Reduction of the corresponding ketones (carbonyl group at the 2, 2, and 8 positions, respectively) exhibited lower stereoselectivity, but the same pattern: an *exo*:*endo* ratio of attack of 75:25 for X, 89:11 for XI, and >99.9:0.1 for XII. On the other hand, the addition of methylmagnesium iodide to the ketones exhibited a very high degree of steric control: 98:2, 99.5:0.5, and >99.9:0.1 preferential *exo* attack, respectively, producing predominantly the corresponding tertiary methyl *endo* alcohols. Similarly, oxymercuration–demercuration of the 2-, 2-, and 8-methylene derivatives of X, XI, and XII, respectively, resulted in the preferential formation of the corresponding tertiary methyl *exo* alcohols: 89:11, 99.5:0.5, and >99.9:0.1, respectively.[6b]

These results are summarized in Table I.

Table I. Comparison of the Relative Stereoselectivities Exhibited by Three Representative U-Shaped Systems (X, XI, and XII)

Reaction	*exo*:*endo* ratios X	XI	XII
Hydroboration–oxidation of olefin	24	200	>1000
Epoxidation of olefin	6.7	200	>1000
Oxymercuration–demercuration of olefin	8	>500	
Lithium aluminum hydride reduction of ketone	3	8.1	>1000
Addition of CH_3MgX to ketone	50	200	>1000
Oxymercuration–demercuration of methylene derivatives	8.1	200	>1000
Solvolysis of the tertiary methyl *p*-nitrobenzoate	17	885	4300

Although individual reactions evidently differ considerably in the stereoselectivities they exhibit, the results reveal a consistent pattern. In all cases, the *cis*-bicyclo[3.3.0]octane system (X) exhibits the least preference for *exo* attack, presumably because of its higher flexibility, and the *endo*-5,6-trimethylenenorbornane system (XII) exhibits the highest stereoselectivity for *exo* attack. Indeed, an examination of a model reveals that the *endo* position in this structure is highly hindered. Finally, the norbornane system (XI) is intermediate.

The exo:endo rate ratios exhibited by the corresponding tertiary methyl p-nitrobenzoates exhibit the same pattern of behavior: 17 for X, 885 for XI, and 4300 for XII (Table I)!

It appears to us that this common pattern of reactivity for carbonium ion and noncarbonium ion reactions makes it necessary to reopen the question as to whether both types of reactions may not have a common physical basis for the unique stereospecificity.[7] Such a common physical basis could well be the greater steric accessibility of the *exo* face of these bicyclic structures and the steric difficulties involved in approaching or leaving the *endo* face. This does not mean that other effects, such as torsional interactions[8] and σ participation, may not contribute to the observed *exo*:*endo* rate ratios. It appears to us that the failure of numerous studies to find significant charge delocalization from the 2 to the 1 and 6 positions in the solvolysis of norbornyl derivatives[9] clearly establishes that σ participation cannot be a major factor in the observed *exo*:*endo* rate ratios. However, the tools available to test for charge delocalization, such as the introduction of substituents in appropriate positions, may not provide a truly satisfactory probe for minor contributions.

In the past, steric effects do not appear to have received serious consideration as a factor in the observed *exo*:*endo* rate ratios in norbornyl and related bicyclic derivatives. It is our opinion that the present results make it necessary to recognize steric effects as a factor in such *exo*:*endo* rate ratios.

(6) (a) H. C. Brown and P. Geoghegan, Jr., *J. Am. Chem. Soc.*, **89**, 1522 (1967); (b) H. C. Brown and W. J. Hammar, *ibid.*, **89**, 1524 (1967); (c) H. C. Brown, J. H. Kawakami, and S. Ikegami, *ibid.*, **89**, 1525 (1967).

(7) It is, of course, possible that this similarity is merely the result of a fortuitous coincidence. We are extending these studies to other systems to test this possibility. In particular, the 7,7-dimethylnorbornane system offers a critical test for the steric interpretation, and the reactions of this system are under intensive study: research in progress with J. H. Kawakami.

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

(9) H. C. Brown, *Chem. Brit.*, **2**, 199 (1966).

(10) Research assistant on grants (G 19878 and GP 6492 X) supported by the National Science Foundation.

(11) Postdoctorate research associate, 1963–1965.

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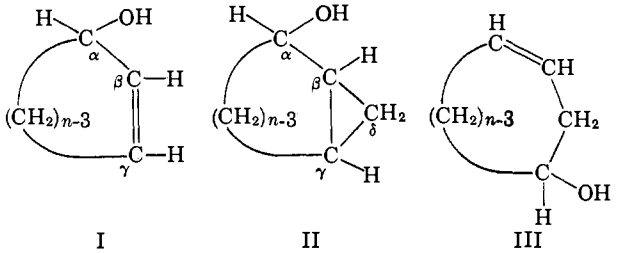
Nonclassical Homoallylic Cations and Homoallylic Ring Expansions[1]

Sir:

Conversion of a cyclic allylic alcohol I to the cyclopropane derivative II, together with acid-catalyzed isomerization of the latter to the homoallylic isomer III, can constitute a useful ring-expansion method.[2a,b] In this communication we describe such homoallylic ring expansions of some medium-size unsaturated ring systems which illustrate a very useful synthetic method and provide important new information about homoallylic rearrangements and nonclassical homoallylic ions.[2d]



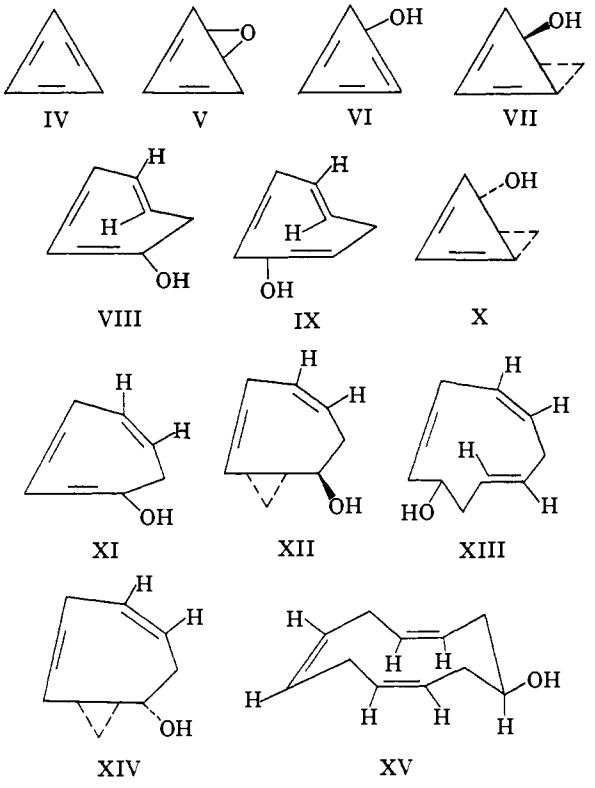
I II III

(1) (a) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research; (b) research supported in part by the National Science Foundation.

(2) (a) E. Friedrich, unpublished work; (b) A. C. Cope, S. Moon, and P. E. Peterson, *J. Am. Chem. Soc.*, **84**, 1935 (1962); (c) H. L. Goering and K. E. Rubinstein, Abstracts, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 28–31, 1966, p 5K; (d) L. Birladeanu, T. Hanafusa, B. Johnson, and S. Winstein, *J. Am. Chem. Soc.*, **88**, 2316 (1966), and references there quoted.

Two of the alcohols subjected to homoallylic ring expansion in the present work were the *anti*- and *syn*-2-bicyclo[7.1.0]deca-4,7-dienols[3] (VII and X), respectively. These were derived from *cis,cis,cis*-2,4,7-cyclononatrienol (VI), mp 39–40°, λ_{max} 223 mμ (ε 3510, MeOH); this alcohol was obtained in good yield from treatment of epoxide V with butyllithium.[4] Epoxide V, mp 50.5–51.5°, was prepared in 80% yield by reaction of *cis,cis,cis*-1,4,7-cyclononatriene[5] (IV) with 1 mole of *m*-chloroperbenzoic acid.

Treatment of trienol VI with CH_2I_2 and Zn–Cu couple yielded the *anti* monoadduct VII, mp 36–38°, ν_{max} 3608 cm^{-1} (CS_2), nmr τ 6.9 (α-H, CCl_4). Oxidation of VII to the ketone, mp 30–33°, ν_{max} 1695 cm^{-1} (CS_2), and reduction of the latter with lithium aluminum hydride yielded an alcohol mixture which contained 2.1% of the *anti* epimer VII and 97.9% of the *syn* epimer[6] X, ν_{max} 3600 cm^{-1} (weak), 3540 cm^{-1} (sharp, strong) (CS_2), nmr τ 5.8 (α-H, CCl_4).



Hydrolysis of the *p*-nitrobenzoate of the *anti*-VII, namely VII-OPNB, mp 126–127°, was carried out in 80% aqueous acetone (Table I). In the presence of sodium acetate as a buffer, the product contained *ca.* 60% of the *anti*-VII and <2% of the *syn* epimer X.[8] While kinetic control in ROPNB solvolysis does not favor homoallylic ring-expanded product, treatment of VII with 0.025 *N* $HClO_4$ in 80% aqueous dioxane yields *ca.* 90% of a thermally unstable ring-expanded trienol, either VIII or IX, containing a *trans* olefinic group as evidenced by a strong 965-cm^{-1} band in its infrared spectrum.[9]

Table I. Solvolysis and Isomerization Rate Constants

System	ROPNB, 80% acetone,[a] 75.0° 10^6k, sec^{-1}	ROH, 80% dioxane, 0.025 *M* $HClO_4$ Temp, °C	10^4k, sec^{-1}
VII	0.328 ± 0.011	100.0	*Ca.* 3
X[b]	1.57 ± 0.03	75.0	*Ca* 1.4
XII	0.99 ± 0.03	90	*Ca.* 2
XIV	8.26 ± 0.20	75.0	*Ca.* 6.5

[a] Some ion-pair return usually detected. [b] Some XI-OPNB isolated.

Solvolysis of *syn*-X-OPNB (mp 66–68°) gave rise to a product containing 13% of *syn*-X (<1% epimeric VII) and 77% of the ring-expanded *cis,cis,cis*-trienol XI[9,10] (mp 45–47°). Treatment of X with dilute perchloric acid in 80% dioxane gave rise cleanly to ring-expanded XI.

In the Simmons–Smith reaction, trienol XI gave rise to the *anti* monoadduct[11] XII, mp 61–63°, ν_{max} 3600 cm^{-1} (CS_2), nmr τ 6.6 (α-H, CCl_4). Oxidation of XII to the ketone, ν_{max} 1680 cm^{-1} (CS_2), and reduction with lithium aluminum hydride afforded *ca.* 98% of the epimeric[11] *syn*-XIV, mp 63–64°, ν_{max} 3600, 3550 (sharp) cm^{-1} (CS_2), nmr τ 5.9 (α-H, CCl_4).

Solvolysis of XII-OPNB, mp 109–111°, yielded, in addition to *ca.* 20% of unidentified hydrocarbon, a mixture[12] of alcohols containing 65% of XII (<2% epimeric XIV) and 15% of a trienol, ν_{max} 3600, 963 cm^{-1} (CS_2), assigned structure XIII with a *trans* olefinic group (strong 963-cm^{-1} infrared band). Treatment of XII with dilute perchloric acid gave rise smoothly to the ring-expanded trienol XIII. Solvolysis of the *syn*-XIV-OPNB, mp 111–112°, gave rise to two alcohols, 34% XIV (<2% epimeric XII) and 66% *cis,cis,cis*-3,6,9-cycloundecatrienol (XV), mp 65–67° (no major infrared absorption at *ca.* 965 cm^{-1}). Very clean conversion of XIV to ring-expanded XV could be accomplished by dilute perchloric acid treatment.

The cyclopropane ring containing alcohol products from the ROPNB solvolyses described above are seen to arise stereospecifically with retention of configuration at C_α. The creation of the olefinic group in the ring-expanded alcohol from ROPNB solvolysis or acid-catalyzed isomerization of the cyclopropylcarbinols is also stereospecific: a *cis* olefinic configuration arises

(3) All new compounds except VIII or IX gave satisfactory elemental analyses or correct mass spectral molecular weights. All new compounds displayed appropriate nmr and infrared spectra.

(4) (a) R. L. Letsinger, *et al.*, *J. Am. Chem. Soc.*, **74**, 399 (1952); (b) J. K. Crandall and L. H. Chang, *J. Org. Chem.*, **32**, 435 (1967).

(5) P. Radlick and S. Winstein, *J. Am. Chem. Soc.*, **85**, 344 (1963).

(6) The *syn* configuration was assigned to X because of the very hindered hydroxyl group, as indicated by rapid elution from alumina, the strong 3540-cm^{-1} infrared absorption, and the deshielding of the α-H from τ 6.9 in VII to τ 5.8 in X. This assignment is supported by the stereochemistry of the ring expansions. Contrary to the situation with smaller rings, the OH group in a medium-sized ring allylic alcohol does not necessarily have a *cis* directing effect[7] in the Simmons–Smith reaction. In fact, inspection of models of medium-sized ring allylic alcohols shows that the alcohol function can be closer to the *anti* side of the olefinic group and can thus be *anti* directing.

(7) (a) S. Winstein and J. Sonnenberg, *J. Am. Chem. Soc.*, **83**, 3235 (1961); (b) W. G. Dauben and G. H. Berezin, *ibid.*, **85**, 468 (1963).

(8) A variety of other hydrocarbon, alcoholic, and ketonic products are also produced, but ring-expanded alcohol VIII or IX is at best only a minor component.

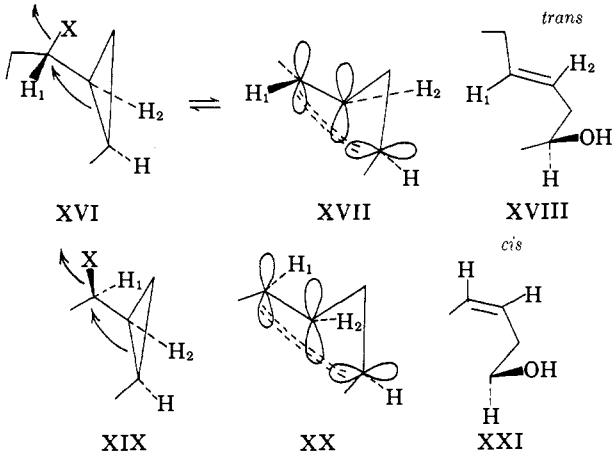
(9) In the various olefinic alcohols without cyclopropane rings encountered in the present work, we invariably observed strong absorption or multiple medium absorptions in the 700-cm^{-1} region for *cis* olefinic groups and strong absorption at *ca.* 965 cm^{-1} for *trans* olefinic groups.

(10) Hydrocarbon (1%) and six other minor products totaling 9% were also observed.

(11) Configurations were assigned to XII and XIV on the same basis outlined for VII and X.

(12) The alcohol mixture contained 20% of an unidentified component which appeared to be a dienol.

from the *syn* starting material, a *trans* from the *anti*. These stereochemical features are just those to be expected from reactions proceeding by way of homoallylic ions[2d] formed by the anchimerically assisted ionization of the cyclopropylcarbinyl derivative which involves mainly participation by the C_β–C_γ secondary–secondary cyclopropane bonding electrons. This is shown in the sequence XVI → XVII → XVIII for an *anti* derivative and XIX → XX → XXI for a *syn* epimer.[13] For the C_β–C_γ bond of the cyclopropane ring of *anti*-XVI to participate in the ionization, rotation about the C_α–C_β bond must occur so as to place H_1 and H_2 in a *trans* relationship in the ion XVII and in the expanded product XVIII. Conversely, a *cis* relationship of H_1 and H_2 is expected in ionization of *syn*-XIX. One additional stereochemical feature is predicted on the basis



of the usual stereoelectronic considerations, namely, inversion of configuration at C_γ. While the cyclopropylcarbinyl compounds described above were insufficiently labeled to test this point, this stereochemical question is dealt with in the following communication.[14]

The present stereochemical results differ considerably from those observed with smaller ring systems. Thus, with I–III where n = 5, 6, or 7, recollection of configuration at C_α of the cyclopropyl carbinol II tends to be largely or completely lost and only a *cis* olefinic group seems to be formed in the ring-expanded III.[2a-c] Until more ring systems are investigated it is not clear which ones can be expected to yield the stereospecific results described.

(13) Homoallylic ions XVII and XX are employed for simplicity, but "symmetrical homoallyl" or "bisected" type ions[2d] could account for the facts if delocalization of the C_β–C_γ cyclopropane electrons is much more important than C_β–C_δ in the transition states.

(14) D. Whalen, M. Gašić, B. Johnson, H. Jones, and S. Winstein, *J. Am. Chem. Soc.*, **89**, 6384 (1967).

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Single and Double Homoallylic Ring Expansions[1]

Sir:

In the preceding communication[2] we reported solvolyses and homoallylic ring expansions of several cyclopropylcarbinyl derivatives which proceeded with retention of configuration at C_α and stereospecific formation of either a *cis* or a *trans* olefinic group depending on the epimer employed for the homoallylic ring expansion. We now report so-called single and double homoallylic ring expansions of the trismethylene adducts of *cis,cis,cis*-2,4,7-cyclononatrienol which show the same stereochemical features but, in addition, demonstrate the inversion of configuration at C_γ expected from a homoallylic intermediate.

Addition of excess zinc–methylene iodide reagent to 2,4,7-cyclononatrienol (I) yielded two bis adducts,[3] bis-A (II), mp 72–73°, and bis-B (III), mp 92–93°, and two tris adducts, tris-A (IV), mp 117–119°, and tris-B (V). Relative to the hydroxyl group, the *anti* disposition of cyclopropane ring 1 in II–V is clear from the previous work. The *syn* disposition of cyclopropane ring 3 in II and IV and the *anti* disposition in III and V is clear from the fact that the bis-A and tris-A adducts are also produced by the Simmons–Smith reaction on alcohol VI,[4] mp 45–46°, λ_{max} 218 mμ (ε 17,800, 95% EtOH), with a *syn* relationship of the cyclopropane ring and OH group. The *trans* relationship of cyclopropane rings 1 and 2 in the tris adducts is clear from the chemical behavior of IV and V (see below).

Solvolysis of IV-OPNB, mp 131–132°, in 80% aqueous acetone or treatment of IV with 0.04 *N* $HClO_4$ in 80% aqueous dioxane (Table I) gave rise cleanly to

Table I. Sovolysis and Isomerization Rate Constants

System	ROPNB, 80% acetone[a] Temp, °C	10^5k, sec^{-1}	ROH, 80% dioxane, 0.025 *N* $HClO_4$, 75.0° 10^4k, sec^{-1}
IV[b]	75.0	2.54 ± 0.05	*Ca.* 85[c]
VII	75.0	0.264 ± 0.007	
IX[d]	75.0	0.717 ± 0.005	1.59 ± 0.1
X	75.0	0.845 ± 0.014	*Ca.* 9
XI	75.0	0.120 ± 0.002	2.69 ± 0.33
XV	100.0	2.53 ± 0.05	*Ca.* 1
XVI	100.0	2.15 ± 0.06	*Ca.* 1.1

[a] Some ion-pair return usually detected. [b] 8% VII-OPNB isolated. [c] 0.041 *N* $HClO_4$. [d] 13% XI-OPNB isolated.

monoexpanded VII, mp 65.5–67.5°, ν_{max} 963 cm^{-1} (CS_2), with a *trans* olefinic group.[5] Less than 1% of the epimer of VII could be detected. The liquid epimeric alcohol was prepared by oxidation of VII to the ketone followed by $LiAlH_4$ reduction (>99% stereospecific). Extended treatment of VII with 0.04 *N* $HClO_4$ in 80% dioxane yielded a mixture containing *ca.* 70% of bis-expanded alcohol VIII, mp 61–62°, with two *trans*

(1) (a) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research; (b) research supported in part by the National Science Foundation.

(2) M. Gašić, D. Whalen, B. Johnson, and S. Winstein, *J. Am. Chem. Soc.*, **89**, 6382 (1967).

(3) All new compounds gave satisfactory elemental analyses and displayed appropriate nmr and infrared spectra.

(4) Alcohol VI was obtained by KOBu-*t*-DMSO treatment of the monoepoxide prepared from the crownlike monomethylene adduct of 1,4,7-cyclononatriene.

(5) With olefinic systems containing cyclopropane rings, we usually observed additional medium absorptions in the 960–990-cm^{-1} region, obscuring somewhat the diagnosis for a *trans* olefinic group based on a strong 965-cm^{-1} band.[2] In some of these cases the corresponding ketones showed only weak absorption in the 960–990-cm^{-1} region. Additional help in assigning olefinic configurations was obtained from vinyl coupling constants and the various chemical interrelationships.