

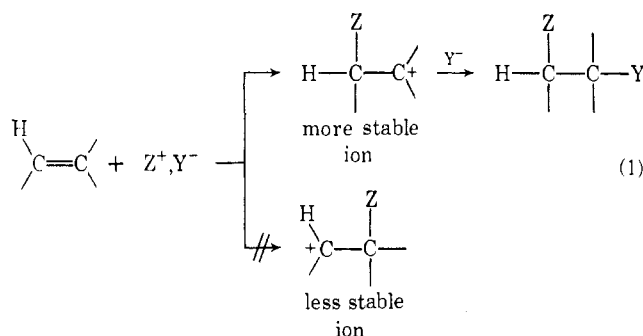
Photosensitized Ionic Additions to Cyclohexenes

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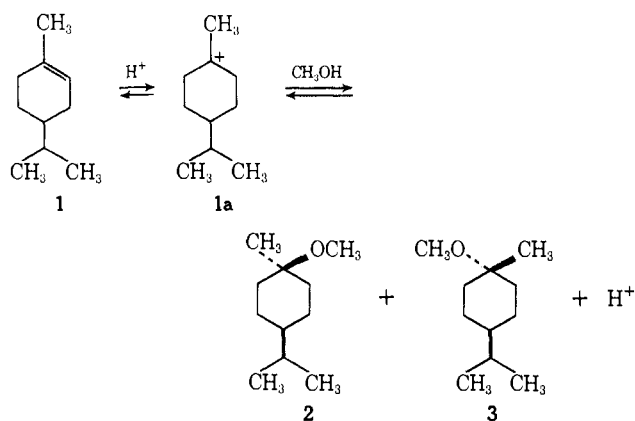
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Markovnikov's rule, one of the longest standing empirically derived rules of organic chemistry, finds its theoretical basis in the fact that ionic additions of unsymmetrical reagents to unsymmetrical olefins proceed *via* the more stable of the two possible carbonium ion intermediates (eq 1).¹ Thus, for example, the



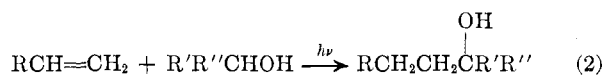
acid-catalyzed addition of methanol to 1-menthene (**1**) affords tertiary ethers **2** and **3** arising *via* the tertiary cation **1a**. In this case two geometric isomers are possible, and since the addition occurs reversibly in the presence of the strongly acidic catalyst, the ratio of these products reflects their relative stabilities (**2**:**3** = 1.5).²

In 1966 we made the astonishing discovery that the addition of methanol to 1-menthene (**1**) in the Markovnikov sense could also be effected in neutral solution provided the reaction was carried out photochemically in the presence of a high-energy photosensitizer such as benzene, toluene, or xylene.³ Since 1-menthene absorbs little or none of the light (λ 220–400 $m\mu$) employed in our experiment, energy transfer from the excited state of the photosensitizer to the ground-state olefin must have occurred, thereby promoting the olefin to a



reactive state. Considering the energies involved and on the basis of previous findings⁴ the first excited triplet state of the olefin seemed a likely intermediate in the addition reaction. Subsequent studies with triplet quenchers supported this presumption.³

The formation of tertiary ethers **2** and **3** from the photochemically initiated addition of methanol to 1-menthene was completely unforeseen. *A priori*, entirely different types of adducts could have been expected. For example, 1-alkenes react photochemically with alcohols to give addition products derived from cleavage of the α -C-H bond of the alcohol (eq 2).⁵



Furthermore, cyclohexene has been found to undergo reduction to cyclohexane upon irradiation with isopropyl alcohol.⁶ These previous examples clearly proceed *via* free-radical pathways. However, the aforementioned addition of methanol to 1-menthene

(1) Cf. F. G. Bordwell, "Organic Chemistry," The Macmillan Co., New York, N. Y., 1963, pp 291–293.

(2) Unpublished findings of R. D. Carroll, Northwestern University.

(3) J. A. Marshall and R. D. Carroll, *J. Am. Chem. Soc.*, **88**, 4092 (1966).

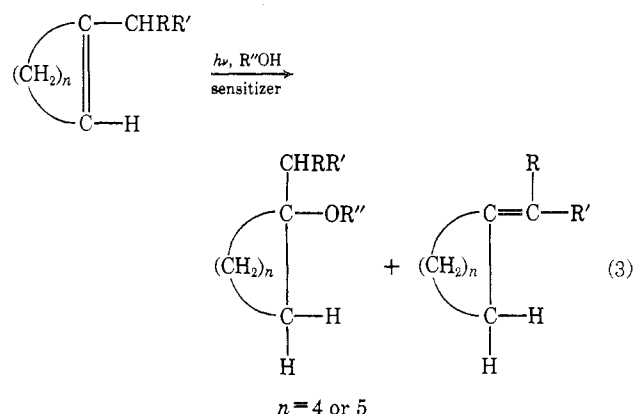
(4) Cf. G. S. Hammond, N. J. Turro, and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1144 (1962); H. Morrison, *J. Am. Chem. Soc.*, **87**, 932 (1965).

(5) Cf. G. Sosnovsky, "Free Radical Reactions in Preparative Organic Chemistry," The Macmillan Co., New York, N. Y., 1964, pp 121–125.

(6) N. C. Yang, D. P. C. Tang, D. M. Thap, and J. S. Sallo, *J. Am. Chem. Soc.*, **88**, 2851 (1966), and references cited therein.

appears to take place by a photochemically induced ionic addition to the isolated carbon-carbon double bond. Apparently this represents a new type of photochemical addition reaction, possibly involving a cationic intermediate.⁷ If such is indeed the case a number of intriguing possibilities, including the chance to examine the behavior of alkyl cations under neutral or even basic conditions, may become available to organic chemists for the first time. Moreover, numerous exciting synthetic applications can also be envisioned for such a reaction.

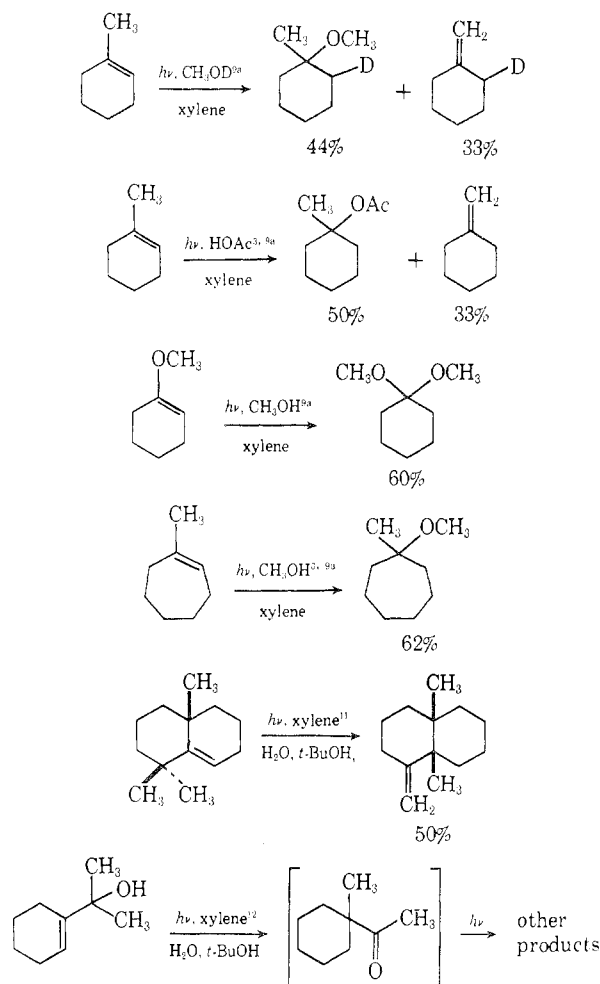
Concurrent⁸ and subsequent studies⁹ showed that water, alcohols, and carboxylic acids undergo the addition reaction, but only with cyclohexenes and cycloheptenes. Acyclic, exocyclic, and larger and smaller ring monoolefins fail to give Markovnikov addition products. Double-bond isomerizations to the exocyclic position accompany additions carried out on 1-alkylcyclohexenes and 1-alkylcycloheptenes (eq 3).



The available evidence suggests that these addition and isomerization reactions proceed by way of a common cationic intermediate derived from the triplet state of the cycloalkene. This conclusion is based on (1) the observed rate retardation of the ionic reaction in the presence of triplet quenchers,³ (2) the isolation of tertiary ethers and esters from photosensitized irradiations of 1-alkylcyclohexenes and 1-alkylcycloheptenes conducted in alcohol and carboxylic acid solvents;^{3,8,9} (3) deuterium-labeling studies which show that protons rather than hydrogen atoms are transferred to the olefins;^{8,9,10} (4) the pH dependence of product formation (often faster at lower pH);^{9b,11} and (5) the occurrence of methyl migrations in highly branched cyclohexenes.^{11,12} The examples in Chart I illustrate the potential scope of the reaction.

Since ionic reactions are observed only with cyclo-

Chart I



(7) A formally analogous reaction has been observed with conjugated dienes: W. G. Dauben and W. T. Wipke, *Pure Appl. Chem.*, **9**, 539 (1964); G. Just and C. Pace-Asciak, *Tetrahedron*, **22**, 1069 (1966), and references cited therein.

(8) P. J. Kropp, *J. Am. Chem. Soc.*, **88**, 4091 (1966).

(9) (a) P. J. Kropp and H. J. Krauss, *ibid.*, **89**, 5199 (1967); (b) J. A. Marshall and M. J. Wurth, *ibid.*, **89**, 6788 (1967).

(10) J. A. Marshall and A. R. Hochstetler, *Chem. Commun.*, 296 (1968).

(11) J. A. Marshall and A. R. Hochstetler, *ibid.*, 732 (1967).

(12) Unpublished findings of A. Greene, Northwestern University.

hexenes and cycloheptenes, it is clear that some special significance must be placed on the ring size. Cyclopentenes yield products of free-radical reactions¹³ while cyclooctenes^{9a} and larger cyclic olefins either polymerize or undergo *cis-trans* isomerization.¹⁴ Kropp and Krauss^{9a} attribute these differences to steric strain. They note that, with cyclohexene and larger ring olefins, the adjacent sp^2 -hybridized carbon atoms can attain the requisite 90° (orthogonal) geometry favored for the triplet state and essential to *cis* \rightarrow *trans* isomerization.¹⁵ With cyclopentene, the angle of twist available to the double bond is restricted to about 40° by steric factors. Thus, cyclopentene should give rise to a highly strained and reactive π, π^* triplet state.

Obviously, a coplanar *trans* double bond cannot be accommodated in six- or seven-membered rings. If formed, such double bonds would suffer considerable

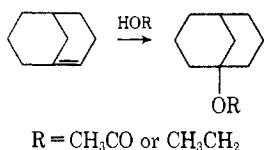
(13) P. J. Kropp, *J. Am. Chem. Soc.*, **89**, 3650 (1967).

(14) Cf. J. K. Crandall and C. F. Mayer, *ibid.*, **89**, 4374 (1967), and references therein. Unfortunately neither the substrates nor the reaction conditions employed in these and related studies would favor ionic processes. The comparisons are therefore somewhat tenuous. However, Kropp's work with 1-methylcyclooctene^{9a} tends to justify the extrapolation to larger ring cycloalkenes. Additional work on larger cycloalkenes is under way in our laboratory.

(15) R. S. Mulliken and C. C. J. Roothaan, *Chem. Rev.*, **41**, 219 (1947).

torsional strain, especially the six-membered case where geometrically the olefin might even resemble the triplet.¹⁶ Electronically, however, the *trans* cycloalkene would conform to a singlet state and may, by virtue of excess vibrational energy, react *via* a hot ground state.¹⁷ Of course the triplet state of the cyclic olefin could decay to the *cis* olefin as well, but in that event no reaction would be observed. In the case of cyclopentene, the orthogonal triplet is already so highly strained that further rotation to a species even remotely resembling a *trans* olefin would be exceedingly unlikely. With eight-membered and larger ring olefins the *trans* isomers can be readily formed and *cis* → *trans* isomerization occurs. The same is true for acyclic olefins. In these cases reactions of the triplet states can also be observed.

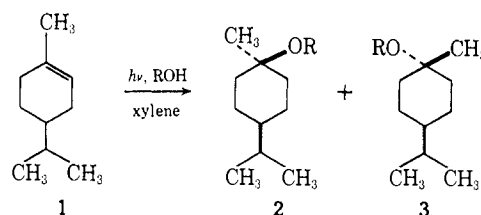
The high degree of torsional and other types of strain inherent in the olefinic bond of *trans*-cyclohexene and *trans*-cycloheptene would undoubtedly endow these substances and their derivatives with unusual chemical reactivity. Some indication of this reactivity can be seen in the chemistry of bicyclo[3.3.1]non-1-ene,¹⁸ a moderately twisted olefin according to molecular models. This olefin quantitatively yields bicyclo[3.3.1]non-1-yl acetate within 15 sec after being dissolved in glacial acetic acid.¹⁹ Even more remarkable is its conversion, albeit slow, to the corresponding ethyl ether in refluxing ethanol.¹⁹ These findings indicate that one reaction pathway available to torsionally strained olefins consists of additions by acidic reagents,



perhaps *via* an intermediate cation.²⁰ The *trans* cycloolefins derived from cycloheptenes and cyclohexenes might therefore reasonably be expected to undergo protonation, even by weak acids such as water and alcohols.

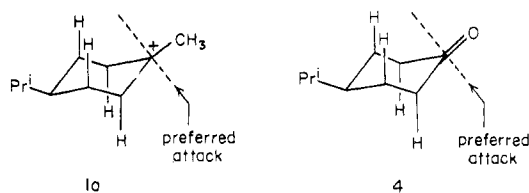
A stereochemical basis for the carbonium ion hypothesis comes from studies on the aforementioned photochemically initiated addition of water and alcohols to 1-menthene (**1**), leading to mixtures of the *cis* and *trans* adducts **3** and **2**. The observed product ratios (**3**:**2** = 1.3–1.7) must represent kinetic distributions of stereoisomers since the methyl and ethyl ethers

afford mixtures containing predominantly the *trans* isomers **2** (**3**:**2** = 0.7) upon acid-catalyzed equilibration.³



R	2 , %	3 , %	3 : 2
H	26	33	1.3
CH ₃	24	37	1.5
C ₂ H ₅	21	28	1.3
(CH ₃) ₂ CH	10	17	1.7

The predominance of *cis* over *trans* isomers in photo-induced additions to 1-menthene can be understood on the basis of the 1-menthyl cation (**1a**) where steric factors favor approach from the bottom face. A similar steric situation obtains in 4-isopropylcyclohexanone (**4**). Here, the addition of methyllithium affords the isomeric alcohols **2** and **3** in a ratio (**2**:**3** = 1.5)³ which reflects nearly the same stereochemical preference for bottom-side attack as the photochemical additions to 1-menthene.



Octalin **5** likewise appears to undergo photoinduced hydration by preferential attack at the less hindered face of the hypothetical tertiary cationic intermediate, as shown by its conversion to a 2:1 mixture of decalols **6** and **7** upon irradiation in aqueous 1,2-dimethoxyethane containing xylene²¹ as the photosensitizer. In this case, isomerization to the exocyclic olefin **10** (63% yield) predominates.²² The equatorial alcohol **6** was independently synthesized by reduction of the oxirane **8** obtained by treating the olefin **5** with *m*-chloroperoxybenzoic acid. The axial alcohol **7** was independently prepared by addition of methyllithium to decalone **9**.²³

Octalin **11** affords a mixture of the isomerized olefin **14** (57%), the equatorial alcohol **12** (19.5%), and the axial alcohol **13** (17.5%) upon irradiation in aqueous 1,2-dimethoxyethane.²² Once again photochemical hydration favors the equatorial alcohol, although not as

(16) Although *trans*-cycloheptene has been generated as an unstable intermediate, attempts to produce *trans*-cyclohexene in the same manner failed: E. J. Corey, F. A. Carey, and R. A. E. Winter, *J. Am. Chem. Soc.*, **87**, 934 (1965).

(17) Cf. N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, pp 186–190.

(18) J. A. Marshall and H. Faubl, *J. Am. Chem. Soc.*, **89**, 5965 (1967); J. R. Wiseman, *ibid.*, **89**, 5966 (1967).

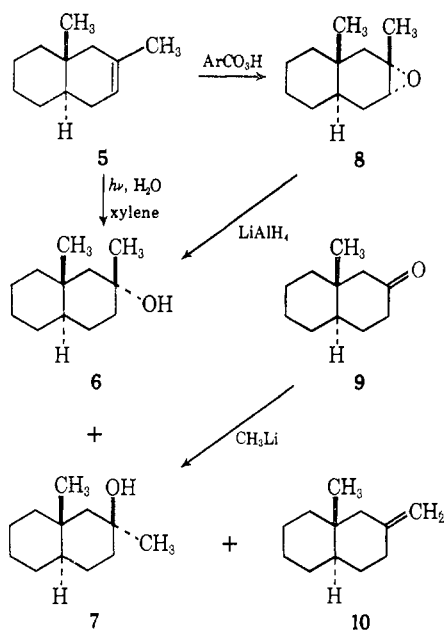
(19) Unpublished findings of H. Faubl, Northwestern University.

(20) Cf. W. G. Dauben and C. D. Poulter, *J. Org. Chem.*, **33**, 1237 (1968), and P. von R. Schleyer, P. R. Isele, and R. C. Bingham, *ibid.*, **33**, 1239 (1968), for quantitative studies on the solvolysis of bicyclo[3.3.1]non-1-yl derivatives.

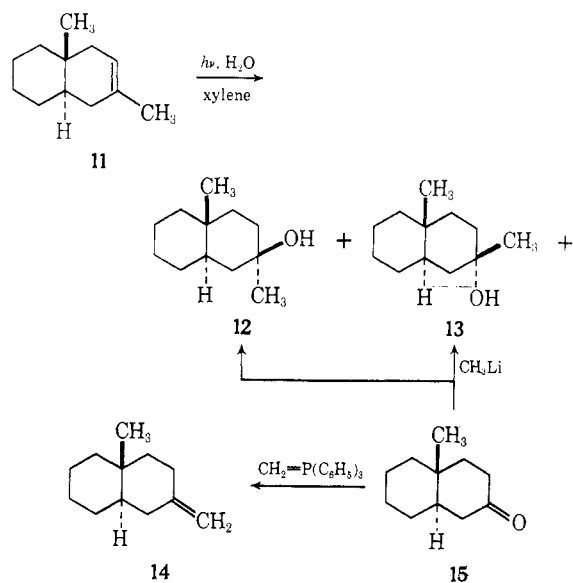
(21) A commercially available mixture of the three isomers containing principally *m*-xylene was employed in these studies. Recent unpublished work (M. Wurth, Northwestern University) has shown that *p*-xylene offers some advantages as a photosensitizer for these reactions owing to its slower conversion to polymeric products.

(22) Unpublished findings of M. Wurth, Northwestern University.

(23) J. A. Marshall and R. D. Carroll, *J. Org. Chem.*, **30**, 2748 (1965).

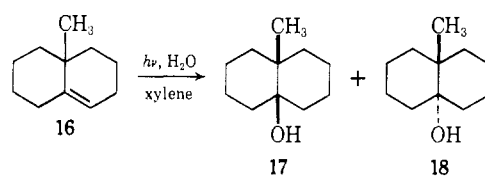


greatly as with octalin 5. On the other hand, treatment of decalone 15²⁴ with methyl lithium gives decalols 12 and 13 with a preponderance (13:12 = 2.3) of the axial alcohol. Here as with 1-menthene and octalin 5, the major alcohol isomer obtained *via* photochemical hydration corresponds to the minor product of methyl-lithium addition to the related ketone.

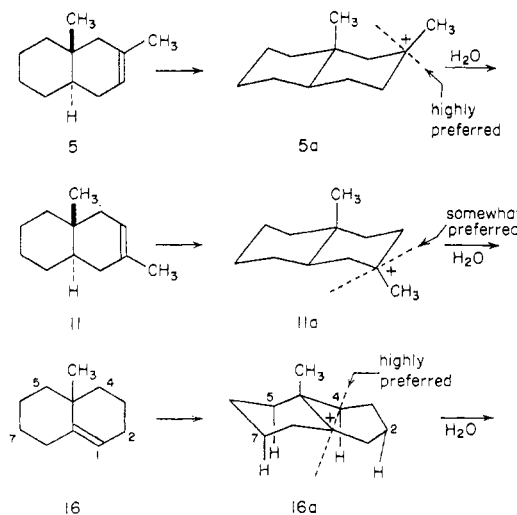


Octalin 16 yields almost entirely (92%) the *cis*-decalol 17 upon photochemical hydration, but a minor amount of the *trans*-decalol 18 (8%) can also be isolated.²² The alcohols were identified through direct comparison with authentic samples.²⁵

The foregoing results can be accommodated on the basis of the cationic intermediates 5a, 11a, and 16a



derived as previously discussed from the corresponding olefins.



The angular methyl grouping effectively shields the top face of cation 5a, thereby causing approach from the bottom face to be the preferred addition pathway. Models suggest that with cation 11a top side approach will be somewhat preferred,²³ in agreement with the results obtained for both photochemical hydration and the addition of methyl lithium to the corresponding decalone 15. The relatively high proportion of elimination to addition products observed with olefins 5 and 11 suggests that the unfavorable steric interactions associated with the related alcohol products contribute somewhat to the over-all transition-state energy for the addition process. However, other factors such as solvent basicity and polarity must also directly influence the reaction pathway. Thus, the photochemical hydration of olefin 5 in aqueous *t*-butyl alcohol leads to a relatively high proportion of alcohols 6 (14%) and 7 (42%) to isomerized olefin 10 (31%) compared with that obtained in aqueous 1,2-dimethoxyethane (30% 6 and 7, 63% 10).

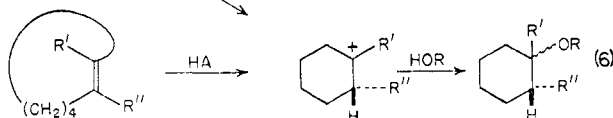
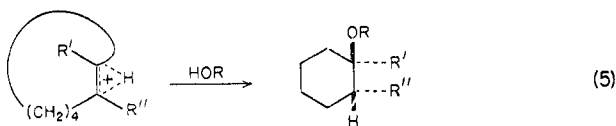
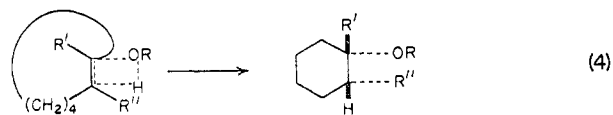
Olefin 16 constitutes a special case since the isomerization reaction cannot occur without invoking energetically unfavorable secondary cations. Molecular models indicate that approach to the top face of cation 16a should be somewhat preferred by virtue of the axial hydrogens at C-2, C-4, C-5, and C-7 which block approach to the bottom face. However the conformational mobility of cation 16a makes this prediction less certain than the previous ones with cations 5a and 11a. Furthermore, no analogy to carbonyl addition reactions can be drawn in this case.

The stereochemical findings outlined above seem adequately accommodated by a mechanism involving a cationic precursor for the photochemical products.

(24) Cf. J. A. Marshall, N. Cohen, and K. R. Arenson, *J. Org. Chem.*, **30**, 762 (1965).

(25) J. A. Marshall and A. R. Hochstetler, *ibid.*, **31**, 1020 (1966).

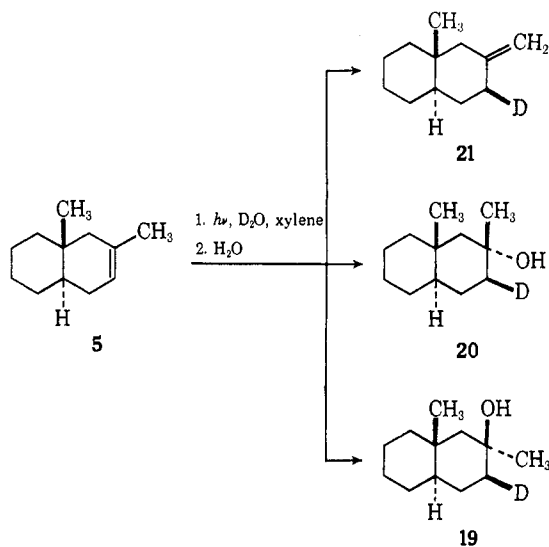
The question remains as to the precise origin of that precursor. As noted earlier, Kropp and Krauss^{9a} have suggested a number of possibilities, including protonation of the π, π^* triplet state of the olefin or addition to a *trans*-cycloalkene. In either event, but particularly with the latter, the following distinct pathways can be envisioned for the addition process. (1) The *trans* olefin could undergo *cis* addition of HOR via a four-center transition state in which C-H bond formation somewhat precedes C-O bond formation (Markovnikov orientation). This pathway would lead to a *trans* adduct (eq 4). (2) The orthogonal triplet or *trans* olefin could be converted to a protonated complex which would undergo backside attack at the more substituted carbon, giving the *cis* adduct with over-all *trans* addition (eq 5). (3) The aforementioned complex could collapse to a cation which then reacts with a nucleophile in a second step to give a mixture of *cis* and *trans* addition products whose composition would depend upon the steric environment of the cation. This reaction could also proceed by direct protonation of the triplet or *trans* olefin without intervention of a protonated complex (eq 6).



Evidence which supports the third possibility was secured from a study of the photoinitiated addition of deuterium oxide to octalins **5**, **11**, and **16**.

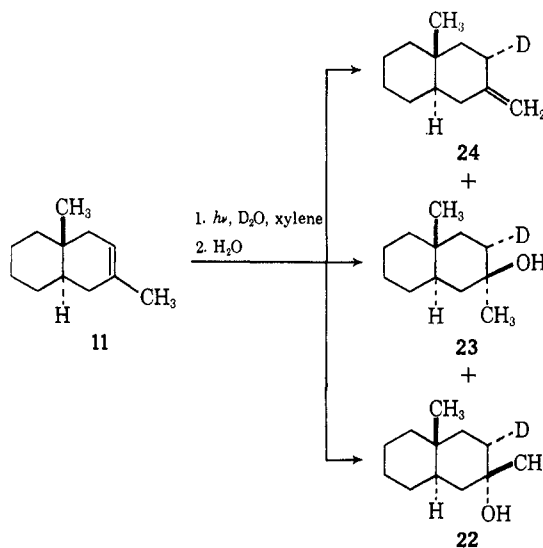
Octalin **5** upon irradiation in D₂O-1,2-dimethoxyethane-xylene, followed by thorough washing of the resulting product with water to remove oxygen-bound deuterium, affords a mixture of isomerized olefin **21** (77%), equatorial alcohol **20** (10%), and axial alcohol **19** (5%).^{22, 26} The product distribution closely resembles that obtained in the hydration of octalin **5**. Product formation, however, is notably slower in the deuterium oxide (*vs.* water) cosolvent. The alcohols **19** and **20** were shown to contain at least 90% of the equatorially deuterated isomers by direct comparison of their infrared and nmr spectra with those of inde-

pendently synthesized authentic samples.²⁶ All three photochemical products contain essentially the same distribution of *d*₀, *d*₁, and *d*₂ species, in keeping with the postulate that the isomerized olefin **21** and alcohols **19** and **20** arise from the same intermediate.



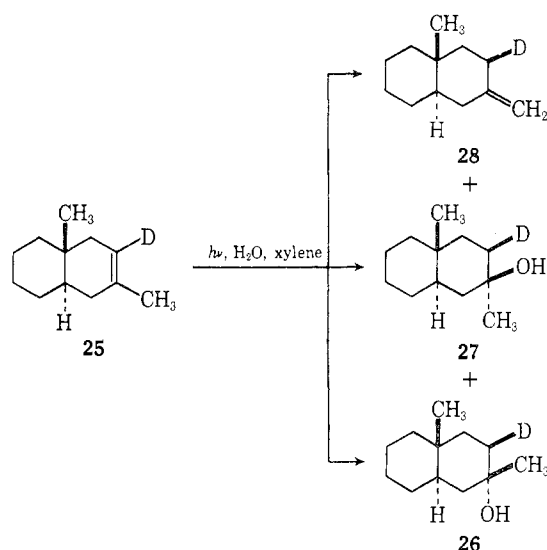
Irradiation of octalin **11** under the conditions employed for octalin **5** leads to a mixture containing the exocyclic olefin **24** (37%), the equatorial alcohol **23** (30%), and the axial alcohol **22** (24%).^{9b} Once again a marked rate decrease is noted in going from water to deuterium oxide. All three photochemical products were shown to be equatorially deuterated (>90%) by comparison with independently synthesized samples.²⁶ The photochemical products were also shown to have essentially identical *d*₀, *d*₁, and *d*₂ distributions (very largely *d*₁). This finding, coupled with the highly specific equatorial orientation of the incorporated deuterium, indicates that these products also share a common (cationic) precursor.

Results complementary to those outlined above were secured by irradiation of the deuterated octalin **25** in aqueous *t*-butyl alcohol-xylene.²² In this case, the axially deuterated alcohols **26** (17%) and **27** (22%) are

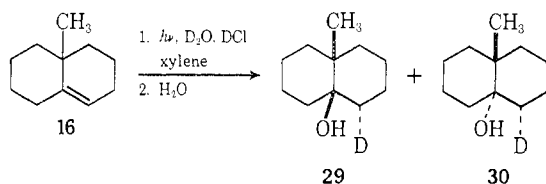


(26) The products of D₂O additions were identified through independent stereoselective syntheses along the lines suggested in a preliminary communication of a portion of this work.^{9b} Owing to space limitations we are unable to present herein the pathways employed in these syntheses. However, the synthetic work leaves no doubt as to the identity of the photochemically derived alcohols.

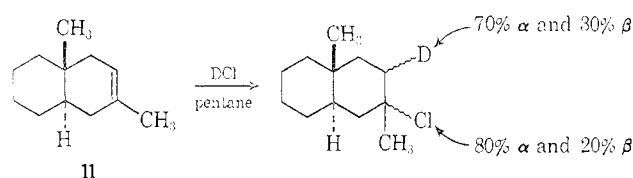
obtained, along with the axially deuterated exocyclic olefin **28** (61%), thereby showing that equatorial protonation has taken place. The stereochemical assignments are based on spectral comparisons with authentic specimens.²⁶



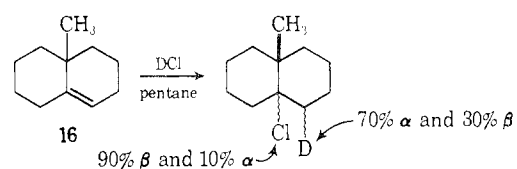
Octalin **16** adds deuterium oxide very slowly under the usual reaction conditions (D_2O -1,2-dimethoxyethane-xylene) and affords mainly polymeric products. However a trace of DCl greatly promotes the addition processes, and the decalols **29** (64%) and **30** (8%) can thus be readily obtained. The distinction between equatorial *vs.* axial deuterium incorporation cannot be made for the major addition product **29** owing to the conformational mobility of the *cis*-decalin ring system. However, the *trans*-decalol **30** possesses an equatorially bound deuterium. Furthermore, both decalols were shown to result from deuteration *trans* to the angular methyl grouping by comparison with authentic samples synthesized independently.²⁶



In the photochemical reactions of octalins **5**, **11**, and **16**, the protonation step appears to be remarkably stereoselective and independent of the environment of the double bond. Octalins **5** and **11** provide a particularly striking comparison since the double bond is identically situated in both compounds and hence subject to the same steric interactions. Thus four-center additions (*e.g.*, hydroboration) and reactions involving olefin π complexes (*e.g.*, epoxidation) proceed mainly by attack at the relatively unhindered bottom face of the double bond in these octalins. Deuterium chloride likewise preferentially attacks the bottom (α) face of octalin **11**, but a considerable proportion of the product arises from top-side (β) attack. Photoinitiated hydration, however, overwhelmingly favors protonation from the bottom face.²²



The kinetically controlled addition of DCl to octalin **16** likewise gives a quantitatively different result than the photochemical addition of D_2O .²²



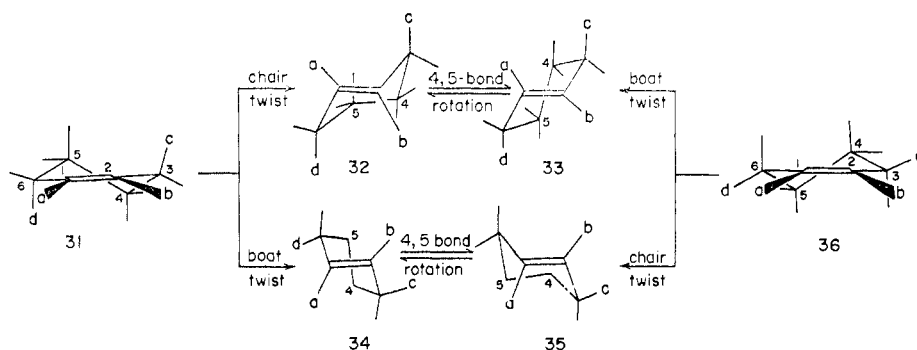
Obviously, the aforementioned nonphotochemical additions all involve *cis*-cyclohexenes. What stereochemical consequences might be expected with the *trans* isomers? An inspection of molecular models²⁷ leads to the following analysis.

With cyclohexene and related olefins, two modes of double bond twisting can be distinguished; both afford the *trans* olefin. The one which causes each of the vinyl substituents (a and b) to become *trans* to its initially axial adjacent group (d and c in **31**) leads to a distorted chair form (**31** \rightarrow **32**). Twisting in the opposite sense causes each vinyl substituent a and b to adopt a *cis* relationship with its initially axial adjacent group and leads to a twist boat form (**31** \rightarrow **34**). In principle, chair-boat interconversion could be achieved either by reversing the olefin twisting process or by rotating the backmost carbon-carbon bond (**32** \rightarrow **33** and **34** \rightarrow **35**). The latter process converts the chair form to the mirror image of its boat-twist-derived counterpart (in the unsubstituted cyclohexene) and *vice versa*. An alternative route to the same enantiomeric *trans* olefins **33** and **35** can be envisioned from the alternative chair conformer **36** of the cyclohexene.²⁸

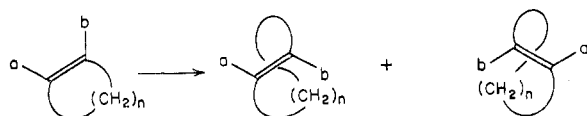
In both *trans*-cyclohexene conformers the favored approach by an electrophile to the π -orbital system no longer involves an attack from the top or bottom face of the cyclohexene ring. Instead, such an attack must proceed, at least initially, from within the ring or outside the ring. This requirement is a direct conse-

(27) The conversion of *cis*- to *trans*-cyclohexenes requires substantial bond angle distortion. Because of their flexible plastic connecting tubes and ready availability, Framework Molecular Models (Prentice-Hall, Inc., Princeton, N. J.) were judged most suitable for constructing the highly strained cyclohexenes under consideration here. Equally satisfactory structures could also be constructed from Dreiding models by changing the internal bond angles as follows: C-1 and C-2 trigonal atoms, compress to 100° ; C-3 and C-6 tetrahedral atoms, compress to 90° ; C-4 and C-5 tetrahedral atoms, expand to 120° . With these modified angles the adjacent trigonal atoms of the *trans* double bond assume a dihedral angle of $\sim 150^\circ$ (twist angle of $\sim 30^\circ$). These parameters do not appear unreasonable in view of known stable compounds such as cyclobutene and *trans*-cyclooctene where analogous bond angle distortions must be present.

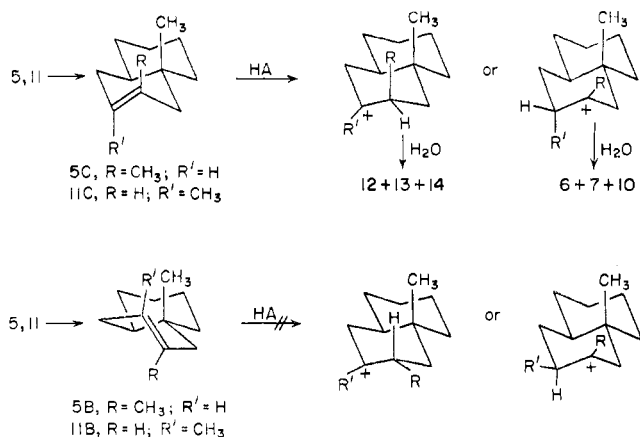
(28) This process (**31** \rightarrow **36**) could not take place with octalins **5** and **11** owing to the *trans* ring fusion. Otherwise the interconversions are essentially equivalent to those described for cyclooctene: G. Binsch and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 5157 (1965).



quence of the necessity for the ring atoms of a relatively small ring cyclic olefin, such as cyclohexene, to pass over one face of the double bond in the *trans* isomer. The smaller the ring, the more closely the carbon chain must approach the double bond. On this basis the protonation of *trans*-cyclohexene might be expected to proceed with a high degree of stereospecificity.²⁹



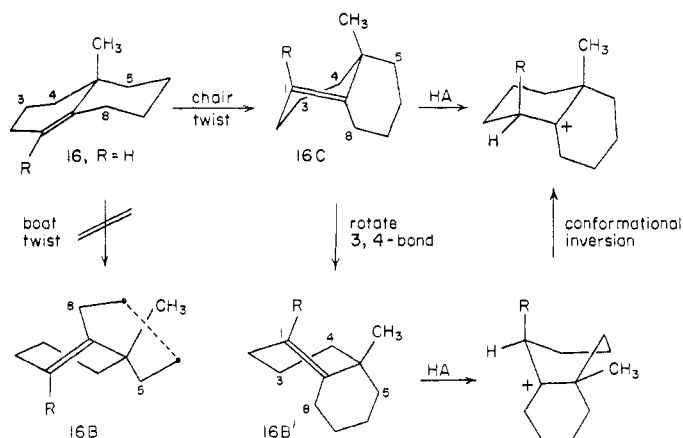
With octalins **5** and **11**, rotation to the *trans* chair form (**5C** and **11C**, respectively) followed by protonation from the outside face of the double bond at the less substituted carbon atom leads to the corresponding tertiary cation with net equatorial introduction of the proton. On the other hand, rotation to the boat form (**5B** or **11B**) followed by attack by an acid in a like manner would lead to net axial protonation. The experimental findings on deuterium oxide additions and isomerizations indicate a distinct preference for the chair pathway. The reasons for this preference are not yet clear.



The stereochemical analysis outlined above could also apply to orthogonal triplet intermediates or to *trans*-cyclohexenes which, owing to torsional strain, more or less resemble the orthogonal triplet in geometry.

In the case of octalin **16**, models show that twisting

to the *trans* chair form **16C** involves no more strain than the like process with octalins **5** and **11**, whereas twisting toward the boat form **16B** increases the dihedral angle between C-8 and C-5 to a point where the saturated ring bonds of the coplanar *trans* olefin are prohibitively stretched. However, an alternative boat form can be attained in this case through rotation of the C-3,C-4 bond of the *trans* chair form **16C**. The analogous chair-boat interconversion cannot take place in the *trans* olefins derived from octalins **5** and **11** as rotation of the requisite carbon-carbon bond would require the formation of a *trans*-diaxial decalin ring fusion. Protonation of either the chair **16C** or boat **16B'** conformer at C-1 from the outside face would give the same stereochemical result. The newly introduced proton would be *trans* to the angular methyl grouping in both cases, in agreement with the experimental findings.

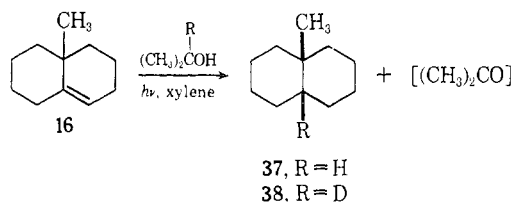


Octalin **16** cannot undergo double-bond isomerization unless protonation leading to the less stable secondary cation takes place at a reasonable rate relative to alternative addition and isomerization reactions. None of the cyclohexenes previously examined gave any indication that such a process could occur. It was therefore of interest to examine the photochemical behavior of this olefin in solvents which favor isomerization.

In *t*-butyl alcohol-xylene neither addition nor isomerization reactions took place, and octalin **16** could be recovered unchanged. However, in isopropyl alcohol-xylene octalin **16** underwent a relatively facile conversion (50% yield) to a new product, identified as *cis*-9-methyldecalin (**37**). The concurrent formation

(29) The same argument holds for the catalytic hydrogenation of *trans*-cyclononene. Cf. R. L. Burwell, Jr., *Chem. Rev.*, **57**, 895 (1957), particularly the discussion on p 912.

of pinacol and free-radical addition products of acetone and octalin **15**³⁰ shows that isopropyl alcohol functions as the reducing agent in this reaction. In 2-deuterio-2-propanol the photosensitized reduction afforded *cis*-9-methyl-10-deuteriodecalin (**38**) as the sole reduction product.¹⁰ Since deuterium adds to the more substituted position of octalin **16**, a mechanism involving deuterium atom abstraction³¹ from the alcohol appears untenable as this pathway would lead to deuterium incorporation at the secondary position. However, the observed results can be accommodated by an ionic pathway involving hydride transfer from isopropyl alcohol to the C-10 cation derived from octalin **16**.

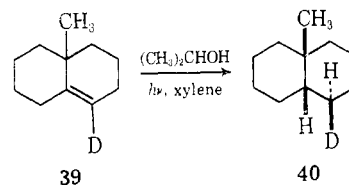


The stereochemistry of the hydrogenation reaction was ascertained through irradiation of the deuterated octalin **39** in isopropyl alcohol-xylene. The resulting *cis*-decalin **40** was identified by comparison with an authentic sample synthesized independently.²⁶ Thus,

(30) Cf. J. S. Bradshaw, *J. Org. Chem.*, **31**, 237 (1966).

(31) Cf. R. R. Sauer, W. Schinski, and M. M. Mason, *Tetrahedron Letters*, 4763 (1967).

protonation of octalin **16** *trans* to the angular methyl grouping appears to be highly preferred in both the photochemical hydration and hydrogenation reactions.



The stereochemical results to date on photosensitized ionic additions to cyclohexene double bonds seem best accommodated by the chair form of a *trans*-cyclohexene intermediate. Protonation of such an intermediate from the outside face must necessarily lead to an equatorially oriented C-H bond in the chair form of the resulting cyclohexyl cation. This cation, or a related ion pair, then reacts with the nucleophilic portion of the addend either by elimination or by addition, depending upon the steric requirements of the nucleophile and the steric environment of the cation.

I am deeply grateful to my collaborators, R. D. Carroll, H. Faubl, A. Greene, A. R. Hochstetler, and M. Wurth, for their dedicated efforts in the pursuit and interpretation of the experimental data which forms the basis of this report. The continued cooperation and interest of Dr. P. J. Kropp has also been of great value. Finally financial assistance from the National Science Foundation, the Hoffmann-La Roche Foundation, and the Alfred P. Sloan Foundation which made this research possible is gratefully acknowledged.

High-Pressure Mössbauer Resonance Studies with Iron-57¹

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The Mössbauer effect is a useful tool for investigating a number of aspects of chemistry and physics, since it allows one to compare very accurately the energy of specific nuclear transitions. The energy of a nuclear transition is slightly modified by surrounding electrons, and by measuring these energy modifications it is possible to deduce information about the chemical nature of the environment. In this paper we discuss the effect of pressure on compounds of iron.

The principles of Mössbauer resonance have been

(1) This work supported in part by the U. S. Atomic Energy Commission under Contract AT(11-1)-1198.

thoroughly discussed,² and will be reviewed only briefly here. The emission or absorption of a γ ray by the nucleus of a free atom involves Doppler broadening and recoil processes. The basic discovery of Mössbauer was that, by fixing the atom in a solid where the momentum is quantized and the motion limited to vibrational modes, these effects might be eliminated. If the lowest allowed quantum of lattice vibrational energy (lowest phonon energy) is large compared with

(2) (a) H. Frauenfelder, "The Mössbauer Effect," W. A. Benjamin, Inc., New York, N. Y., 1963; (b) G. K. Wertheim, "Mössbauer Effect: Theory and Applications," Academic Press, New York, N. Y., 1964.