Addition Reactions of *cis,trans*-1,5-Cyclodecadiene[1]

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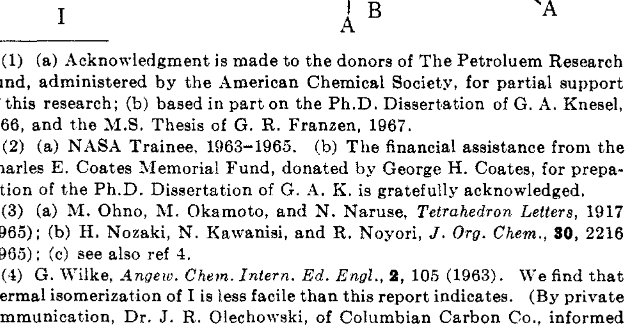
Various olefin addition reagents have been used with *cis,trans*-1,5-cyclodecadiene. A high degree of selectivity for addition to the *trans* double bond in the diene has been detected for reagents which transfer the added atoms or groups in a single step. Among these reactions are diimide reduction, diborane addition, ozonation, epoxidation, and methyleneation. Ionic reagents, such as bromine, lead tetraacetate, methanesulfenyl chloride, and mercury salts, which add in steps, lead to transannular cycloadditions producing substituted *cis*-decalins as products.

Two reports of several selective reactions of *cis,trans,-trans*-1,5,9-cyclododecatriene recently appeared.[3,3] At that time we were investigating similar selectivity for reactions of *cis,trans*-1,5-cyclodecadiene (I), a medium-ring diene which might be expected to respond differently to various reagents than the larger ring triene. Although some of the reagents used with cyclododecatriene added selectively to the *trans* double bond, even those which did not discriminate between *cis* and *trans* double bonds still gave normal 1,2-addition products. We have observed high selectivity for the *trans* double bond in cyclodecadiene by some reagents, and the formation of transannular products, substituted *cis*-decalins, with others.

No systematic investigation of the reactions of I has been reported. The diene undergoes thermal isomerization to *cis*-1,2-divinylcyclohexane.[4] Monoepoxidation[5,1b] and 1:1 complex formation with gold(I) chloride[6] involve principally the *trans* double bond. Preliminary investigations of complexes between I and silver nitrate and copper halides indicate that both double bonds of the diene are involved in the coordination.[7] We have now made a systematic survey of various types of reactions of I and here summarize our results.

1,2 Additions.—Like cyclododecatriene,[3] *cis,trans*-1,5-cyclodecadiene (I) reacts with several addition reagents principally at the *trans* double bond. Among the reactions for which high selectivity is obtained are reduction with diimide, addition of diborane, epoxidation with *m*-chloroperoxybenzoic acid, and methyleneation with methylene iodide and zinc-copper couple.



Each of these additions probably proceeds through a transition state with little or no ionic character;[8,9] that is, the transfer or addition is accomplished essentially in one step to give a product of *cis* addition.

The preferential reaction of such reagents with the *trans* double bond in both cyclododecatriene[3] and cyclodecadiene indicates that relative strain in the alkene linkage itself probably plays little part in determining the selectivity of the addition reactions. In the monoolefins, *trans*-cyclododecene and *cis*-cyclodecene are favored over their corresponding geometrical isomers.[10] Although the relative strain in *cis* and *trans* alkene linkages may well be different in the monoenes and the di- and trienes considered here, there are no data to indicate this difference. Models certainly do not suggest that the *trans* linkage has become the favored one in I.

Reduction of the diene with diimide is so selective and convenient that we have used it to prepare pure *cis*-cyclodecane from the relatively easily accessible diene.[11] Catalytic hydrogenation[12-14] of the diene is selective with a pyridine-poisoned palladium-on-carbon catalyst,[15] but is unselective in the absence of the poison.

Ozone attacks I preferentially at the *trans* double bond also. The products obtained depend on the solvent employed for the reaction. In carbon tetrachloride and chloroform at low temperature, low molecular weight polymeric ozonides were obtained, but from acetic acid solution the simpler product, 4-decenedial (isolated as the bis-2,4-dinitrophenylhydrazone),

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[1] (a) Acknowledgment is made to the donors of The Petroluem Research Fund, administered by the American Chemical Society, for partial support of this research; (b) based in part on the Ph.D. Dissertation of G. A. Knesel, 1966, and the M.S. Thesis of G. R. Franzen, 1967.

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[3] (a) M. Ohno, M. Okamoto, and N. Naruse, *Tetrahedron Letters*, 1917 (1965); (b) H. Nozaki, N. Kawanisi, and R. Noyori, *J. Org. Chem.*, **30**, 2216 (1965); (c) see also ref 4.

[4] G. Wilke, *Angew. Chem. Intern. Ed. Engl.*, **2**, 105 (1963). We find that thermal isomerization of I is less facile than this report indicates. (By private communication, Dr. J. R. Olechowski, of Columbian Carbon Co., informed us that he has data which lead to the same conclusion.) A sample of I was barely changed after being heated for 8 hr at 100° but was completely isomerized after being heated overnight at 140°. We have preliminary evidence for catalysis of this transformation and are investigating such rearrangements more extensively.

[5] W. Dittmann and F. Stuerzenhofetker, *Ann.*, **688**, 57 (1965).

[6] R. Heuttel, H. Reinheimer and H. Distl, *Chem. Ber.*, **99**, 462 (1966).

[7] J. C. Trebellas, J. R. Olechowski, and H. B. Jonassen, *Inorg. Chem.*, **4**, 1818 (1965).

[8] (a) Diimide reduction: E. W. Garbish, Jr., S. M. Schildcrout, D. B. Patterson, and C. M. Sprecher, *J. Am. Chem. Soc.*, **87**, 2932 (1965); (b) diborane addition: H. C. Brown and G. Zweifel, *ibid.*, **83**, 2544 (1961); (c) epoxidation: K. D. Bingham, G. D. Meakins, and G. H. Whitham, *Chem. Commun.*, 445 (1966); (d) methyleneation: J. Hine, "Divalent Carbon," Ronald Press Co., New York, N. Y., 1964, pp 25–28.

[9] Evidence for a 1,3-dipolar addition mechanism (without significant charge development on the olefinic carbons) has been presented: (a) H. Kwart and D. M. Hofmann, *J. Org. Chem.*, **31**, 419 (1966); (b) H. Kwart, P. S. Starcher, and S. W. Tinsley, *Chem. Commun.*, 335 (1967).

[10] A. C. Cope, P. T. Moore, W. R. Moore, *J. Am. Chem. Soc.*, **81**, 3153 (1959).

[11] Two samples of I were generously supplied by Dr. J. R. Olechowski of Columbian Carbon Co., Lake Charles, La. Another sample was prepared by us from butadiene, ethylene, and nickel biscyclooctadiene;[4] we gratefully acknowledge gifts of butadiene from Copolymer Corp., Baton Rouge, La.

[12] Although catalytic hydrogenation of alkenes is a complex series of reactions involving half-hydrogenated species, the over-all mode of addition is *cis*. See T. I. Taylor, *Catalysis*, **5**, 557 (1957).

[13] At the pressures employed by us, the half-hydrogenated state probably figures importantly in the product-determining step of the reaction.[14] The same factors that lead to a preference for the *trans* double bond in the single-step diimide reduction[8a] would favor the *trans* double bond for formation of the half-hydrogenated state ("an essentially saturated structure"[14]).

[14] S. Siegel, M. Dunkel, G. V. Smith, W. Halpern, and J. Cozort, *J. Org. Chem.*, **31**, 2802 (1966).

[15] An earlier report by G. Wilke on selective reduction of the *trans* double bond of the diene with hydrogen and a pyridine-poisoned palladium catalyst was relayed to us by Dr. William C. Baird, Jr.

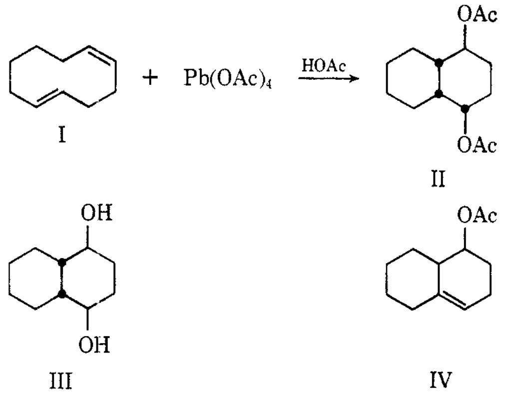
was obtained. Nuclear magnetic resonance (nmr) spectra were used to establish that the alkene linkage remaining in the dial derivative was *cis*.

Although conversion of alkene to ozonide is a multistep process,[16] the initial *cis* addition leads to preferential attack on the *trans* rather than the *cis* double bond.[16a] The factors controlling relative rates of formation of intermediates from *trans* and *cis* double bonds will be quite similar for ozonations and epoxidation.

Transannular Additions.—In contrast to the *cis* additions to the *trans* double bond of I described above, reactions of I with several ionic addition reagents involve both double bonds, and the products formed are 1,4-disubstituted *cis*-decalins.

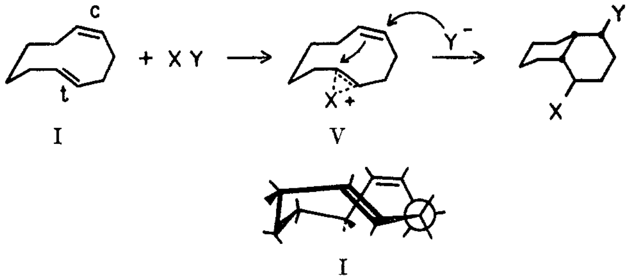
Lead tetraacetate reacts with alkenes by an initial attack by $Pb(OAc)_3^+$ or its equivalent,[17] and the products isolated are generally diacetates. Dienes give both 1,2- and 1,4-addition products. The cationic nature of the intermediates in the reaction is supported by the reports that *cis*-cyclooctene gives a large amount of transannular product[18a] and norbornene and nonbornadiene give only rearrangement products.[18b] Reaction of I (Scheme I) with lead tetraacetate is far more vigorous and exothermic than the description of the related reaction of cyclooctene[18a] led us to expect; the reaction proceeds smoothly, however, when the temperature is controlled with an ice bath. The major product was identified as *trans*-1,4-diacetoxy-*cis*-decalin.[19] The distilled product also contained some unsaturated acetate, tentatively identified on the basis of nmr data (relative intensity of signal for C=CH) and expected relative stability as bicyclo[4.4.0]dec-5-en-2-yl acetate (IV). This acetate is apparently formed by an elimination reaction during distillation, for an acetoxylation carried out with molar equivalents of lead tetraacetate and I in an nmr tube led to a mixture whose nmr spectrum was devoid of ethylenic absorptions.

SCHEME I



The CCC bond angles in the ten-membered ring are appreciably larger than the normal tetrahedral angle,[20] and conversion of the cyclodecadiene to a substituted *cis*-decalin is accompanied by substantial strain relief. Addition to a monoene, even a medium-ring one, does not yield a comparable amount of angle strain relief (in fact, conversion of medium ring cycloalkenes to substituted cycloalkanes probably leads to an increase in strain). The rapid acetoxylation of I may signal a significant amount of concerted character in the addition (Scheme II).

SCHEME II



Conversion of the intermediate organolead cationic intermediate (represented by V, X = $Pb(OAc)_3$) to a 1,4-disubstituted *cis*-decalin is quite similar to the hydrolysis of *trans*-5,6-epoxy-*cis*-cyclodecene (*trans*-monoepoxide of I).[5] Hydrolysis of that epoxide produces *cis*-decalin-*trans*-1,4-diol (III) in high yield.[5] Treatment of a sample of the diol[21] with acetic anhydride produced a diacetate identical with the product obtained in the acetoxylation of I.

Additions of bromine to I, both in acetic acid and in carbon tetrachloride, also lead to transannular cycloaddition products (disubstituted *cis*-decalins).[22–24] In acetic acid solvent, the product is a bromo acetate (which was reduced by lithium aluminum hydride to the bromo alcohol), and in carbon tetrachloride, a dibromide. Structure identifications depended primarily on nmr spectra, which corresponded closely (except for signals for HCBr) to the nmr spectra for the diacetate (II) and the diol (III).[25] The addition in carbon tetrachloride was conducted in an nmr tube, and

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[16] (a) P. S. Bailey, *Chem. Rev.*, **58**, 925 (1958); (b) R. W. Murray, R. D. Youssefyeh, and P. R. Story, *J. Am. Chem. Soc.*, **88**, 3143, 3144 (1966); (c) F. L. Greenwood, *ibid.*, **88**, 3146 (1966).

[17] R. Criegee, in "Newer Methods of Preparative Organic Chemistry," Vol. II, Academic Press Inc., New York, N. Y., 1963, pp 367–386.

[18] (a) A. C. Cope, M. Gordon, S. Moon, and C. H. Park, *J. Am. Chem. Soc.*, **87**, 3119 (1965); (b) K. Alder, R. H. Flock, and H. Wirtz, *Chem. Ber.*, **91**, 609 (1958).

[19] (a) W. Hückel and W. Kraus, *Chem. Ber.*, **95**, 233 (1962). (b) For a report of (apparently slower) cyclooxidation of 1,5-hexadiene, see I. Tabushi and R. Oda, *Tetrahedron Letters*, 2487 (1966).

[20] (a) J. D. Dunitz and H. M. M. Shearer, *Helv. Chim. Acta*, **43**, 18 (1960); (b) J. D. Dunitz and V. Prelog, *Angew. Chem.*, **72**, 896 (1960); (c) J. Sicher, M. Svoboda, J. Zavada, R. B. Turner, and P. Goebel, *Tetrahedron*, **22**, 659 (1966); these authors indicate that the most stable conformations of unsaturated ten-membered rings exhibit "the minimum essential deviation from that of cyclodecane."

[21] A sample of *cis*-decalin-*trans*-1,4-diol was kindly supplied to us by Dr. J. R. Olechowski, Columbian Carbon Co., Lake Charles, La.

[22] The ease of ionic additions to I contrast with the reported "inactivity of tetraethyl *cis,cis*-3,8-cyclodecadiene-1,1,6,6-tetracarboxylate toward conventional tests for olefinic groups."[23]

[23] R. M. Gipson, H. W. Guin, S. H. Simonsen, C. G. Skinner, and W. Shive, *J. Am. Chem. Soc.*, **88**, 5366 (1966). These authors report that the substituted *cis,cis*-1,6-cyclodecadiene does not react with bromine in carbon tetrachloride, but it does add bromine in methanol to form a 4-bromo-8-methoxy-*cis*-decahydronaphthalene (transannular cycloaddition).

[24] J. M. Greenwood, J. K. Sutherland, and A. Torre (*Chem. Commun.*, 410 (1965)) have reported that humulene (2,6,6,9-tetramethyl-*trans,trans,*-*trans*-1,4,8-cycloundecatriene) reacts with N-bromosuccinimide in aqueous acetone to form a 5-bromotricyclo[7.2.0.$0^{2,4}$]undecan-9-ol (transannular cycloaddition) as well as monocyclic products.

[25] In some experiments, the crude bromo acetate and bromo alcohol products were shown by gas chromatography to consist of two isomers. Since the nmr spectra suggest only *cis*-decalin frameworks, and acetoxylation apparently gives a single *trans*-1,4-diacetoxy-*cis*-decalin product, we consider these bromo acetates (and bromo alcohols) to be noninterconvertible conformational isomers of *trans*-1-acetoxy-4-bromo-*cis*-decalin (bromine *cis* or *trans* to ring fusion), formed by initial attack at both alkene linkages. Bromine addition to *cis,trans,trans*-1,5,9-cyclododecatriene was likewise shown to be unselective.[3a] Unselective attack during acetoxylation ($Pb(OAc)_4$) would lead to a single *trans*-1,4-diacetoxy-*cis*-decalin because of the identity of the two substituents.

spectra were recorded intermittantly during titration with bromine. The total signal for ethylenic protons (*cis* and *trans*) diminished during the addition of bromine, but the shape of the signal did not change. We consider this observation to be strong evidence that both alkene linkages are involved directly in the addition reaction, and that a 1,2 addition of bromine followed by a rearrangement is not a good description of the reaction. The nmr spectrum of the addition product clearly excludes a tetrabromocyclodecane.

Mercury(II) acetate (1 molar equiv) reacts rapidly with a methanolic solution of I to cause complete loss of all ethylenic proton absorption in the nmr spectrum, which resembled closely in the region above −3 ppm the spectrum of the diacetate (II). It appears that none of the methoxymercuration has occurred to give a 1,2-addition product, as would be expected of a *cis*-addition reagent.[26] The implications of this nmr tube experiment were confirmed by preparative hydration of I by the recently described procedure of oxymercuration followed by reductive demercuration.[27] Gas chromatography of the product mixture revealed the presence of two isomeric alcohols in proportions 17:83. The major component (60% yield) was isolated by crystallization and identified as *cis,cis*-1-decalol.[28] Formation of this alcohol is consistent with attack by cationic mercury on the *trans* alkene linkage of I and bonding of water at the *cis* linkage, both from pseudo-equatorial directions. Bonding of mercury at this *cis* linkage and water at the *trans* one would produce *cis,trans*-1-decalol.[23] This alcohol is apparently produced as the minor product in the mercuration–demercuration experiment, for oxidation of the alcohol mixture with chromic acid in aqueous acetone produced a single ketone, *cis*-1-decalone.[29]

In preliminary screening experiments in nmr tubes, 1 molar equiv of methanesulfenyl chloride reacted with I in methylene chloride solution at −25° to form a product mixture whose nmr spectrum was completely devoid of ethylenic proton signals. Although this product has not been isolated and identified, its nmr spectrum indicates clearly that it is also formed by transannular cycloaddition. Like the reaction with lead tetraacetate, this one is strongly exothermic, even at −25°. The absence of any 1,2-addition product (which would require that some ethylenic protons remain in the product mixture) is particularly interesting here, because methanesulfenyl chloride additions have been described in terms of strong bridging by sulfur in intermediate cations,[30] and 1,2 additions to conjugated dienes have been reported.[30c]

These several reactions of I may be summarized as follows. Reagents apparently effecting the transfer of the addend in one step without the intervention of cationic intermediates form 1,2-addition products by preferential attack at the *trans* alkene linkage. Stepwise additions to I proceeding through intermediate cations (V), whether formed by attack of metal ions, bromine, or methsulfenyl chloride, lead to transannular additions and substituted *cis*-decalins as products. Reactions of I may prove to be of considerable diagnostic value for clarification of olefin reaction mechanisms.

Experimental Section

Capillary melting points were obtained on a Thomas–Hoover apparatus and are uncorrected. Infrared spectra were obtained with Beckman IR-5 and Perkin-Elmer 137 spectrophotometers. Gas chromatographic analyses were performed on a Barber–Coleman Model 20 instrument equipped with a 100-ft SE-96 silicone capillary column and with Micro-Tex GC-1600 and Beckman GC-5 instruments with $^1/_8$-in. columns of Carbowax 20 M or SE-30 silicone on 60–80 solid support. Microanalyses were performed by Mr. R. Seab in these laboratories. Nmr spectra were obtained with a Varian Associates HA-60 spectrometer operated by Mr. W. Wegner in these laboratories; all chemical shifts are relative to internal tetramethylsilane (TMS) reference.

***cis,trans*-1,5-Cyclodecadiene** (I) (98% pure) was obtained by reduced pressure distillation of a hydrocarbon mixture (92% I) provided by Columbian Carbon Co. and by cyclooligomerization of 1,3-butadiene and ethylene with nickel bis-1,5-cyclooctadiene catalyst.[4] The infrared spectrum of the diene included absorptions at 10.27 and 14.25 μ, characteristic of *trans* and *cis* C=C, respectively. The nmr spectrum of the diene consisted of a complex multiplet centered at −5.28 ppm (C=CH, area equivalent to 4 H), a broad multiplet centered at −1.93 ppm ($C{=}CCH_2$, 8 H), and a broad multiplet centered at −1.55 ppm ($CH_2CH_2CH_2$, 4 H).

Diimide Reduction.—A stream of air was bubbled vigorously through a mixture of *cis,trans*-1,5-cyclodecadiene (1.5 moles), 85% hydrazine hydrate (7.5 moles), 95% ethyl alcohol (2 l.), and copper sulfate (2 g).[31] The progress of the reduction of the diene was followed by gas chromatography; after 6 hr, the reaction was over 90% complete; after 8 hr, little diene remained and a trace of cyclodecane was detected. The cyclodecene isolated was shown by infrared spectral[32a] and gas chromatographic[32b] analyses to be the *cis* isomer contaminated only with a trace of cyclodecane.

Catalytic Hydrogenation. Hydrogenation of a methanol solution of *cis,trans*-1,5-cyclodecadiene with hydrogen and palladium-on-carbon catalyst in a Parr medium pressure apparatus (40 psig) proceeded readily to give a mixture of *cis*-cyclodecene, *trans*-cyclodecene, and cyclodecane. Gas chromatographic analysis indicated a ratio of *cis–trans* of 49:51.

When a little pyridine (0.5 ml/20 mg of catalyst) was added to the alcoholic solution of diene along with palladium-on-carbon catalyst, no *trans*-cyclodecene was obtained.[15] The product mixture consisted only of *cis*-cyclodecene contaminated with cyclodecane.

Hydroboration.[5b]—A solution of boron trifluoride etherate (9.5 g, 0.067 mole) in diglyme (diethylene glycol dimethyl ether, 25 ml) was added during 1.5 hr to a well-stirred mixture of I (27.2 g, contaminated with some cyclododecatriene), sodium borohydride (1.9 g, 0.05 mole), and diglyme (55 ml) protected by a nitrogen atmosphere. The reaction was carried out at room temperature. After an additional hour of stirring, gas chromatographic analysis indicated that only about two-thirds of the cyclodecadiene had been consumed, so additional sodium borohydride (0.6 g, 0.017 mole) and boron trifluoride etherate (3.2 g, 0.022 mole) in diglyme (10 ml) were added to the mixture. After addition of the boron trifluoride solution was complete, gas chromatographic analysis indicated that very little diene remained in the mixture. Propionic acid (29.5 g, 0.41 mole) was added cautiously, and the mixture was refluxed for 2.5 hr. The mixture was diluted with petroleum ether (bp 60–70°, 300 ml) and washed thoroughly with water (five

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[26] Methoxymercuration has been described as an ionic, *trans* addition (H. J. Lucas, F. R. Hepner, and S. Winstein, *J. Am. Chem. Soc.*, **71**, 3102 (1939)) as a four-centered, *cis* addition (A. Rodgman and G. F Wright, *J. Org. Chem.*, **18**, 1617 (1953)), and as an ionic, *cis* addition (T. B. Traylor and A. W. Baker, *Tetrahedron Letters*, 14 (1959)).

[27] H. C. Brown and P. Geoghegan, Jr., *J. Am. Chem. Soc.*, **89**, 1522 (1967).

[28] H. L. Goering, H. H. Espy, and W. D. Glosson, *ibid.*, **81**, 329 (1959). Stereoisomeric 1-decalols are readily distinguished by the melting points of the alcohols and their *p*-toluenesulfonate derivatives.

[29] (a) C. D. Gutsche and H. H. Peter, *ibid.*, **77**, 5971 (1955); (b) J. M. Conia and F. Rouessac, *Tetrahedron*, **16**, 45 (1961).

[30] (a) W. H. Mueller and P. E. Butler, *J. Am. Chem. Soc.*, **88**, 2866 (1966); (b) see also, N. Kharasch, in "Organic Sulfur Compounds," Vol. I, Kharasch, N., Ed., Pergamon Press Inc., New York, N. Y., 1961, pp 375–396; (c) W. H. Mueller and P. E. Butler, *Chem. Commun.*, 646 (1966).

[31] M. Ohno and M. Okamoro, *Tetrahedron Letters*, 2423 (1964).

[32] (a) Absorption at 14.25 μ for *cis*- and at 10.29 μ for *trans*-cyclodecene. (b) J. G. Traynham, D. B. Stone, and J. L. Couvillion, *J. Org. Chem.*, **32**, 510 (1967).

times) to remove propionic acid and diglyme. The petroleum ether solution was dried and distilled. The hydrocarbon product (19.0 g, about 86% yield), bp 63–66° (6.5 mm), was shown by gas chromatographic analysis to be a mixture of *cis*-cyclodecene (86%), *trans*-cyclodecene (11%), and cyclodecane (3%).

Epoxidation.[5]—A solution of *m*-chloroperoxybenzoic acid[33] (17.2 g, 0.085 mole) in ethyl acetate (60 ml) was added in 30 min to a well-stirred solution of I (13.6 g, 0.1 mole) in ethyl acetate (10 ml). The temperature of the reaction mixture was maintained at about 25° by external cooling. After 5 min more of stirring, the mixture was diluted with petroleum ether (100 ml) and extracted three times with dilute sodium bicarbonate solution. The organic solution was washed with water, dried, and concentrated on a rotary evaporator. The infrared spectrum of the residue (15.2 g) indicated that some ethyl acetate remained in the mixture and that the absorption at 14.25 μ (*cis* C=C) was much stronger than that at 10.29 μ (*trans* C=C). Reduced pressure distillation led to the recovery of some diene (3.3 g) and the isolation of a mixture of monoxides, bp 49–50 (0.5 mm), 10.5 g (91%). Gas chromatographic analysis indicated that the monoxide mixture consisted of 85–90% *trans*-epoxide and 10–15% *cis*-epoxide.

Methyleneation of I was accomplished with methylene iodide and zinc–copper couple (molar equivalents of the three reagents) in anhydrous ethyl ether.[34] After the prescribed work-up,[34] the petroleum ether extract was concentrated on a rotary evaporator. The infrared spectrum of the residue included strong absorption for *cis* C=C, but virtually none for *trans* C=C. Gas chromatography revealed that the methyleneation product produced a single signal peak with a small shoulder (estimation <3%). Distillation at reduced pressure failed to afford pure bicyclo-[8.1.0]undec-5-ene, but gas chromatographic analysis of the distillate fractions indicated that together they contained a 48% yield of the methyleneation product.

Ozonation. A. In Acetic Acid.—Ozone (13 mmoles, about 3% in a stream of oxygen from a Welsbach T-23 ozonator) was passed through a capillary tube into an ice-chilled solution of I (2.5 g, 13 mmoles) in glacial acetic acid (10 ml). The mixture, which became homogeneous during the ozonation, was diluted with water (3 ml), the ozonide was reduced with a slurry of zinc dust in ice water until the solution no longer gave a positive test with starch–iodide paper, and the mixture was extracted with two 30-ml portions of ethyl ether. The combined extract was washed thoroughly with saturated sodium bicarbonate solution, dried over calcium chloride, and concentrated on a rotary evaporator. A portion of the concentrate was treated with alcoholic 2,4-dinitrophenylhydrazinium hydrogen sulfate; the yellow-orange solid which was obtained was recrystallized twice from a mixture of ethyl alcohol and ethyl acetate; it decomposed at 94–103°. The nmr spectrum of a sample of the solid in dimethyl sulfoxide-d_6 (DMSO-d_6) included a multiplet centered at −5.45 ppm (C=CH, area equivalent to 2 H) which virtually duplicated the C=CH signal from oleic acid but was quite different from the broad, unresolved signal from eladic acid (DMSO-d_6 solutions of the acids).[35] We therefore assign *cis* geometry to the olefinic linkage remaining in the ozonation product.

B. In Carbon Tetrachloride.—Ozone (73 mmoles, approximately 3% in O_2) was passed into a solution of I (10 g, 73 mmoles) in carbon tetrachloride (80 ml) at −45°. The mixture, which contained some suspended solid, was then allowed to warm to room temperature, solvent was removed at reduced pressure, and the remaining spongy solid was washed thoroughly with ether. After being dried over phosphorus pentoxide in a drying pistle at 65°, the solid melted at 114–116° with gas evolution and darkening: $\lambda_{\max\,(\mathrm{KBr})}$ 2.97 (s), 3.72 (w), 5.84 (s), 6.10 (w), and 9.02 (br) μ. The solid was insoluble in ether, benzene, carbon tetrachloride, chloroform, ethanol, methanol, water, and petroleum ether.

Anal. Calcd for $C_{30}H_{50}O_{10}$: C, 63.65; H, 8.77. Found: C, 63.65; H, 8.72.

C. In Chloroform.—When chloroform was substituted for carbon tetrachloride in B above, the product was a very viscous liquid, whose infrared spectrum was virtually a duplicate of that for the solid obtained in B.

Anal. Calcd for $C_{20}H_{34}O_7$: C, 62.17; H, 8.81. Found: C, 61.53; H, 8.73.

Acetoxylation.—A solution of I (10.0 g, 73 mmoles) in acetic acid (100 ml) was added to a stirred slurry of lead tetraacetate (32.4 g, 73 mmoles) in acetic acid (100 ml) during 1.5 hr. The mixture was kept at about 18° with a water bath. After complete addition of the diene solution, the mixture, which had become homogeneous, was stirred for 2 hr longer, diluted with water (400 ml), and extracted with three 150-ml portions of petroleum ether. The combined extract was washed with saturated sodium bicarbonate solution, dried over Drierite, and concentrated on a rotary evaporator. The residual liquid showed infrared absorptions at 5.80 and 8.08 μ, indicative of acetoxy groups. Distillation gave two main fractions: (1) 3.1 g, bp 75.5–83° (0.7–0.9 mm); and (2) 8.8 g, bp 123–124.5° (0.9 mm). Fraction 1 reduced aqueous permanganate and gave nmr signals for ethylenic protons (area equivalent to 1 H); fraction 2 did neither. Both fractions gave infrared (5.80 and 8.08 μ) and nmr (−1.95 ppm, sharp singlet) absorptions for acetoxy groups. Gas chromatography (SE-30 silicone rubber, 6 ft × $^1/_8$ in. column) at different temperatures (145–225°) demonstrated that the single component fraction 2 could be pyrolyzed to the two more volatile components constituting fraction 1. A portion of 2 crystallized from aqueous acetone melted at 66–68°; mixture melting point with authentic *trans*-1,4-diacetoxy-*cis*-decalin was 66–68°. Gas chromatography of an acetone solution of the solid product at column temperatures above 145° reproduced the component peaks obtained with both of the distillate fractions.

When the acetoxylation was carried out in an nmr tube (0.5 mmole each of I and lead tetraacetate, 0.5 ml of acetic acid), the nmr spectrum obtained immediately after complete solution (15 min) was devoid of signals attributable to C=CH.

A sample of *cis*-decalin-*trans*-1,4-diol[21] was esterified in refluxing acetic anhydride. The viscous liquid remaining after removal of extracting solvent gave an infrared spectrum virtually identical with the one from distillate fraction 2 above. The product crystallized after several days and, after recrystallization from pentane, melted at 65–66° (lit.[19] mp 69–70°). The infrared and nmr spectra for this sample of *trans*-1,4-diacetoxy-*cis*-decalin and those from acetoxylation of I were identical.

Addition of Bromine. A. In Acetic Acid.—A solution of bromine (12.0 g, 75 mmoles) in glacial acetic acid (100 ml) was added slowly to a stirred solution of I (10.0 g, 74 mmoles) in glacial acetic acid (50 ml) at room temperature in the dark. After the solution had been stirred overnight and treated with saturated sodium bisulfite solution to remove excess bromine, it was diluted with water (200 ml) and extracted with two 100-ml portions of petroleum ether. The combined extract was washed three times with saturated sodium bicarbonate solution, dried over calcium chloride, and concentrated on a rotary evaporator. The brown liquid remaining (18.7 g) showed infrared absorption at 5.80 (s), 8.10 (s), 9.60 (m), and 9.78 (ms) μ. The nmr spectrum included a sharp singlet (−1.94 ppm, $\mathrm{OCOC}H_3$) superimposed on a broad multiplet (*cis*-decalin framework) but no C=CH absorption. Upon storage in a freezer for 2 days, the liquid product partially crystallized. The solid was recrystallized from 95% ethyl alcohol: mp 96.5–99°; $\lambda_{\max\,(\mathrm{KBr})}$ 5.79 (s), 8.10 (s), 9.54 (m), 9.72 (s), and 13.92 (m) μ. The nmr spectrum consisted of a broad multiplet at −4.80 ppm (*H*COAc, 1 H), another at −4.22 ppm (*H*CBr, 1 H), and a sharp singlet at −1.96 ppm ($\mathrm{OCOC}H_3$) on a broad multiplet at −2.5 to −1.0 ppm (*cis*-decalin framework, 18 H together). The sample gave a precipitate with alcoholic silver nitrate.

Anal. Calcd for $C_{12}H_{19}BrO_2$: C, 52.36; H, 6.91. Found: C, 52.37; H, 7.01.

A portion of the solid 1-acetoxy-4-bromo-*cis*-decalin (1.4 mmoles) was reduced with lithium aluminum hydride (1.3 mmoles) in refluxing ether solution (20 ml). Conventional work-up gave a solid bromo alcohol which was sublimed at 90° (0.14 mm), mp 122–124°. The infrared spectrum of the solid included strong absorption for OH but none for carbonyl; its nmr was very similar to that of authentic *cis*-decalin-*trans*-1,4-diol.

Anal. Calcd for $C_{10}H_{17}BrO$: C, 51.50; H, 7.29. Found: C, 51.54; H, 7.51.

B. In Carbon Tetrachloride.—Bromine was added from a capillary pipet to a solution of I (1.3 mmoles) in an equal volume of carbon tetrachloride in an nmr tube until the signal for C=CH in the nmr spectrum was absent. The spectrum then con-

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[33] Obtained from FMC Corp and used as supplied; assay, 85% peroxy acid.

[34] R. D. Smith and H. E. Simmons, *Org. Syn.*, **41**, 72 (1961).

[35] Six other multiplets and a singlet which completed the nmr spectrum were assigned by comparison of this spectrum with one obtained for butyraldehyde 2,4-dinitrophenylhydrazone in DMSO-d_6. For a complete description, see ref 1b (G. R. Franzen).

sisted of a broad multiplet at −4.38 ppm (*H*CBr, 2 H) and a broad multiplet characterisic of the *cis*-decalin framework (14 H).

Methoxymercuration.—A mixture of I (0.80 mmole), methanol (approximately 0.3 ml), and mercury(II) acetate (0.80 mmole) immediately became homogeneous when shaken in an nmr tube. The nmr spectrum consisted of a broad singlet at −5.30 ppm (MeO*H* and AcO*H* exchanging), a broad singlet at −3.30 ppm (OC*H*$_3$), a sharp singlet at −1.95 ppm (OCOC*H*$_3$), and broad, overlapping multiplets at −2.5 to −1.1 ppm (*cis*-decalin framework). The spectrum was devoid of signals for C=CH.

Oxymercuration–Demercuration[27] of I.—When 10 mmoles of I was mixed with a solution of mercury(II) acetate (10 mmoles) in aqueous tetrahydrofuran (10 ml of each solvent), the yellow color of the mixture disappeared within 30 sec. After reduction with sodium borohyride and extraction with ether, the reaction product mixture was shown by gas chromatography (10 ft × $^1/_8$ in. Carbowax 20 M column, 160°) to consist of two components in proportions 17:83 (minor component, shorter retention time). The major component was isolated (60% yield) by distillation and recrystallization and was identified as *cis,cis*-1-decalol,[28] mp 90–91.5°. Its *p*-toluenesulfonate derivative[28,36] melted at 89–89.5° (lit.[28] mp 88–88.5°), and its 3,5-dinitrobenzoate derivative at 122.5–124° (lit.[37] 123.8°). When a small sample of the alcohol mixture in acetone solution was oxidized with chromic acid,[38] gas chromatography (Carbowax 20 M and silicone SE-30 columns, 160°) of the product mixture revealed that both alcohols had been converted into a single ketone[39] identified as *cis*-1-decalone[40−43] by its 2,4-dinitrophenylhydrazone derivative (mp 170.5–172.5°; lit.[29a] mp 176–177°).

Addition of Methanesulfenyl Chloride.—A solution of methanesulfenyl chloride was prepared by adding chlorine (20 mmoles) to dimethyl disulfide (20 mmoles) in chloroform (1 ml) at −10° and then diluting the mixture to 5.0 ml with chloroform.[44] When a portion of that solution (0.2 ml, 1.6 mmoles) was added to a solution of I (1.4 mmoles) in an equal volume of chloroform in an nmr tube at 25°, an exothermic reaction took place. The nmr spectrum of the mixture was devoid of C=CH signals.

Registry No.—I, 1124-78-3; acetic aeid, 64-19-7; carbon tetrachloride, 56-23-5; chloroform, 67-66-3; 1-acetoxy-4-bromo-*cis*-decalin, 13976-54-0; bromo alcohol $C_{10}H_{17}OBr$, 13976-55-1.

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[36] A. C. Cope, R. J. Cotter, and G. G. Roller, *J. Am. Chem. Soc.*, **77**, 3598 (1955).

[37] W. Hückel, D. Mancher, O. Fechtig, J. Kurz, M. Heinzel, and A. Hubele, *Ann.*, **645**, 115 (1961).

[38] K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, **39** (1946).

[39] *cis*- and *trans*-1-decalones are reported to be separated by gas chromatography on a 1.5-m silicone column at 250°.[29b] We find that the *trans* ketone has a retention time about 1 min shorter than that of the *cis* isomer on a 10 ft × $^1/_8$ in. Carbowax 20 M column at 160°.

[40] *cis*-1-Decalone is easily converted to *trans*-1-decalone,[29a] and preparation of derivatives certain to be those of the *cis* isomer rather than the trans one is difficult. For example, *cis*-1-decalone 2,4-dinitrophenylhydrazone has been (mistakenly) reported to melt at 225°,[41] approximately the melting point of the *trans* derivative,[42] and two different preparations by us of the 2,4-dinitrophenylhydrazone from the same sample of *cis*-1-decalone (infrared spectral identification[29]) gave material melting after recrystallization at 159.5–162 and 216–219°, respectively. Repeated recrystallizations of the lower melting product did not raise the melting point to 176°, and sometimes led to a lower melting point. The isomerization of the ketone occurs much more easily than we had expected. When an ether solution of *cis*-1-decalone (infrared absorption at 938 cm^{-1} but not at 906 cm^{-1} [29]) extarcted from the chromic acid oxidation mixture was mixed with calcium chloride and neglected for 10 days, the ketone was nearly completely isomerized to *trans*-1-decalone (infrared absorption at 906 cm^{-1} but not at 938 cm^{-1} [29]). The 2,4-dinitrophenylhydrazone derivative of the *trans* ketone melted at 230–231° (lit. 225.2–227.8,[42a] 234–235,[42b] and 238–239°[29a]), and the semicarbazone derivative melted at 224–226.5° (lit.[43] mp 227–229°). Identification of this isomerization product actually reinforces the identification of the initial oxidation product, *cis*-1-decalone.

[41] I. N. Nazarov, L. A. Kazitsyna, and I. I. Zaretskaya, *Zh. Obschch. Khim.*, **27**, 606 (1957); *Chem. Abstr.*, **51**, 1638*h* (1957).

[42] (a) W. G. Dauben and R. C. Tweit, *J. Am. Chem. Soc.*, **76**, 3197 (1954); (b) A. L. Wilds and N. A. Nelson, *ibid.*, **75**, 5360 (1953).

[43] H. Muele and Ch. Tamm, *Helv. Chim. Acta*, **45**, 1475 (1962).

[44] The chlorinolysis of dimethyl disulfide at −78° without solvent was described by I. B. Douglas and D. A. Koop, *J. Org. Chem.*, **27**, 1398 (1962).

Enamines. II. Factors Determining the Structure of Enamines of 2-Substituted Ketones[1]

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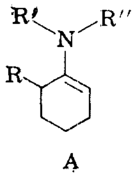
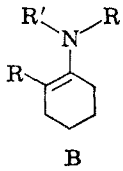
Enamines derived from 2-substituted ketones can and do exist as a mixture of the more and less substituted double-bond isomers. The isomer ratio is determined by various steric and electronic factors which affect the overlap between the nitrogen lone pair and the double bond of the enamine. In general, the greater the overlap, the greater the proportion of less substituted double-bond isomer. In addition, the position of the vinyl proton in the nmr is a reflection of the amount of overlap. Evidence supporting these proposals is presented.

It was previously shown by us[2] that enamines of 2-substituted cyclohexanones do not exist solely as the less substituted double-bond isomer A as was commonly believed,[3] but as a mixture of the two isomers A and B



A



B

with the R groups determining the composition of the mixture. Specifically we proposed that overlap of the lone pair of electrons on nitrogen with the π electrons of the double bond is appreciable with pyrrolidine, but less so with other amines. We further stated that the position of the vinyl hydrogen absorption in the nmr spectrum was an indication of the amount of overlap.

We here offer evidence that the ratio of isomers will be determined by a balance of factors which affect the conjugation between the nitrogen lone pair and the double bond of an enamine. Specifically, within a given series, as the amount of overlap increases, the proportion of less substituted double-bond isomer A increases.

In addition, we give further proof that the position of the vinyl proton reflects the amount of overlap, *i.e.*,

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[1] Presented at the 153rd National Meeting of The American Chemical Society, Miami, Beach, Fla., April 9–14, 1967, Abstracts, p 80-O.

[2] Enamines I: W. D. Gurowitz and M. A. Joseph, *Tetrahedron Letters*, 4422 (1965).

[3] See, for example (a) G. Stork, *et al.*, *J. Am. Chem. Soc.*, **85**, 207 (1963); (b) H. A. P. de Jongh, *J. Org. Chem.*, **30**, 1409 (1965); L. F. Fieser and M. Fieser, "Current Topics in Organic Chemistry," Vol. 1, Reinhold Publishing Corp., New York, N. Y., 1964, p 25; H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, N. Y., 1965, p 197; J. Szmuszkovicz, *Advan. Org. Chem.*, **4**, 21 (1963); K. Blaha and O. Cervinka, *Advan. Heterocyclic Chem.*, **6**, 167 (1966).