1965); the ketone precurser to exo and endo III absorbs at 1756 ± 1 cm^{-1} corresponding to a predicted [P. von R. Schleyer, ibid., **86**, 1854, 1856 (1964)] rate retardation of ca. 4.

(9) The ketone corresponding to exo and endo V absorbs at 1743 cm^{-1} corresponding to rate enhancement of ca. 10. This, however, does not include a correction for the substituent effect of the neighboring cyclopropane. This correction is complex and is

likely to depend on the relative orientation of the two groups. The few model systems available suggest that *without* ring strain the carbonyl frequency might be lowered by 10-20 cm^{-1} indicating that the cyclopropyl group does *not* introduce any significant geometric distortion. It thus appears that the observed rate enhancement must arise from other sources.

(10) C. F. Wilcox, Jr., M. Sexton, and M. F. Wilcox, *J. Org. Chem.*, **28**, 1079 (1963).

(11) Calculations using the extended Hückel model [R. Hoffmann, *J. Chem. Phys.*, **40**, 2480 (1964)] predicts no significant participation from a cyclopropyl group at C_7 but does predict stabilization energies of 8.1 kcal (*exo* sp^3 orbital) and 6.8 kcal (*endo* sp^3 orbital) for that group at C_3. The same calculations predict considerable charge development at C_2' and C_3' for the C_3 cyclopropane. Interestingly in the *exo* transition state the C_1'' atom develops much more positive charge (+0.12) than the C_3' atom (+0.07). We are indebted to Professor Hoffmann for making his program available.

(12) P. von R. Schleyer, *J. Am. Chem. Soc.*, **89**, 699, 701 (1967).

(13) H. C. Brown and K. Takeuchi, *ibid.*, **88**, 5336 (1966).

(14) For example, it might be argued that the *endo* isomer is fortuitously close to the *exo* isomer because easier participation of a cyclopropyl bond across the *exo* face of the norbornyl system just cancels the increased steric repulsion of an *endo* departure. This interpretation would require that both *exo* and *endo* be slow relative to a cyclopropyl system that did not develop steric strain on going through the transition state. Unfortunately, the 20-50-fold faster rate of the spiro[2,4] system (Table I) compares favorably with 100-fold rate difference of cyclopentyl over *endo* norbornyl. Suitable bulky substitution at C_7 might provide a distinction.

Note added in proof. Subsequent to the submission of this manuscript a dramatic cemonstration of edge-wise participation of a cyclopropane ring has been presented with the solvolysis of the endo isomer of II; H. Tanida, T. Tsuji, and T. Irie, *J. Am. Chem. Soc.*, **89**, 1953 (1967); M. A. Battiste, C. L. Deyrup, R. E. Pincock, J. Haywood-Farmer, *ibid.*, **89**, 1954 (1967).