ml portions of pentane. The combined pentane extracts were washed with aqueous DMSO (50:50 v/v) and half-saturated sodium chloride solution, and dried over magnesium sulfate. Evaporation of the pentane gave an oil which was shown to contain a trace amount of **4** by glpc analysis. Accordingly, the crude product was chromatographed on alumina (80–200 mesh), and **3** was eluted with pentane. The product was distilled (Kugelrohr, 30–45°, 0.05 mm) to give 0.252 g of **3** (54% yield) as a colorless liquid, $n^{20}D$ 1.5654, $[\alpha]^{23}D$ +138° (*c* 0.91, isooctane). The neat ir spectrum of **3** features olefinic absorption at *ca.* 1665 and *ca.* 885 cm^{-1}. The nmr spectrum featured the following resonances: aromatic multiplet at τ 2.80–3.15 (4 H), olefinic protons at 4.87–5.08 and 5.28–5.48 (2 H) as broadened signals, 6.30–6.50 and 6.55–6.80 (2 H) bridgehead protons as broadened signals, methylene multiplet at 7.30–8.45 (4 H). The ultraviolet absorption spectrum in isooctane solution exhibited the following features [λ_{max} (ϵ)]: 273.8 (1220), 267 (1170), 261 (760), 254 sh (410), 228 sh (5400), 224 sh (7800), 216 sh (9200), 196 (34,000). The ORD characteristics in isooctane (*c* 0.0790 g/100 ml at λ >225 mμ, *c* 0.00316 g/100 ml at λ <225 mμ), corrected to optical purity, were: $[\phi]_{276}$ +10,600°, $[\phi]_{274}$ +11,200°, $[\phi]_{271}$ +8200°, $[\phi]_{269}$ +9500°, $[\phi]_{268}$ +10,300°, $[\phi]_{264}$ +8000°, $[\phi]_{262}$ +9200°, $[\phi]_{231}$ +74,000°, $[\phi]_{225}$ 0, $[\phi]_{213}$ −105,000°, $[\phi]_{206}$ 0. The CD in isooctane, corrected to optical purity (*c* 0.0644 g/100 ml at λ >235 mμ, *c* 0.00644 g/100 ml at 220–235 mμ, *c* 0.002576 g/100 ml at λ <220 mμ), was as follows [λ_{max}, mμ ($[\theta] \times 10^{-4}$)]: 280 (0), 272 (+0.46), 265 (+0.50), 260 sh (+0.3), 253 sh (+0.2), 227 (+11), 224 (+12), 215 (0), 207 (−8).

Anal. Calcd for $C_{12}H_{12}$: C, 92.25; H, 7.75. Found: C, 92.13; H, 7.95.

Circular Dichroism of (+)-*exo*-2-Benznorbornenol (5).[8] The sample of **5** used had $[\alpha]^{25}D$ +12.6° (*c* 4.7, chloroform) and was 46% optically pure.[8] The ultraviolet absorption spectrum in isooctane solution exhibited the following features [λ_{max} (ϵ)]: 272.5 (1050), 265.5 (930), 259 (580), 252 sh (300), 226.5 (1400), 220.5 sh (3500), 216 sh (4800), 211 (5600). The CD in isooctane, corrected to optical purity (*c* 0.00882 g/100 ml), was as follows: $[\theta]_{226}$ +4400. No Cotton effect was observed in the long-wavelength region, and $[\theta]_{max}$ (observed) < 360 (*c* 0.00882 g/100 ml, *l* 1.0 cm).

Photosensitized Isomerizations of 10-Methyl-1(9)-octalins

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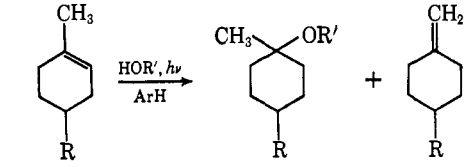
Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. *Received August 7, 1968*

Abstract: 8,8,10-Trimethyl-, *trans*-8,10-dimethyl-, and *cis*-8,10-dimethyl-1(9)-octalin (**7**, **11**, and **13**) were prepared and subjected to ultraviolet irradiation in isopropyl alcohol containing xylene as the photosensitizer. The first two octalins required an added proton source (acetic acid) for isomerization to occur. The first afforded mainly 1-methylene-*cis*-9,10-dimethyldecalin (**18**) and the second gave chiefly 1-methylene-*cis*-10-methyldecalin (**30**) under these conditions. The *cis*-dimethyloctalin **13** isomerized smoothly without added acetic acid and gave 1-methylene-*trans*-10-methyldecalin (**35**) as the sole product. These findings suggest a pathway for isomerization involving conversion of the 1(9)-octalin to an incipient C-9 cation followed by a stereospecific migration of an adjacent methyl or hydrogen to give a new tertiary cation which then ultimately loses a proton from the α-methyl grouping to give the observed exocyclic olefin. Internal hydride migration was confirmed for the *cis*-dimethyloctalin **13** by means of a deuterium-labeling experiment. The photochemical isomerizations of the 10-methyl-1(9)-octalins are contrasted with their behavior in strong acid and a scheme is presented which accommodates the observed reactions in terms of cationic intermediates.

Recent studies have shown that cyclohexenes exhibit rather unusual behavior upon photosensitized irradiation in protic solvents insofar as products which appear to arise *via* ionic reaction pathways are produced. For example, 1-methylcyclohexene (**1a**) and 1-menthene (**1b**) yield the corresponding alcohols (**2**, R′ = H), ethers (**2**, R′ = CH_3 or C_2H_5), acetates (**2**, R′ = CH_3CO_2), and exocyclic olefin isomers (**3**) upon irradiation with ultraviolet light in water, alcohols, or acetic acid in the presence of aromatic hydrocarbons such as benzene, toluene, or xylene.[2] Deuterium-labeling experiments indicate that both the addition and isomerization reactions proceed through a common intermediate resulting from proton transfer to the olefin by the protic solvent.[2c] These findings as well as the stereochemical outcome of additions to 1-menthene[2b] can all be understood in terms of a photochemically derived cationic intermediate.

Since acyclic olefins, cyclopentenes, and cyclooctenes and larger ring olefins fail to undergo analogous addition and isomerization reactions, some special significance must be placed on the ring size. Kropp and Krauss[2c] have attributed the unique photochemistry of cyclohexenes and cycloheptenes to ring strain. They propose that upon excitation these olefins afford orthogonal triplets possessing appreciable, albeit not prohibitive, steric strain. Conceivably this strain factor imparts unusual reactivity to these triplet states enabling them to abstract a proton from even such weak acids as alcohols and water thereby leading to cationic species. Alternatively, the orthogonal triplets could play their usual role as intermediates in *cis–trans* isomerization



1a, R = H
b, R = *i*-Pr
2
3

(1) (a) Fellow of the Alfred P. Sloan Foundation, 1966–1968. (b) National Institutes of Health Predoctoral Fellow, 1965–1968.

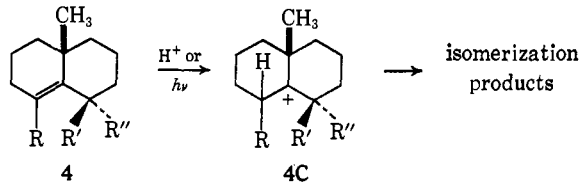
(2) (a) P. J. Kropp, *J. Am. Chem. Soc.*, **88**, 4091 (1966); (b) J. A. Marshall and R. D. Carroll, *ibid.*, **88**, 4092 (1966); (c) P. J. Kropp and H. J. Krauss, *ibid.*, **89**, 5199 (1967).

and thereby give rise to highly strained *trans*-cyclohexenes and cycloheptenes as intermediates. These *trans*-cycloalkenes, because of their excessive strain energy, may abstract a proton from the hydroxylic solvent to yield the cationic intermediates which give rise to the observed products.

Cyclopentenes afford dimers and products of free-radical reactions upon irradiation in protic solvents containing triplet sensitizers.[3] Although the singlet → triplet transition may be allowed in this case, *cis* → *trans* isomerization would be precluded by prohibitive strain factors. On the other hand, cyclooctene and larger ring olefins, as well as acylic olefins, suffer relatively little steric strain in their orthogonal triplet or *trans*-singlet states, and according to the aforementioned tenets would expectedly show no unusual photochemical behavior.

In carrying out the investigation described in this report we hoped to gain additional insight regarding the nature of the presumed cationic intermediates in photosensitized isomerizations of cyclohexenes. We were particularly interested in comparing the chemical behavior of these cations with those generated *via* protonation of the corresponding cyclohexene in strong acid. Possibly the greater vibrational energy initially available to the photochemically derived cation would promote reactivity differences between the two species. The marked contrast in reaction media could also lead to contrasting chemical characteristics for cations generated by the two routes. Inasmuch as the photochemically derived cations, for the reasons stated above, may afford unique products not otherwise readily accessible these studies were of practical as well as theoretical importance.

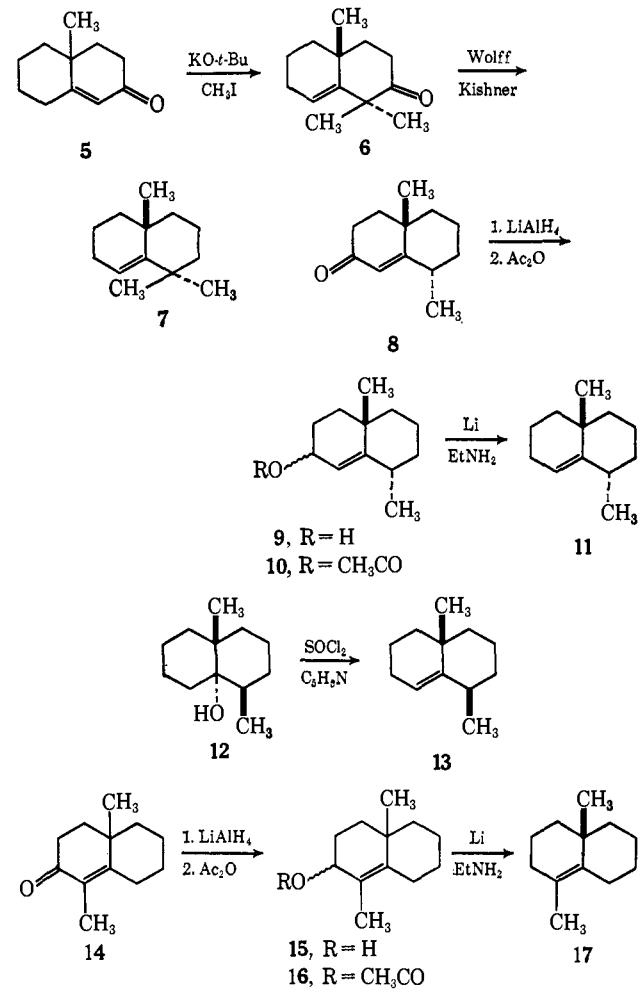
We decided to concentrate our initial efforts on the 10-methyl-1(9)-octalin system **4**. This system was of particular interest because the initially derived cation **4C** cannot simply lead to a photochemically inert exocyclic olefin and therefore rearrangements or multistep elimination processes would presumably occur. Hopefully these would vary from one octalin to the next and thus truly characterize the reactivity pattern of each. The octalin system **4** also provided an opportunity to examine stereochemical aspects of the isomerization reaction as the various products could be independently synthesized by stereorational reaction pathways. Finally, it should be noted that the basic octalin system **4** bears a close relationship to various sesquiterpene natural products. Studies on this system were therefore of interest in connection with synthetic efforts in this area.[4]



4 4C

The octalins **7**, **11**, **13**, and **17** chosen for these studies were prepared in routine fashion according to the routes outlined in Chart I.

Chart I



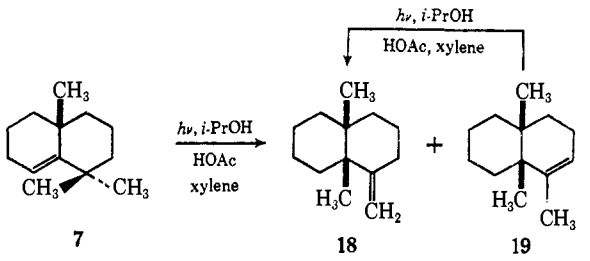
Our previous findings indicated that photosensitized olefin isomerizations could be most efficiently conducted in isopropyl alcohol where alcohol addition, perhaps for steric reasons, is relatively unfavorable.[2b] Surprisingly, the trimethyloctalin **7** gave no indication of either isomerization or addition reactions upon irradiation under these conditions. However, at the somewhat lower pH attained by the addition of acetic acid to the reaction medium photosensitized isomerization did take place leading to two products in 1 and 50% yield.[5] The major product showed strong infrared absorption bands at 6.11 and 11.18 μ indicative of an exocyclic methylene grouping. The nmr spectrum supported this indication and, in addition, showed two quaternary methyl signals. These data suggested that methyl migration had accompanied double bond isomerization and pointed to one of the 1-methylene-9,10-dimethyldecalin stereoisomers as the major rearrangement product. Subsequent synthetic work outlined below confirmed the structure of this product as the *cis*-decalin **18**. The apparent yield of the minor product rose to 3% early in the photochemical reaction and then gradually decreased indicating its possible conversion to decalin **18**. This transformation,

(3) *Cf.* P. J. Kropp, *J. Am. Chem. Soc.*, **89**, 3650 (1967), and references therein.

(4) For a relevant application of the isomerization reaction, see J. A. Marshall and M. T. Pike, *J. Org. Chem.*, **33**, 435 (1968). For the first and only other application in the sesquiterpene field, see F. J. McQuillin and J. D. Parrack, *J. Chem. Soc.*, 2973 (1956).

(5) In most cyclohexenes thus far examined we have found that low concentrations of acids favor the ionic reaction pathway. Suitable controls have been employed to exclude the possibility of direct acid catalysis involving the ground-state *cis*-olefin. *Cf.* J. A. Marshall and M. J. Wurth, *J. Am. Chem. Soc.*, **89**, 6788 (1967).

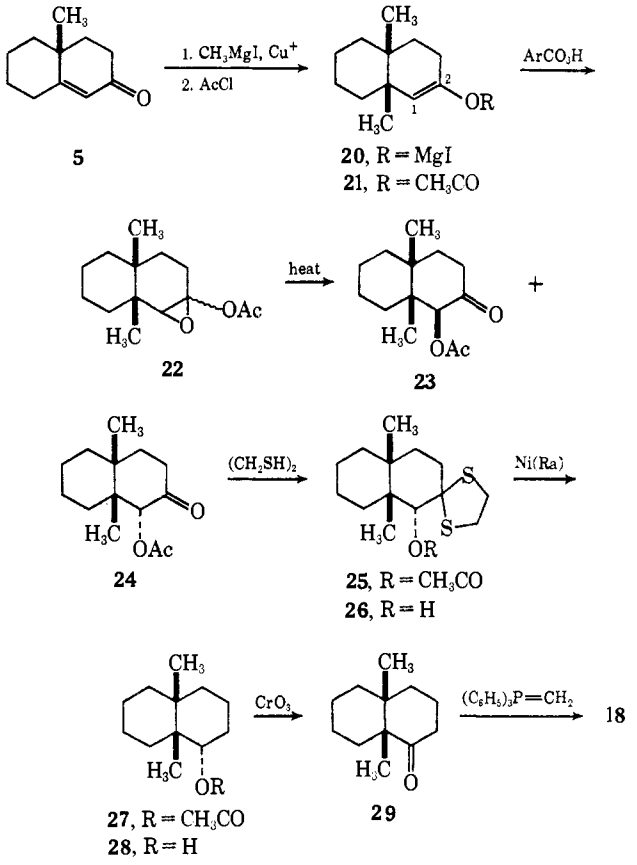
which was experimentally verified with a pure sample of the minor olefin, coupled with spectral data, supports structure **19** for the minor product.



7 18 19

Chart II outlines an independent stereoselective synthesis of olefin **18**. We have previously shown that the copper-catalyzed addition of CH_3MgI to octalone **5** affords *cis*-9,10-dimethyl-2-decalone.[6] The problem in synthesizing olefin **18** then simply involves a trans-

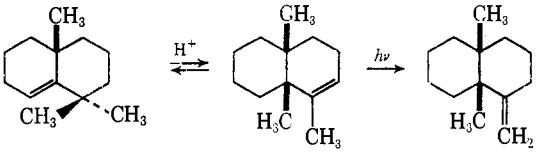
Chart II



5
20, R = MgI
21, R = CH_3CO
22
23
24
25, R = CH_3CO
26, R = H
27, R = CH_3CO
28, R = H
29

position of the oxygen function from C-2 to C-1 in the 1,4 adduct of octalone **5**. This transposition was readily effected by treating the enolate **20**, obtained *via* the 1,4-addition reaction, with acetyl chloride and subjecting the resulting enol acetate **21** to epoxidation followed by thermal rearrangement.[7] This sequence yielded a mixture of isomeric acetoxy ketones **23** and **24** from which the major isomer **24** crystallized. The tentative stereochemical assignment is based on the expected (from models) preferred direction of epoxidation and the known steric course of the thermal rearrangement.[8] Ketone **24** afforded a crystalline thioketal derivative **25** which underwent desulfurization to the expected acetate **27**. However, this reaction gave a significant amount of deacetoxylation products and a more efficient over-all conversion could be realized through desulfurization of the alcohol derivative **26**. Subsequent oxidation with Jones reagent[9] and treatment of the resulting ketone **29** with methylenetriphenylphosphorane in dimethyl sulfoxide[10] afforded the methylenedecalin **18** identified as the major photochemical rearrangement product of octalin **7** by comparison of infrared and nmr spectra and gas chromatographic retention times.

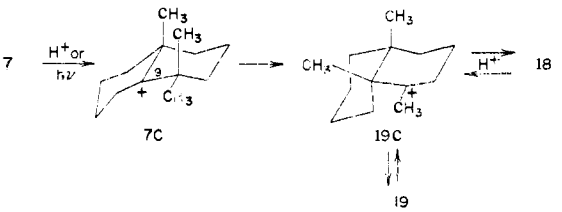
In 5% sulfuric acid–acetic acid the trimethyloctalin **7** afforded an equilibrium mixture containing 94% of octalin **19**, the minor irradiation product, and 6% of unchanged octalin **7**. Octalin **19** was converted to its exocyclic isomer **18** upon irradiation in isopropyl alcohol–xylene.



7 **19** **18**

Thus, both the photochemical and acid-catalyzed isomerizations of octalin **7** appear to follow the same pathway insofar as both can be viewed as proceeding *via* a stereospecific methyl migration (**7C** → **19C**) to an incipient cationic center at C-9. In the former case proton loss in the direction of the exocyclic olefin leads to a photochemically inert product whereas the alternative proton loss gives the endocyclic olefin which photochemically isomerizes to the exocyclic isomer. Since protonation of both isomers **18** and **19** can take place in strong acid, the more stable olefin **19** would be expected to predominate under these conditions. The preferred formation of *cis*-fused products in the photochemical reaction can be understood on stereoelectronic grounds. As shown in Scheme I, axial methyl migration in the all-chair conformation of cation **7C** leads to the *cis*-decalin system. Apparently this system is also the more stable one since it predominates at equilibrium as well.

Scheme I

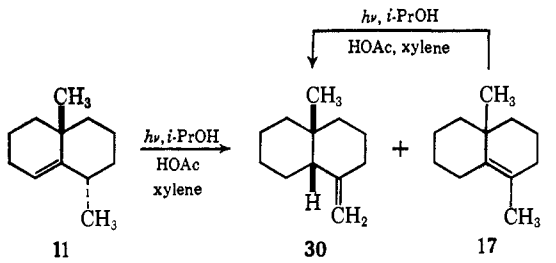


7C **19C** **19**

The *trans*-dimethyloctalin **11**, like its trimethyl counterpart **7**, proved relatively inert to photosensitized isomerization in isopropyl alcohol. However, with added acetic acid or, alternatively, in *t*-butyl alcohol–

(6) J. A. Marshall, W. I. Fanta, and H. Roebke, *J. Org. Chem.*, 31, 1016 (1966).
(7) *Cf.* H. J. Shine and G. E. Hunt, *J. Am. Chem. Soc.*, 80, 2434 (1958).
(8) *Cf.* K. L. Williamson and W. S. Johnson, *J. Org. Chem.*, 26, 4563 (1961).
(9) K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).
(10) R. Greenwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, 28, 1128 (1963).

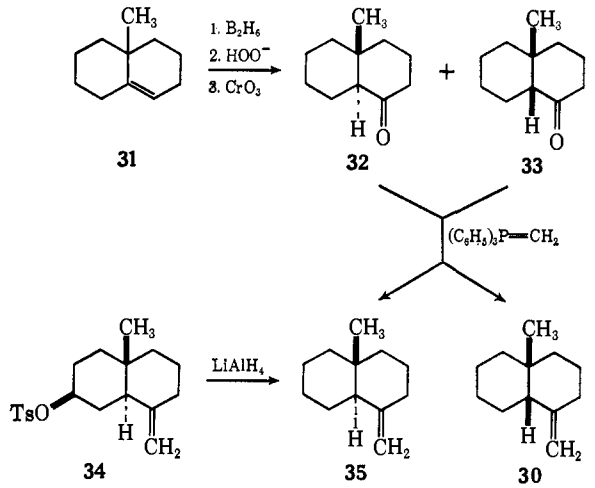
acetic acid the photoisomerization occurred readily affording two products in 53 and 2% yield. The major product showed infrared and nmr spectral characteristics indicative of an exocyclic methylene grouping and was subsequently identified as *cis*-1-methylene-10-methyldecalin (**30**) *via* independent synthesis (Chart III). The minor product was shown (Chart I) to be 1,10-dimethyl-1(9)-octalin (**17**). The relative yield of octalin **17** rose to 15% early in the reaction and then gradually decreased implying that it may be an intermediate in the isomerization reaction. In keeping with this possibility, irradiation of octalin **17** in acetic acid–*t*-butyl alcohol afforded the *cis*-decalin **30** in 70% yield. None of the corresponding *trans*-decalin **35** could be detected. The isomerization of octalin **17**, like that of octalins **7** and **11**, could not be effected without added acid.



11 **30** **17**

An authentic sample of the *cis*-decalin **30** was secured according to the sequence outlined in Chart III. Hydro-

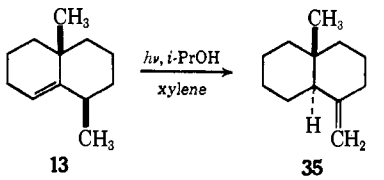
Chart III



31 **32** **33** **34** **35** **30**

boration of the octalin **31** followed by oxidation first with alkaline hydrogen peroxide and then with Jones reagent[9] afforded a 1:2 mixture of the decalones **32** and **33** favoring the *cis* isomer. Equilibration in refluxing methanolic sodium carbonate gave a 2:1 mixture favoring the *trans* isomer **32**.[11] Upon treatment with methylenetriphenylphosphorane in dimethyl sulfoxide[10] this mixture afforded a mixture of the corresponding olefins containing 13% of the *cis* isomer **30** and 87% of *trans* isomer **35**. Evidently, decalones **32** and **33** must interconvert under these reaction conditions and the *trans* isomer **32** must preferentially condense with the phosphorane. We have encountered this phenomenon previously in connection with a similar conversion.[12] The isomeric decalins **35** and **30** were purified by preparative gas chromatography. The *trans* isomer could also be prepared *via* reduction of the known tosylate **34**[12] with lithium aluminum hydride.

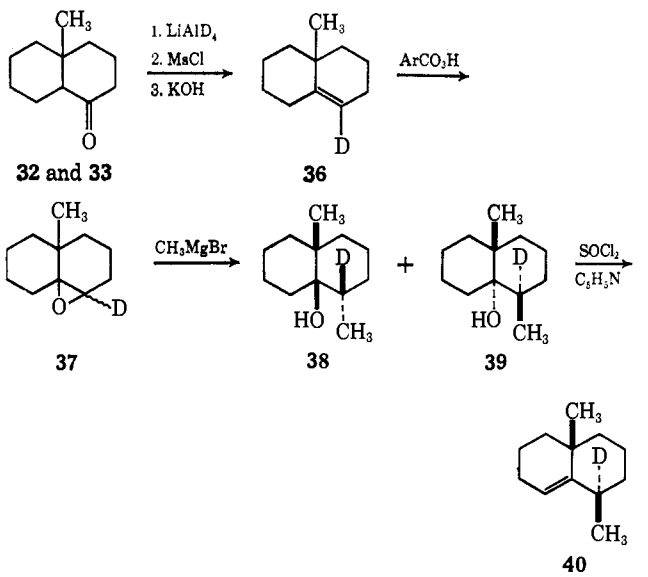
The *cis*-dimethyloctalin **13** exhibited a substantially higher propensity for photosensitized isomerization than the corresponding *trans* isomer. Irradiation in isopropyl alcohol–xylene afforded a single product in 83% yield. Spectral evidence combined with the independent synthesis outlined above in Chart III identified this product as *trans*-1-methylene-10-methyldecalin (**35**). Interestingly, neither the *cis*-decalin **30** nor the tetrasubstituted olefin **17** could be detected, even in trace amounts, from this photoisomerization reaction.



13 **35**

These findings suggested that the isomerization of octalin **13** to the decalin **35** may proceed *via* a stereospecific hydride migration. To examine this possibility we synthesized the deuterated octalin **40** and subjected it to the isomerization reaction. Chart IV outlines the

Chart IV



32 and 33 **36** **37** **38** **39** **40**

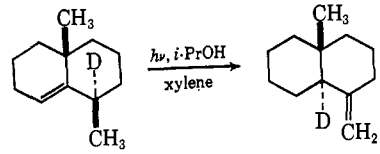
synthetic sequence. The aforementioned equilibrium mixture of decalones **32** and **33** was successively reduced with lithium aluminum deuteride and treated with methanesulfonyl chloride in pyridine and then with methanolic potassium hydroxide to give the deuterated octalin **36**. Epoxidation with *m*-chloroperoxybenzoic acid and treatment of the resulting oxide mixture **37** with methylmagnesium bromide yielded the dimethyldecalols **38** and **39** which could be separated by column elution chromatography. The stereochemistry of these decalols can be assigned on the basis of previous work on their nondeuterated counterparts.[13] Decalol **39** afforded mainly the desired olefin **40** upon dehydration with thionyl chloride in pyridine.

(11) *Cf.* F. Sondheimer and D. Rosenthal, *J. Am. Chem. Soc.*, **80**, 3995 (1958).

(12) J. A. Marshall, M. T. Pike, and R. D. Carroll, *J. Org. Chem.*, **31**, 2933 (1966).

(13) J. A. Marshall and A. R. Hochstetler, *ibid.*, **33**, 2593 (1968).

The photosensitized isomerization of octalin **40** proceeded quite slowly in comparison to its nondeuterated equivalent and the rearranged olefinic product was formed in only 5.2% yield. The only other detectable product was not produced in sufficient amounts to be isolated. However, it can tentatively be regarded as the hydrogenation product[14] of octalin **40** on the basis of its gas chromatographic retention time. The isomerization product was identified as the deuterated *trans*-decalin **41** by comparison with an independently synthesized sample.

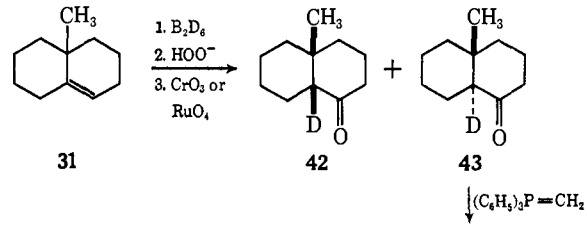


40 **41**

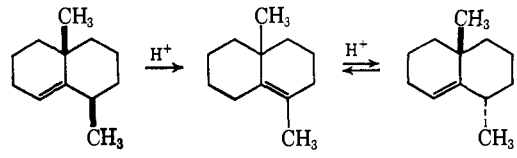
These findings raise two noteworthy points. First, the observed deuterium isotope effect shows that hydride migration must be involved in at least one of the rate-limiting steps of the isomerization reaction and that the transition state for this transfer is fairly symmetrical. Second, the relatively large rate retardation of the observable ionic process imposed by this isotope effect enables other photochemical reactions to compete for octalin **40**. These mainly lead to a variety of high molecular weight, ill-defined materials and may occur *via* triplet and free-radical pathways.

An authentic specimen of the deuterated decalin **41** was prepared from octalin **31** *via* deuterioboration and oxidation as outlined below. The *cis*- and *trans*-decalones **42** and **43** were isolated by preparative gas chromatography. In this way, a sample of *trans*-decalone **43** containing 66% d_1 and 34% d_0 was secured. The relatively low deuterium content must reflect the isotopic composition of the deuterioborane employed in this synthesis rather than exchange during the oxidation since the same distribution of d_1 and d_0 resulted when ruthenium tetroxide was used to oxidize the initial decalol mixture.[15] The decalin **41** obtained upon treatment of decalone **43** with methylenetriphenylphosphorane in ether (to circumvent reversible enolate formation leading to exchange[12]) contained 66% d_1 and 34% d_0 and gave an infrared spectrum superimposable with that of a 2:1 mixture of the photochemical product **41** and the authentic d_0 *trans*-decalin **35**.

Upon treatment with 5% sulfuric acid in acetic acid octalins **11**, **13**, and **17** were each converted to the equilibrium mixture containing **17** (33%), **11** (11%), **46** (3%), **47** (45%), and two unidentified components (8%) according to the gas chromatogram. Octalins **46** and **47** readily afforded their exocyclic isomers **35** and **30** upon sensitized irradiation in isopropyl alcohol. Interestingly, small amounts of the *trans*-dimethyloctalin **11** (2%) and the tetrasubstituted olefin **17** (3%) were formed on irradiation of the *cis*-fused octalin **47** but the corresponding *trans*-fused octalin **46** gave only its exocylic isomer **35**. An authentic specimen of the *trans*-octalin **46** was secured *via* base treatment of the tosylhydrazone derivative **45** of decalone **44**. This reaction also gave some of the *trans*-decalin **35** and the isomeric octalin **48**. Chart V outlines these transformations.

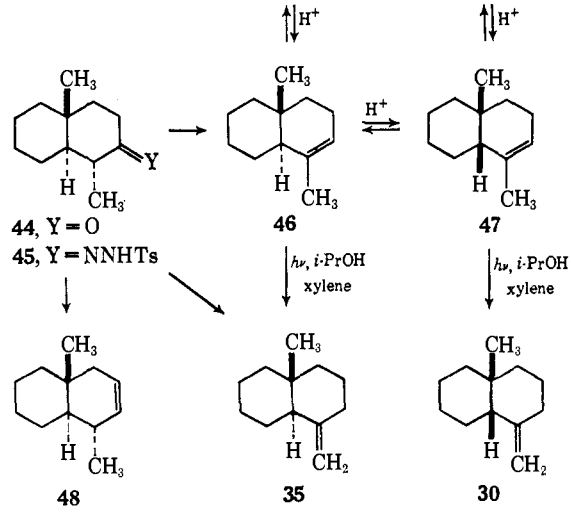


31 **42** **43** **41**



13 **17** **11**

Chart V



48 **35** **30**

The observed equilibrium distribution of disubstituted olefins **11**, **13**, **46**, and **47** can be understood in terms of conformational analysis. Of the two 8,10-dimethyl-1(9)-octalins, the *trans* isomer **11** should be greatly preferred to the *cis* isomer **13** by virtue of the 1,3-diaxial methyl groupings present in the latter. As for the *cis*- and *trans*-1,10-dimethyloctalins **46** and **47**, the former suffers from an $A^{(1,2)}$ methyl–methylene interaction[16] not present in the latter. Because of its *cis* ring fusion, octalin **47** should also be favored by entropy factors.

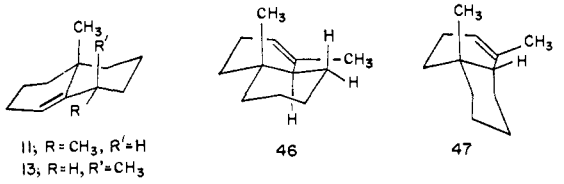
Scheme II correlates the experimental findings on isomerizations of the dimethyloctalins **11**, **13**, and **17**. The *cis*-dimethyloctalin **13** yields only the *trans*-decalin **35** *via* the photosensitized reaction but affords a mixture of the tetrasubstituted olefin **17**, the *cis*- and *trans*-fused octalins **47** and **46**, and the *trans*-dimethyloctalin **11** upon acid-catalyzed isomerization. These contrasting results indicate that the photochemically derived cation **13C** can isomerize to cation **46C** (*via* hydride migration—possibly through the boat conformer **13C′**) but, once formed, cation **46C** does not undergo measurable proton loss to give the tetrasubstituted olefin **17**.

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

(15) *Cf.* E. J. Corey, J. Casanova, Jr., P. A. Vatakencherry, and R. Winter, *J. Am. Chem. Soc.*, **85**, 169 (1963).

(16) F. Johnson and S. K. Malhotra, *ibid.*, 87, 5492 (1965).

Loss of a primary or secondary α-proton leading to the exocyclic olefin **35**, or the endocyclic isomer **46** which rapidly isomerizes to **35**, appears to be highly preferred.



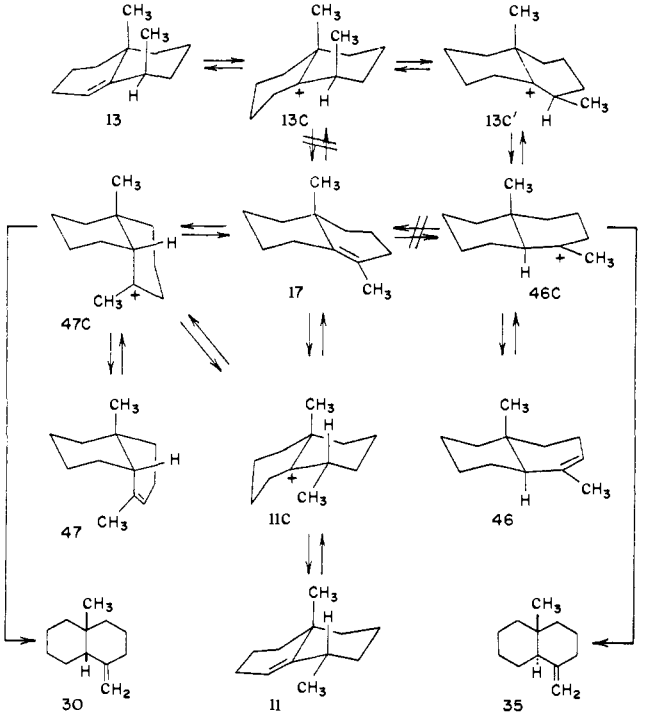
11; R = CH_3, R' = H
13; R = H, R' = CH_3

46 47

In acidic solution, protonation of the tetrasubstituted olefin **17** must afford the cations **47C**, **46C**, and **11C** evidenced by the isolation of olefins **47**, **46**, and **11**. Photochemically, however, the tetrasubstituted olefin **17** seems to give only cations **47C** or **11C** (net topside protonation) since the *cis*-decalin **30** is the sole product. Therefore cations **46C** or **13C** (net bottomside protonation) must not be formed.

The *trans*-dimethyloctalin **11** yields a mixture of the tetrasubstituted olefin **17** and the *cis*-decalin **30** upon photosensitized isomerization indicating the preferential formation of cation **47C**, presumably *via* hydride migration from cation **11C**. In this case, **11C** undergoes proton loss to give the tetrasubstituted olefin **17** in distinct contrast to the related cation **13C** derived from the *cis*-dimethyloctalin **13**. Likewise, cation **47C** generated photochemically from octalin **47** appears capable of proton loss, leading to the tetrasubstituted olefin **17**, and hydride migration, leading to the cation **11C** and thence the *trans*-dimethyloctalin **11**. However, the analogous cation **46C**, generated photochemically from octalin **46**, once again shows no comparable tendencies and leads only to the exocyclic olefin **35**.

Scheme II

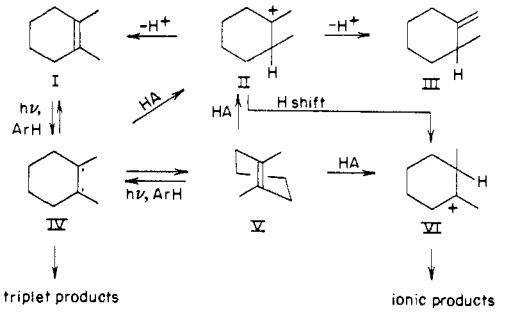


13 13C 13C' 47C 17 46C 47 11C 46 30 11 35

The major distinction between the reaction pathways followed by the dimethyloctalins **11**, **13**, and **17** under photosensitized *vs.* strongly acidic conditions appears to center about the protonation and deprotonation steps involving the tetrasubstituted isomer **17**. In the photochemical process, net topside protonation of **17** seems to be overwhelmingly more favorable than net bottomside protonation whereas in acid, both processes evidently occur. Of course, this distinction may be more apparent than real since the photochemical isomerization features irreversible steps while strong acid effects complete equilibration of the octalins.

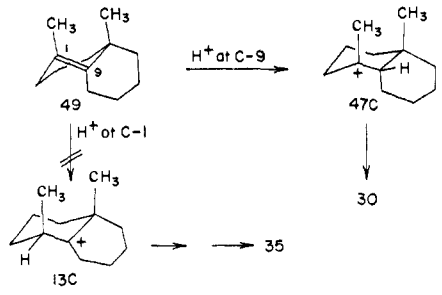
We have summarized elsewhere[17] evidence which supports the formation of *trans*-cyclohexene intermediates in photosensitized ionic reactions of cyclohexenes. Our present findings also seem amenable to this proposal which is elaborated in Scheme III. Accordingly, excitation of the cyclohexene I affords the triplet species IV which, depending on steric factors and the reaction medium, can go on to dimeric and free-radical reaction pathways (triplet products). Alternatively, the triplet IV could undergo intersystem crossing leading to the *trans*-cyclohexene V which then protonates leading to the cation II. The ease of this protonation step will also be governed by steric factors in the olefin and the acidity of the medium. Once formed the cyclohexyl cation appears to react rather discriminately either by stereospecific hydride or alkyl migration leading to a new cation VI or by proton loss giving the starting olefin I or the exocyclic isomer III. Whether or not the cyclohexyl cation II reacts by elimination or nucleophilic addition appears to be governed by the medium and the structure of the cation. An alternative scheme with comparable stereochemical consequences can be envisioned whereby the triplet species IV undergoes protonation leading directly to the cation II. The results of this study do not allow a choice between the two pathways.

Scheme III



Assuming the tetrasubstituted olefin **17** is photochemically converted to its *trans* isomer **49** we could *a priori* expect two possible cationic intermediates, **47C** and **13C**, arising *via* proton addition to the outside face of the *trans* double bond at C-9 and C-1, respectively. The inside face of this double bond would, of course, be inaccessible to external reagents for steric reasons. Thus, the stereochemistry of protonation could reasonably be controlled by the geometry of the intermediate. The factors which control the site of protonation (C-9 *vs.* C-1) are less clear. Conceivably C-9 may be more accessible to an acidic reagent by virtue of steric factors. Alternatively, cation **47C** may arise from a particular conformation of the triplet state of the olefin whose geometry would favor protonation at C-9.

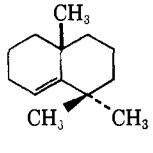
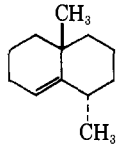
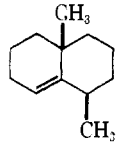
(17) J. A. Marshall, *Accounts Chem. Res.*, in press.



In summary, octalins **7**, **11**, and **13** exhibit comparable chemical behavior in their acid-catalyzed and photoinduced isomerization reactions. The observed differences can be accounted for by the greater stability of the endocyclic olefinic products **11**, **17**, **19**, **46**, and **47** under equilibrating conditions contrasted with the photochemical lability of these products (particularly **19**, **46** and **47**). Furthermore, in strong acid protonation and deprotonation no doubt occur rapidly and reversibly whereas photochemically this is probably not the case as the exocyclic isomers build up fairly quickly and are photochemically inert. Thus, the photochemical process more nearly approximates kinetic control of product formation. One additional difference concerns the actual species undergoing protonation. The acid-catalyzed reactions involve protonation of the *cis* olefins while the photochemical reactions probably proceed *via trans* olefins or the corresponding orthogonal triplet states. This difference is most clearly evident from the photosensitized isomerization of the tetrasubstituted olefin **17** where C-9 protonation appears to be highly specific contrasted with the isomerization in strong acid where both C-1 and C-9 protonation must take place.

Finally it is of interest to compare the photochemical reactivities of the 1(9)-octalins **7**, **11**, and **13**. Table I shows the relative amounts of unchanged octalin, ionic

Table I. Relative Reactivities of 1(9)-Octalins[a]

	 7	 11	 13
Unchanged octalin	55	35	5
Ionic products[b]	30	40	80
Nonionic products[c]	15	25	15

[a] Irradiation in isopropyl alcohol–acetic acid–xylene for 2 hr; all values in per cent. [b] Isomerized olefins. [c] Unaccounted for material.

products, and unaccounted for octalin after 2 hr of irradiation under identical reaction conditions. The unaccounted for material is presumably that which goes to triplet products *via* dimerization and free-radical pathways.

The trimethyloctalin **7** and the *trans*-dimethyloctalin **11** exhibit comparable rates of isomerization. Moreover, neither isomerizes without added acid. On the other hand, the *cis*-dimethyloctalin **13** isomerizes fairly rapidly even in neutral solution. These findings point to a rate-retarding effect of the equatorial methyl grouping of octalins **7** and **11** on the ionic pathway. The overall slower disappearance of the trimethyloctalin **7** by both pathways may stem from steric factors which retard the excitation process or which adversely affect reactions of the triplet such as dimerization. The added acid appears to enhance ionic reactions relative to the reactions which lead to those ill-defined, nonvolatile materials referred to as triplet products in Scheme III. This finding can be accommodated on the basis of a *trans*-cyclohexene intermediate which is not readily protonated by a weak acid such as isopropyl alcohol so that photochemical conversion back to the triplet could presumably take place. In this event, a stronger acid such as acetic acid would appear sufficient to effect protonation. Alternatively the "triplet products" could arise from the presumed *trans*-cyclohexene intermediate *via* reaction pathways not involving protonation, such as dimerization or hydrogen atom abstraction. Were this the situation, an added proton source would likewise favor ionic products.

In no case did we observe the addition of acetic acid to the octalins employed in this study, although such additions occur with 1-methylcycloheptene.[2] No doubt steric factors render the addition process less favorable in the 1,9-octalin system.

Experimental Section[18]

1,1,10-Trimethyl-8-octal-2-one (6). A solution of 50.9 g (0.31 mol) of octalone **5** in 50 ml of *t*-butyl alcohol was added to 515 ml (0.68 mol) of 1.3 *M* potassium *t*-butoxide in *t*-butyl alcohol and the mixture was stirred for 2 hr at room temperature.[18a] The solution was then cooled to 10°, 395 g (2.78 mol) of methyl iodide was added over 10 min, and the cooling bath was removed. After the mixture had stirred for 2 hr, most of the solvent was removed at reduced pressure and the product was isolated with hexane.[18b] Distillation afforded 55.9 g (94%) of colorless oil, bp 76–80° (0.5 mm). Fractionation through a spinning-band column gave 44.0 g of material, bp 131.5–132.5° (11.5 mm), which was judged 95% pure according to gas chromatography.[19] The 2,4-dinitrophenylhydrazone derivative exhibited mp 160–161° after crystallization from ethanol (lit.[20] mp 160.8–161.5°).

8,8,10-Trimethyl-1(9)-octalin (7). A mixture of 25.0 g (0.137 mol) of ketone **6**, 600 ml of triethylene glycol, 170 ml of hydrazine hydrate, and 15 g of hydrazine dihydrochloride was heated at 125° for 3.3 hr.[18a] To the hot solution was cautiously added 50 g of solid potassium hydroxide and the temperature of the mixture was slowly increased to 230° over a 1-hr period. Stirring was continued at this temperature for 2.5 hr whereupon nitrogen evolution ceased. The mixture was cooled and the product was isolated with hexane[18b] and distilled affording 17.8 g (78%) of a mobile oil, bp 95–99° (11 mm) (lit.[20] bp 97–99° (10 mm)). The gas chromatogram showed peaks at 6.7 min (19%) and 7.6 min (81%).[19] The major component was isolated by preparative gas chromatography:[21] n^{24}D 1.4998;

(18) (a) The apparatus described by W. S. Johnson and W. P. Schneider [*Org. Syn.*, **30**, 18 (1950)] was used to maintain a nitrogen atmosphere over reaction mixtures. (b) The isolation procedure consisted of thoroughly extracting the reaction mixture with the specified solvent, washing the combined extracts with saturated brine, and drying the extracts over anhydrous magnesium sulfate. The solvent was removed under reduced pressure. Lithium aluminum hydride reductions were processed by carefully adding 1.0 ml of water and 0.8 ml of 10% aqueous sodium hydroxide for each 0.5 g of hydride initially present. The mixture was efficiently stirred to effect granulation of the salts and filtered. (c) Gas chromatography was performed on F&M Model 700 or 720 instruments equipped with thermal conductivity detectors. (d) Microanalyses were performed by Micro-Tech Laboratories, Inc., Skokie, Ill.

(19) A 19 ft × 0.25 in. column of 15% 1:4 potassium hydroxide–Carbowax 20M on 60–80 mesh Chromosorb W was used for this analysis.

(20) W. G. Dauben and A. G. Ashcraft, *J. Am. Chem. Soc.*, **85**, 3673 (1963).

(21) A 10 ft × 0.5 in. column of 20% Carbowax 20M on 60–80 mesh Chromosorb W was employed.

λ_{max}^{film} 6.09 (C=C), 10.02, 10.25, 11.39, and 12.55 μ; $\delta_{TMS}^{CCl_4}$ 5.49 (H-1 triplet, J = 3.5 Hz), 1.18, 1.10, 1.05 ppm (C-8 and C-10 CH_3's).

Anal. Calcd for $C_{13}H_{22}$: C, 87.56; H, 12.44. Found: C, 87.8; H, 12.2.

cis-**8,10-Dimethyl-1(9)-octalin (13).** To a solution of 1.50 g (8.25 mmol) of decalol **12**[22] in 50 ml of anhydrous pyridine at 0° was added 4.0 ml (55 mmol) of freshly distilled thionyl chloride.[18a] After stirring at 0° for 1 hr the solution was poured onto cracked ice and acidified with 10% aqueous hydrochloric acid, and the product was isolated with ether[18b] and distilled affording 1.22 g (90%) of a mobile oil, bp 85–87° (3.5 mm). The gas chromatogram[23] showed peaks at 10.5 min (**13**, 72.5%), and 11.2 min (**17**, 27.5%). The major component, octalin **13**, was secured *via* preparative gas chromatography:[24] $n^{25}D$ 1.4960; λ_{max}^{film} 6.03 (C=C), 9.29, 9.62, 9.72, 10.04, 10.14, 10.55, 11.43, 12.37, 12.60, and 15.05 μ; $\delta_{TMS}^{CCl_4}$ 5.30 (H-1, multiplet), 1.13 (C-10 CH_3), 1.12 ppm (C-8 CH_3, doublet, J = 7.5 Hz).

Anal. Calcd for $C_{12}H_{20}$: C, 87.73; H, 12.27. Found: C, 87.8; H, 12.4.

1-Methylene-*cis*-9,10-dimethyldecalin (18). A. From Decalone 29. A solution of 43 mg (0.24 mmol) of decalone **29** in 1.0 ml of dimethyl sulfoxide was treated with 2.2 ml of 0.5 M methylenetriphenylphosphorane according to the procedure of Corey and coworkers.[10] The product was isolated with pentane and chromatographed on alumina affording 28 mg (67%) of an oil: $n^{26}D$ 1.5120; λ_{max}^{film} 6.11 (C=C), 8.49, 8.60, 8.94, 9.96, 10.80, and 11.18 μ; $\delta_{TMS}^{CCl_4}$ 4.68 (C=CH_2), 1.05, and 0.83 ppm (C-9 and C-10 CH_3's). The analytical sample, mp 45–50°, was secured *via* preparative gas chromatography.[21]

Anal. Calcd for $C_{13}H_{22}$: C, 87.56; H, 12.44. Found: C, 87.5; H, 12.3.

B. Irradiation of Octalin 7. A solution containing 495 mg (2.78 mmol) of octalin **7**, 1.2 ml of *m*-xylene, and 15 ml of glacial acetic acid in 85 ml of isopropyl alcohol was irradiated[25] for 8 hr. The gas chromatogram[26] of an aliquot showed 19% of unchanged octalin **7**, 40% of decalin **18**, and 1% of octalin **19**. This last component constituted 3% of the product olefins after 1 hr of irradiation. The major peak was collected[21] and found to be decalin **18** by comparison with the authentic specimen synthesized in part A.

In a comparable experiment without added acetic acid, irradiation of octalin **7** for 3 hr failed to produce any identifiable products. Products likewise could not be detected upon irradiation of octalin **7** in isopropyl alcohol–acetic acid without xylene. Octalin **7** was completely stable to the reaction conditions in the dark.

C. From Octalin 19. A solution containing 600 mg (3.36 mmol) of octalin **19**, 1.2 ml of *m*-xylene, and 100 ml of isopropyl alcohol was irradiated[25] for 35 hr. The gas chromatogram[26] showed that 12% of octalin **19** remained and 74% of decalin **18** had been formed at this time. The product was isolated with ether[18b] and purified by preparative gas chromatography[21] affording 340 mg (65%) of decalin **18** identified by comparison with an authentic specimen. Comparable results were obtained upon irradiation of octalin **19** as above except with added acetic acid. In this case, however, a somewhat higher conversion was achieved after only 7.5 hr.

cis-**1,9,10-Trimethyl-1-octalin (19).** A solution of 1.83 g of octalin **7** in 20 ml of 5% sulfuric acid–acetic acid was stirred at room temperature for 50 min. The product was isolated with hexane[15b] and distilled affording 1.65 g (90%) of a 94:6 mixture of **7** and **19**[19] which was purified by preparative gas chromatography:[21] $n^{24}D$ 1.5074; λ_{max}^{film} 6.01 (C=C), 9.23, 9.96, 11.94, and 12.45 μ; $\delta_{TMS}^{CCl_4}$ 5.27 (H-2), 1.59 (C-1 CH_3 doublet, J = 1.7 Hz), 0.89 ppm (C-9 and C-10 CH_3's).

Anal. Calcd for $C_{13}H_{22}$: C, 87.56; H, 12.44. Found: C, 87.8; H, 12.2.

cis-**9,10-Dimethyl-1-octal-2-yl Acetate (21).** A solution of 25.0 g (0.152 mol) of octalone **5** and 4.57 g (0.023 mol) of cupric acetate monohydrate in 480 ml of tetrahydrofuran was added over 0.5 hr to a solution of 650 ml (0.39 mol) of 0.6 M methylmagnesium iodide at −10°.[18a] The mixture was stirred at room temperature for 2 hr and at reflux for 20 min, then it was cooled to 5° and 53 ml (0.74 mmol) of acetyl chloride in 500 ml of ether was added over 20 min. The mixture was diluted with ether, aqueous sodium bicarbonate and aqueous ammonium chloride were added, and the product was isolated with ether[18b] and distilled affording 10.12 g (30%) of the enol acetate **21**, bp 75–80° (0.2 mm); λ_{max}^{film} 5.70 (CO), 5.91 (C=C), 7.32, 8.20, 8.42, 8.62, 9.08, and 9.19 μ; $\delta_{TMS}^{CCl_4}$ 4.94 (H-1, triplet, J = 1.2 Hz), 2.00 (CH_3CO), and 0.92 ppm (C-9 and C-10 CH_3's).

Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.94. Found: C, 75.6; H, 10.2.

trans-**1-Acetoxy-*cis*-9,10-dimethyl-2-decalone (24).** A solution of 10.1 g (46.5 mmol) of enol acetate **21** and 27.0 g (133 mmol) of 86% *m*-chloroperoxybenzoic acid in 650 ml of benzene was stirred in the dark for 18 hr. The solution was washed with 10% aqueous sodium hydroxide and the product was isolated with benzene[18b] and distilled affording 8.60 g (80%) of a mixture of epoxy acetate stereoisomers **22**: λ_{max}^{film} 5.73 (CO), 8.09, 8.54, 9.63, 10.64, and 11.95 μ; $\delta_{TMS}^{CCl_4}$ 2.80, 2.71 (H-1 singlets), 1.98 (CH_3CO), 1.06, 0.96 (C-9 and C-10 CH_3's), 0.86, and 0.81 ppm (C-9 and C-10 CH_3's). The integrated nmr spectrum of this material indicated a 2:1 mixture, presumably favoring the *trans*-acetoxy isomer.

The above mixture of epoxy acetates **22** was heated at 165° for 25 min and the resulting mixture was crystallized from hexane affording 4.02 g (47%) of keto acetate **24**, mp 142–143°; λ_{max}^{KBr} 5.75, 5.80 (CO), 7.71, 8.05, 8.60, 9.38, 9.50, 9.71, and 10.34 μ; $\delta_{TMS}^{CHCl_3}$ 5.26 (H-1), 2.14 (CH_3CO), 1.20, and 1.08 ppm (C-9 and C-10 CH_3's).

The analytical sample, mp 142.5–143°, was obtained by an additional recrystallization followed by sublimation at 65° (0.02 mm).

Anal. Calcd for $C_{14}H_{22}O_3$: C, 70.56; H, 9.30. Found: C, 70.8; H, 9.2.

An additional 0.14 g (2%) of keto acetate **24**, mp 138–140°, was obtained as a second crop of crystals.

cis-**1-Acetoxy-*cis*-9,10-dimethyl-2-decalone (23).** The mother liquor from the above crystallization yielded a residue which was crystallized from pentane affording 0.10 g of keto acetate **23**, mp 75–78°; λ_{max}^{KBr} 5.75, 5.80 (CO), 7.85, 8.07, 9.24, 9.85, and 10.74 μ; $\delta_{TMS}^{CHCl_3}$ 5.71 (H-1), 2.15 (CH_3CO), 1.05, and 0.83 ppm (C-9 and C-10 CH_3's).

Anal. Calcd for $C_{14}H_{22}O_3$: C, 70.56; H, 9.30. Found: C, 70.6; H, 9.15.

Ethylene Thioketal Derivative of *trans*-1-Acetoxy-*cis*-9,10-dimethyl-2-decalone (25). To a solution of 3.66 g (15.4 mmol) of keto acetate **24** in 50 ml of glacial acetic acid was added 4.6 ml of 1,2-ethanedithiol and 4.6 ml of boron trifluoride etherate. The solution was allowed to stand for 3.5 hr and the product was isolated with ether[18b] affording 4.80 g (99%) of crystalline thioketal **25**, mp 118–123°; λ_{max}^{KBr} 5.77 (CO), 7.30, 8.10, 8.28, 9.66, 9.92, 10.05, and 12.63 μ; $\delta_{TMS}^{CCl_4}$ 5.33 (H-1), 3.20 (-SCH_2CH_2S-), 2.03 (CH_3CO), 0.99, and 0.89 ppm (C-9 and C-10 CH_3's).

The analytical sample, mp 124–125°, was secured by recrystallization from hexane followed by sublimation at 75° (0.02 mm).

Anal. Calcd for $C_{16}H_{26}O_2S_2$: C, 61.11; H, 8.33; S, 20.39. Found: C, 61.35; H, 8.15; S, 20.3.

Ethylene Thioketal Derivative of *trans*-1-Hydroxy-*cis*-9,10-dimethyldecalin (26). A solution of 3.30 g (10.5 mmol) of thioketal **25** in 10 ml of ether was added with stirring to a suspension of 1.0 g (26 mmol) of lithium aluminum hydride in 150 ml of ether. After 1 hr the product was isolated[18b] affording 2.80 g (99%) of alcohol **26**, mp 74–77°; λ_{max}^{KBr} 2.92 (OH), 7.88, 9.48, 9.60, 9.93, and 10.41 μ; $\delta_{TMS}^{CCl_4}$ 3.34, 3.22 (H-1, two equal peaks), 3.25–3.20 (-SCH_2-CH_2S-), 2.36 (OH), 1.03, and 0.90 ppm (C-9 and C-10 CH_3's).

The analytical sample, mp 77–79°, was obtained by recrystallization from pentane followed by sublimation at 60° (0.02 mm).

Anal. Calcd for $C_{14}H_{24}OS_2$: C, 61.71; H, 8.88; S, 23.54. Found: C, 61.6; H, 8.7; S, 23.4.

cis-**9,10-Dimethyl-*trans*-1-decalol (28).** A solution of 2.20 g (8.1 mmol) of thioketal **26** in 60 ml of ethanol was stirred with 12 g of W-2 Raney nickel[27] at room temperature for 2 hr and at reflux for 5 hr. The cooled mixture was filtered and the product was isolated with hexane[18b] affording 1.17 g (80%) of semicrystalline material. A sample exhibited mp 115–117° after two recrystallizations from pentane; λ_{max}^{KBr} 3.00 (OH), 8.42, 9.40, 9.57, 9.75, 10.00, and 10.65 μ; $\delta_{TMS}^{CCl_4}$ 3.60 (H-1, multiplet), 2.36 (OH), 1.00, and 0.85 ppm (C-9 and C-10 CH_3's).

(22) J. A. Marshall and A. R. Hochstetler, *J. Org. Chem.*, **31**, 1020 (1966).

(23) A 13 ft × 0.25 in. column of 20% Carbowax 20M on 60–80 mesh Chromosorb W was used for this analysis.

(24) A 13 ft × 0.5 in. column of 20% Carbowax 20M on 60–80 mesh Chromosorb W was employed.

(25) A Hanovia 450-W, high-pressure mercury arc (Type L) was used in a water-jacketed Vycor immersion well. Stirring was effected by a stream of nitrogen introduced through a gas dispersion tube fitted in the bottom of the reaction vessel.

(26) A 40 ft × 0.125 in. column of 3.5% Carbowax 20M on 60–80 mesh Chromosorb W was used for this analysis.

(27) H. R. Billica and H. Adkins, *Org. Syn.*, **21**, 15 (1941).

Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.06; Found: C, 79.3; H, 12.3.

***cis*-9,10-Dimethyl-1-decalone (29).** A solution of 1.07 g of the crude alcohol **28** in 20 ml of acetone at 5° was swirled while 2.0 ml of Jones reagent[9] was added dropwise. The excess oxidizing agent was destroyed with isopropyl alcohol and the product was isolated with ether[18b] affording 1.00 g of an oil whose infrared spectrum showed a strong ketonic band at 5.88 μ and a weaker conjugated ketone band at 5.98 μ. Evidently the thioketal **26** affords some of the allylic alcohol derived from abstraction of a β-hydrogen upon desulfurization with Raney nickel. Oxidation then affords the corresponding conjugated ketone (**29**, double bond at C-2, C-3).

Chromatography of this mixture on 100 ml of alumina afforded 690 mg (65%) of crystalline ketone, mp 88–96°, from the early fractions eluted with 1:1 hexane–benzene; λ_{max}^{KBr} 5.88 (CO), 7.60, 8.65, 9.50, 9.88, 10.48, 10.62, and 12.14 μ; $\delta_{TMS}^{CCl_4}$ 1.01, 0.94 ppm (C-9 and C-10 CH_3's).

Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.7; H, 11.3.

1-Methylene-*cis*-10-methyldecalin (30). A. From the Decalone Mixture 32 and 33. A solution of 1.50 g (9.0 mmol) of the decalone equilibrium mixture (2:1 in favor of the *trans* isomer **32**) in 8 ml of dimethyl sulfoxide was treated with 40 ml of 0.6 *M* methylenetriphenylphosphorane.[10] After 3 hr at 35° the reaction mixture was diluted with water and the product was isolated with ether[18b] affording 1.32 g (89%) of a mixture of the *cis*-decalin **30** (13%) and the *trans*-decalin **35** (87%)[19] which was separated by preparative gas chromatography.[28]

In this manner, 150 mg (10%) of the shorter retention time minor component was isolated as a colorless oil: $n^{25}D$ 1.4914; λ_{max}^{film} 6.06 (C=C), 8.63, 10.30, 10.54, 11.23, and 11.63 μ; $\delta_{TMS}^{CCl_4}$ 4.65, 4.64 (C=CH_2), and 0.87 ppm (C-10 CH_3).

Anal. Calcd for $C_{12}H_{20}$: C, 87.73; H, 12.27. Found: C, 87.9; H, 12.05.

The longer retention time major olefin (1.03 g, 70%) was likewise isolated and shown to be the *trans* isomer **35** by comparison with an authentic sample.

B. Irradiation of Octalin 11. A solution of 500 mg (3.04 mmol) of octalin **11**,[29] 1.3 ml of *m*-xylene, 15 ml of glacial acetic acid, and 85 ml of isopropyl alcohol was irradiated[25] for 8 hr affording a mixture containing 8% of unchanged octalin **11**, 2% of the tetrasubstituted olefin **17**, and 53% of the *cis*-decalin **30**.[28] No product corresponding to the *trans*-decalin **35** could be detected at any point in the reaction. An aliquot removed after 1 hr contained octalin **17** as 15% of the isomerized products. This percentage gradually decreased as the irradiation proceeded. Control experiments showed that no reaction took place in the absence of xylene or acetic acid or ultraviolet light.

The major product (180 mg, 36%) isolated with hexane[18b] and purified by preparative gas chromatography[24] was identified as the *cis*-decalin **30** by comparison with an authentic sample.

C. Irradiation of Octalin 17. A solution of 50 mg (3.04 mmol) of octalin **17**[22] was irradiated as described above for 4 hr after which no more starting material remained and the *cis*-decalin **30** constituted the only observable product (70% yield).[28] This material was isolated by preparative gas chromatography[24] and identified by comparison with an authentic specimen.

D. Irradiation of Octalin 47. A solution of 410 mg (2.50 mmol) of octalin **47** and 1.3 ml of *m*-xylene in 100 ml of isopropyl alcohol was irradiated[26] for 4 hr whereupon a mixture containing 13% unchanged starting material, 2% of the *trans* dimethyloctalin **11**, 3% of the tetrasubstituted olefin **17**, and 67% of the *cis*-decalin **30** was obtained with an apparent 15% loss of material. The major product was isolated by preparative gas chromatography[24] and identified by comparison with an authentic specimen.

***trans*- and *cis*-10-Methyl-1-decalones (32 and 33).** The hydroboration sequence of Brown and coworkers[30] was applied to 35.2 g (0.234 mol) of 10-methyl-1(9)-octalin (**31**).[22] The resulting mixture of alcohols was oxidized with 58.5 ml of Jones reagent[9] affording 35.2 g (90%) of colorless oil, bp 72–73° (0.7 mm), containing principally the *cis*-decalone **33** (63%) and the *trans*-decalone **32** (31.5%).[31] The pure ketones, separated by preparative gas chromatography,[21] displayed the following properties.

***trans*-10-Methyl-1-decalone (32):** $n^{25}D$ 1.4895; λ_{max}^{film} 5.85 (CO), 7.22, 7.29, 7.61, 7.80, 8.26, 8.62, 9.11, 9.47, 9.57, 10.49, 10.74, 12.01, and 12.18 μ; $\delta_{TMS}^{CCl_4}$ 0.80 ppm (C-10 CH_3).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.6; H, 11.0.

***cis*-10-Methyl-1-decalone (33):** $n^{25}D$ 1.4902; λ_{max}^{film} 5.85 (CO), 7.25, 7.59, 8.10, 8.39, 8.53, 9.18, 9.30, 9.50, 10.42, and 12.02 μ; $\delta_{TMS}^{CCl_4}$ 1.05 ppm (C-10 CH_3).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.5; H, 11.1.

Equilibration was effected by heating a solution of 15.0 g (90 mmol) of the above decalone mixture and 5.0 g of sodium carbonate in 90 ml of water and 500 ml of methanol at reflux for 20 hr.[18a] The product was isolated with pentane[18b] and distilled affording 14.65 g (98%) of colorless oil, bp 65–66° (0.3 mm), containing 67% of the *trans*-decalone **32** and 33% of the *cis*-decalone **33**.[31] The composition was unaffected upon treatment of a sample of this mixture under the above conditions for an additional 24 hr.

1-Methylene-*trans*-10-methyldecalin (35). A. From Tosylate 34. A solution of 310 mg (0.43 mmol) of tosylate **34**[12] and 100 mg (2.62 mmol) of lithium aluminum hydride in 20 ml of 1,2-dimethoxyethane was heated at reflux for 13 hr. The cooled mixture was diluted with 50 ml of ether and the product was isolated[18b] and chromatographed on 10 ml of Florisil affording 113 mg (75%) of a colorless mobile oil: $n^{24}D$ 1.4945; λ_{max}^{film} 6.07 (C=C), 8.09, 8.55, 10.25, 10.33, 10.71, 11.27, and 11.61 μ; $\delta_{TMS}^{CCl_4}$ 4.70 4.59 (C=CH_2), and 0.73 ppm (C-10 CH_3).

Anal. Calcd for $C_{12}H_{20}$: C, 87.73; H, 12.27. Found: C, 87.6; H, 12.2.

B. Irradiation of Octalin 13. A solution of 220 mg (1.34 mmol) of octalin **13** and 0.6 ml of *m*-xylene in 105 ml of isopropyl alcohol was irradiated[25] for 2 hr at which time 6% of octalin **13** remained and 80% of decalin **35** had been formed as the sole detectable product.[28] This product was isolated by preparative gas chromatography[24] and identified by comparison with an authentic sample.

C. Irradiation of Octalin 46. A solution of 500 mg (3.04 mmol) of octalin **46** and 1.0 ml of *m*-xylene in 120 ml of isopropyl alcohol was irradiated as described above. After 1 hr no starting material could be detected and decalin **35** had formed in 83% yield.[23] Isolation by preparative gas chromatography[24] afforded 340 mg (68%) of decalin **35** identified by comparison with an authentic sample.

1-Deuterio-10-methyl-1(9)-octalin (36). A 14.1-g (85 mmol) sample of the equilibrium mixture of decalones **32** and **33** in 20 ml of ether was added over 20 min to a stirred mixture of 1.40 g (33.2 mmol) of lithium aluminum deuteride in 200 ml of ether. The mixture was stirred for 22 hr and the product was isolated as usual[18b] affording 14.2 g of crude decalol.

The entire decalol mixture was dissolved in 50 ml of pyridine, cooled to 0°, and treated with 11.5 g (100 mmol) of methanesulfonyl chloride. After 3 hr the product was isolated with pentane.[18b]

The above mesylate was heated at reflux with 75 g of potassium hydroxide in 450 ml of methanol for 14 hr.[18a] The product was isolated with pentane[18b] and distilled affording 10.25 g (80%) of a mobile oil, bp 76–78° (11 mm); λ_{max}^{film} 4.48 (vinylic C—D), 6.01 (C=C), 8.39, 8.55, 9.20, 9.55, 10.12, 11.15, and 12.10 μ; mass spectrum, M = 151 (Calcd for $C_{11}H_{17}D$: M = 151), 96% d_1, 4% d_0. The nmr spectrum indicated the presence of about 20% of an isomeric olefin, presumably 1-deuterio-10-methyl-1-octalin resulting from loss of H-2 in the above mesylate.

8-Deuterio-*cis*-8,10-dimethyl-1(9)-octalin (40). The sequence employed for the preparation of this octalin is essentially that used for the nondeuterated counterpart, octalin **13**, which is described above and elsewhere.[22] Accordingly, 7.0 g (46.4 mmol) of octalin **36** was converted to 7.2 g (93%) of the epoxide mixture **37** upon treatment with 11.8 g (54.5 mmol) of *m*-chloroperoxybenzoic acid (85%) in 230 ml of benzene for 3 hr. The epoxide mixture was treated with 150 ml of 4.5 *M* methylmagnesium bromide in tetrahydrofuran at reflux for 68 hr.[18a] The products were isolated with ether[18b] and carefully chromatographed on silica gel affording, on elution with 1.5% ether–hexane, 2.92 g (73%) of decalol **39**: λ_{max}^{film} 2.87 (OH), 4.72 (C–D), 8.64, 9.30, 9.80, 10.49, 11.35, 11.85, and 12.44 μ; $\delta_{TMS}^{CCl_4}$ 1.06 (C-10 CH_3) and 1.00 ppm (C-4 CH_3).

Continued elution of the above column with 1.5% ether–hexane afforded 400 mg of a mixture of decalols **38** and **39** and finally, 0.99 g (13%) of decalol **38**: λ_{max}^{film} 2.87 (OH), 4.65 (C–D), 9.30, 9.53, 9.92, 10.34, 10.63, 11.05, 11.42, and 11.62 μ; $\delta_{TMS}^{CCl_4}$ 0.91 (C-10 CH_3) and 0.81 (C-4 CH_3) ppm.

(28) A 50 ft × 0.125 in. column of 2% LP-118 silicone gum rubber SE-30 on 60–80 mesh Chromosorb G was used for this analysis.

(29) J. A. Marshall and A. R. Hochstetler, *J. Org. Chem.*, **33**, 2593 (1968).

(30) H. C. Brown, K. J. Murray, L. J. Murray, J. A. Snover, and G. Zweifel, *J. Am. Chem. Soc.*, **82**, 4233 (1960).

(31) A 24 ft × 0.125 in. column of 20% Carbowax 20M on 60–80 mesh Chromosorb W was used for this analysis.

A 2.0-g sample of decalol **39** was treated with 5.0 ml of thionyl chloride, as described for decalol **12**, affording 1.55 g of an olefin mixture containing 77% of the *cis*-dimethyloctalin **40** purified *via* preparative gas chromatography:[24] λ_{max}^{film} 4.65 (C—D), 6.05 (C=C), 9.91, 10.02, 10.92, 11.40, 12.31, 12.61, and 15.24 μ; $\delta_{TMS}^{CCl_4}$ 5.33 (H-1, triplet, J = 3.5 Hz) and 1.15 ppm (C-10 and C-4 CH_3's); mass spectrum, M = 165 (Calcd for $C_{12}H_{19}D$: M = 165), 5% d_0, 95% d_1.

1-Methylene-*trans*-9-deuterio-10-methyldecalin (41). A. From Decalone 43. A mixture of 1.80 g (5.0 mmol) of methyltriphenylphosphonium bromide, 3.0 ml (4.8 mmol) of 1.6 M *n*-butyllithium in hexane, and 20 ml of ether was stirred at room temperature for 4 hr.[18a] A solution of 365 mg (2.18 mmol) of decalone **43** in 2 ml of ether was added and, after 13 hr, the product was isolated with ether[18b] and chromatographed on 20 ml of alumina. Elution with pentane gave 205 mg (55%) of decalin **41**: λ_{max}^{film} 4.80 (C—D), 6.08 (C=C), 11.28, 11.68, and 11.94 μ; mass spectrum, M = 165 (calcd for $C_{12}H_{19}D$: M = 165), 34% d_0, 66% d_1.

B. Irradiation of Octalin 40. A solution of 230 mg (1.39 mmol) of octalin **40** and 0.6 ml of *m*-xylene in 105 ml of isopropyl alcohol was irradiated[25] for 8 hr at which time 13% of octalin **40** remained and 5.2% of decalin **41** had been formed along with 3.5% of an unidentified product (presumably dihydro-**46**[14]).[32] The major product, isolated by preparative gas chromatography,[24] was found to contain 78% d_1 and 22% d_0 by mass spectrometry. A sample adjusted to 66% d_1 and 34% d_0 by the addition of decalin **35** gave a superimposable infrared spectrum with that of the material prepared in part A.

The infrared spectrum of the recovered starting octalin **40** was identical with the spectrum before irradiation.

***trans*-9-Deuterio-10-methyl-1-decalone (43).** The hydroboration sequence of Brown and coworkers[30] was applied to 4.0 g (26.5 mmol) of 10-methyl-1(9)-octalin (**31**)[22] using 10 ml of 0.75 M trideuterioborane in tetrahydrofuran. The product was isolated with ether[18b] and chromatographed on 75 ml of Florisil. Elution with hexane gave 1.8 g (45%) of recovered octalin **31**. Elution with 1:1 ether–hexane gave 2.35 g of decalols which was directly oxidized with Jones reagent[9] at 0° affording 1.75 g (75% based on alcohols) of decalones **42** and **43**, bp 65–70° (0.05 mm). The minor isomer, decalone **43**, was purified by preparative gas chromatography[24] and found to contain 67% d_1 and 33% d_0 species according to the mass spectrum.

Analogous results were obtained when the Jones oxidation[9] was carried out at −20° or when ruthenium tetroxide[15,33] was employed for the oxidation.

***trans*-1,10-Dimethyl-*trans*-2-decalone (44).** A solution of 20.3 g (0.114 mol) of octalone **14**[22] in 110 ml of ether and 600 ml of liquid ammonia was treated with 5.0 g (0.72 g-atom) of lithium wire. After 2 hr, 100 ml of 1:1 ether–ethanol was added over a 0.5-hr period, the mixture was stirred for an additional 2 hr, and the blue color was discharged with solid ammonium chloride. The ammonia was allowed to evaporate and the product was isolated with ether[18b] and directly oxidized with Jones reagent[9] affording 18.6 g (91%) of decalone **44**, bp 59–61° (0.10 mm); λ_{max}^{film} 5.86 (CO), 8.43, 8.62, 8.88, 9.40, 9.87, and 10.22 μ; $\delta_{TMS}^{CCl_4}$ 1.07 (C-10 CH_3) and 0.84 ppm (C-1 CH_3, doublet, J = 6 Hz).

Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.9; H, 11.0.

***p*-Toluenesulfonylhydrazone Derivative of *trans*-1,10-Dimethyl-*trans*-2-decalone (45).** A solution of 5.0 g (27.8 mmol) of decalone **44**, 5.17 g (27.8 mmol) of *p*-toluenesulfonylhydrazine, and 0.25 ml of concentrated hydrochloric acid in 70 ml of ethanol was stirred at reflux for 4 hr.[18a] The product was isolated with hexane[18b] and recrystallized from methanol affording 4.3 g (45%) of crystals, mp 145–147° dec; λ_{max}^{KBr} 3.21 (NH), 6.23 (C=N), 7.50, 8.52, 9.10, 9.80, 10.78, and 12.26 μ. A second crop of 1.4 g (15%) was obtained.

Anal. Calcd for $C_{19}H_{28}N_2O_2S$: C, 65.49; H, 8.10; N, 8.04; S, 9.20. Found: C, 65.3; H, 8.0; N, 8.0; S, 9.4.

***trans*-1,10-Dimethyl-1-octalin (46).** A 2.0-g (87 mg-atom) portion of sodium was allowed to react with 70 ml of ethylene glycol whereupon 8.0 g (23 mmol) of tosylhydrazone **45** was added and the temperature was raised to 175°.[18a] After 15 min, the temperature was raised to 210° and after 0.5 hr nitrogen evolution subsided. The product was isolated with pentane[18b] and distilled affording 2.1 g (55%) of a mobile oil, bp 67–77° (0.5 mm), which consisted of four components in relative amounts of 22%, 6.5%, 18%, and 52%.[31] Partial separation was effected by preparative gas chromatography[24] to give 405 mg of a mixture of the first two components (largely octalin **48**: λ_{max}^{film} 6.04 (C=C), 13.85, and 14.60 μ) and 1.15 g of a mixture of the latter two components. This mixture was chromatographed on 75 ml of silver nitrate impregnated silica gel. Elution with pentane afforded 810 mg (21%) of the octalin **46**: $n^{25}D$ 1.4940; λ_{max}^{film} 6.01 (C=C), 8.70, 10.71, 11.75, 12.05, and 12.56 μ; $\delta_{TMS}^{CCl_4}$ 5.36 (H-2, multiplet), 1.61 (C-1 CH_3, doublet, J = 1.4 Hz), and 0.81 ppm (C-10 CH_3).

Anal. Calcd for $C_{12}H_{20}$: C, 87.73; H, 12.27. Found: C, 87.5; H, 12.2.

Elution of the above column with 20% ether–hexane afforded 260 mg (7%) of the *trans*-decalin **35**, identified by comparison with an authentic sample.

***cis*-1,10-Dimethyl-1-octalin (47).** A solution of 1.40 g of octalin **17** in 20 ml of 5% sulfuric acid in acetic acid was stirred at room temperature for 40 min. The product was isolated with pentane[18b] and purified *via* preparative gas chromatography[24] affording 650 mg (46%) of octalin **47**: $n^{25}D$ 1.4903; λ_{max}^{film} 5.99 (C=C), 8.18, 9.20, 9.26, 10.03, 10.53, 11.62, 12.38, and 13.93 μ; $\delta_{TMS}^{CCl_4}$ 5.21 (H-2), 1.62 (C-1 CH_3, doublet, J = 1.8 Hz), and 0.86 ppm (C-10 CH_3).

Anal. Calcd for $C_{12}H_{20}$: C, 87.73; H, 12.27. Found: C, 87.4; H, 12.3.

Acid-Catalyzed Equilibration of Olefins 11, 13, 17, 30, 35, 46, and 47. Each of the pure title olefins (50 mg, 0.30 mmol) was dissolved in 0.5 ml of 5% sulfuric acid in acetic acid and stirred at room temperature for 40 min. The solutions were neutralized with 10% aqueous sodium hydroxide and the products were isolated with pentane.[18b] The material balances ranged from 84 to 90%. The composition was determined by gas chromatography on two columns.[26,29] The results are summarized in Table II.

Table II. Acid-Catalyzed Equilibration of Olefins

	Equilibrium composition, %				
Starting olefin	**11**	**17**	**46**	**47**	Unidentified (2 peaks)
11	13	33	3	43	8
13	11	33	3	45	8
17	10	35	3	45	7
30	12	32	3	45	8
35	12	34	2	45	7
46	10	35	3	45	7
47	11	33	3	45	8

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(32) A 17 ft × 0.25 in. column of Carbowax 20M on 60–80 mesh Chromosorb W was used for this analysis.

(33) The procedure of J. A. Caputo and R. Fuchs, *Tetrahedron Letters*, 4729 (1967).