respectively, formed in the reaction of 4-methylcyclohexene with peracid.[26] As a control, a known mixture of the two isomeric ketones was subjected to the oxidizing solution for a comparable period of time; the recovered mixtures had the same composition as the starting material.

Epoxides of 3-Methylcyclohexene.—Mixed hydride reduction of this epoxide mixtures gave all four possible alcohol products; *cis*-2- (53%), *cis*-3- (4%), *trans*-3- (28%), and *trans*-2-methylcyclohexanol (15%). Lithium aluminum hydride alone gave comparable results. In view of the failure of the mixed reagent to give cleanly axial products, it is not possible to assign unequivocably the precursor epoxide of each alcohol.[30] However, the preponderance of *cis* alcohols suggests strongly that *cis* epoxide is the major product of the peracid reaction.

Kinetic Procedure.—Rates were determined by following loss of peracid iodometrically. Aliquots of ethereal solution were removed periodically from tightly stoppered flasks held in a constant temperature bath at 25.0°. Good second-order plots were obtained through at least 80% of reaction.

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[30] Assuming only diaxial opening with the mixed reagent, the present data suggest that axial alkyl conformations are contributing appreciably to the reduction transition states.

The Simmons–Smith Reaction of *trans,trans,cis*-1,5,9-Cyclododecatriene

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The title reaction was carried out with varying mole ratios of methylene iodide to obtain mono- (II), bis- (III and IV), and triscyclopropane derivatives (V). The Simmons–Smith reagent attacks preferentially one of the *trans* olefinic bonds of the triene I and then the *cis* double bond of the diene II. Reductive cleavage of the cyclopropane ring of these products (II and V) under various conditions failed to afford the corresponding ring-enlargement products.

As a step in attempted ring-enlargement of *trans,trans,cis*-1,5,9-cyclododecatriene (I)[1] the Simmons–Smith reaction[2] of this triene has been examined and the results, as summarized in Table I, are discussed in the present paper.

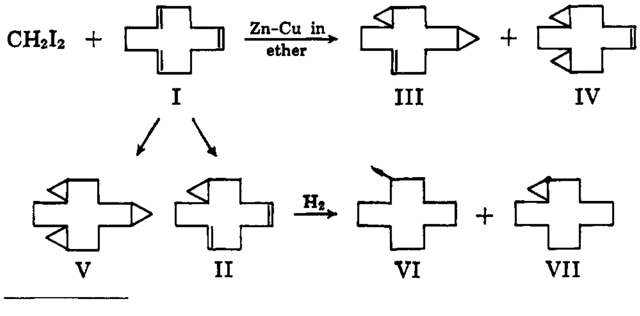
TABLE I

MOLE RATIOS OF REAGENTS AND COMPOSITION OF PRODUCTS

Methylene iodide to I, mole ratio	% yield[a]		
	II[b]	III and IV[c]	V
1	58	8	Trace
2	25	30	7
10	0	0	54[d]

[a] The yields were calculated based on the weight of isolated mixture and peak areas in the analytical gas chromatogram. [b] The fraction contains less than 5% of an isomer. See the text. [c] This is a mixture of III and IV in 4:1 mole ratio, respectively. [d] A single peak.

The methylenation was carried out in the standard way[2] with varying mole ratios of methylene iodide to I and the products were subjected to analytical gas chromatography. Each component was isolated by preparative gas chromatography and information concerning the sites of attack during methylenation was obtained by examination of the infrared spectra.



The monocyclopropane fraction (II) was practically homogeneous upon gas chromatography, although a small shoulder (less than 5% in its area) appeared at the high retention time side of the peak. The infrared spectrum showed both the *trans* and *cis* double bond absorptions at 960 and 700 cm.$^{-1}$, respectively. Therefore, II is formed by the attack of one of the *trans* bonds of the triene I. The minor component would probably have arisen from the attack of the *cis* bond of I, but attempted isolation of this isomer failed. Hydrogenation of II with 10% palladium-on-charcoal catalyst gave a mixture of methylcyclododecane (VI) and *trans*-bicyclo[10.1.0]tridecane (VII), VII being converted into VI by exhaustive hydrogenation. The *trans*-bicyclotridecane (VII) thus obtained was clearly distinguished from the authentic *cis* isomer which was prepared by the Simmons–Smith reaction of *cis*-cyclododecene.[3] The differentiation was made on the basis of the retention times in gas chromatography and comparison of the infrared spectra.

With 2 moles of the Simmons–Smith reagent a mixture of biscyclopropane derivatives III and IV was obtained as a major fraction, which gave two peaks in the ratio of 4:1 upon gas chromatography. Methylenation of the pure monoadduct (II) also gave a product which showed an identical gas chromatogram. The substance giving the predominant peak (III) was preparatively isolated and its infrared spectrum was examined. No *cis* absorption was detected in the neighborhood of 700 cm.$^{-1}$, while the *trans* absorption at 960 cm.$^{-1}$ and the cyclopropane absorption at 1020 cm.$^{-1}$ were clearly recognized. The substance giving the minor peak could not be isolated pure, but the presence of *cis* absorption at 700 cm.$^{-1}$ in the crude biscyclopropane fraction indicated that this was very probably the isomer IV. Accordingly, the further attack of II by the Simmons–Smith reagent takes place at the *cis* bond rather than at the *trans* bond. The selectivity (4:1), however, is not so sharp as the attack of the original triene I.

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[1] G. Wilke, *Angew. Chem.*, **75**, 10 (1963).

[2] (a) E. P. Blanchard and H. E. Simmons, *J. Am. Chem. Soc.*, **86**, 1337 (1964); (b) H. E. Simmons, E. P. Blanchard, and R. D. Smith, *ibid.*, **86**, 1347 (1964).

[3] For the preparation of cyclododecene, see H. Nozaki and R. Noyori, *J. Org. Chem.*, **30**, 1652 (1965).

The triscyclopropane fraction was completely homogeneous upon gas chromatography. Two cyclopropane rings must be *trans* fused and the remaining one *cis* fused. Attempted hydrogenolysis of the triscyclopropane V under chemical and catalytic conditions failed to afford cyclopentadecane or related 15-membered ring compounds. Instead, however, the appearance of methyl absorption at 1380 cm.$^{-1}$ in the reduction products indicated cleavage of the cyclopropane ring without ring enlargement.

No preferential attack of the three double bonds of I has been recorded in the *trans* additions of halogen,[4] hydrogen chloride,[5] acetic acid,[5] *etc.*, but the *cis* additions[6] generally occur with predominant attack at *trans* bonds. Thus, diimide reduction[3,7] of I takes place at the two *trans* bonds only, affording *cis*-cyclododecene exclusively. Oxidation of I with osmium tetroxide[8] proceeds similarly even in the second attack, or, in the reaction of the *trans,cis*-cyclododecadiene system, the *trans* double bond is attacked. In contrast to these *cis* additions affording monocyclic compounds, the Simmons–Smith reaction described above is closely analogous to the epoxidation of I.[4b] Both reactions occur initially at one of the *trans* bonds of I and then preferentially at the *cis* bond of the *trans,cis*-cyclododecadiene ring of the bicyclic system.

This difference in the selectivity of *cis* additions prompted examination of the diimide reduction of the monocyclopropane compound II. It was found to be completely inert to this reaction under conditions sufficient to convert I into *cis*-cyclododecene. It is concluded that the reactivity of the two double bonds in the *trans,cis*-cyclododecadiene system is greatly influenced by the presence of a fused three-membered ring, the *trans* double bond being rendered less reactive to reagents adding in the *cis* manner.

Experimental

All temperatures were uncorrected. The microanalyses were performed at the Elemental Analyses Center of Kyôto University.

Methylenation of *trans,trans,cis*-1,5,9-Cyclododecatriene.—To a suspension of 6.5 g. (0.1 g.-atom) of zinc–copper couple[9] in 50 ml. of dry ether a few crystals of iodine were added and the mixture was stirred until the brown color disappeared. To this mixture a solution of 16.2 g. (0.1 mole) of *trans,trans,cis*-1,5,9-cyclododecatriene (I)[10] in 26.8 g. (0.1 mole) of freshly distilled methylene iodide was added in one portion and the reaction mixture was stirred and refluxed for 15 hr. After cooling, the inorganic precipitates were filtered off and washed with ether thoroughly. The combined ether soluion was washed with saturated ammonium chloride solution, sodium bicarbonate solution, and water and then dried over anhydrous magnesium sulfate. Distillation *in vacuo* gave 15.1 g. of colorless oil boiling at 105–135° (10 mm.), which was shown by gas chromatography (high vacuum silicone grease, He, 180°) to consist of unchanged cyclododecatriene (I), mono- (II), bis- (III and IV), and a trace of trismethylenated products (V). Yields of mono- and diadducts based on consumed I were 58 and 8%, respectively. *trans*-Bicyclo[10.1.0]-trideca-*trans*-4,*cis*-8-diene (II), the chief component, was separated by preparative gas chromatography and was purified by distillation: b.p. 112–114° (10 mm.); n^{20}D 1.5038; infrared absorptions (neat), 1020 (cyclopropane ring), 960 (*trans* olefin), and 700 cm.$^{-1}$ (*cis* olefin). This sample was practically homogeneous on gas chromatography (high vacuum silicone or PEG–$AgNO_3$) and was shown to be contaminated by less than 5% of another isomer.

Anal. Calcd. for $C_{13}H_{20}$: C, 88.56; H, 11.44. Found: C, 88.27; H, 11.64.

Methylenation of I (0.1 mole) with 2 equiv. of methylene iodide and zinc–copper couple afforded 12.6 g. of a volatile fraction boiling below 110° (3 mm.). Yields of mono- (II), di- (III and IV), and triadducts (V) were 25, 30, and 7%, respectively. Isolation of the diadduct fraction by preparative gas chromatography (high vacuum silicone), followed by distillation *in vacuo*, gave an analytical sample, b.p. 95–97° (3 mm.), n^{20}D 1.5022.

Anal. Calcd. for $C_{14}H_{22}$: C, 88.35; H, 11.65. Found: C, 88.59; H, 11.39.

Analytical gas chromatography of this fraction showed two peaks in the ratio of 1:4 (relative retention times, 1.00 and 1.10, respectively). The substance giving the major peak was isolated pure by gas chromatography. Strong bands at 1020 (cyclopropane ring) and 960 cm.$^{-1}$ (*trans* olefin) and the absence of *cis* olefin absorption indicated this to be tricyclo[11.1.0(*trans*).0^{4,6}(*cis*)]tetradec-*trans*-9-ene (III). Although the minor component could not be isolated, the absorption at 700 cm.$^{-1}$ of the original mixture indicating the presence of a *cis* double bond suggested that this component was probably tricyclo[11.1.0(*trans*).0^{4,6}(*trans*)]tetradec-*cis*-9-ene (IV).

Reaction with a large excess of methylene iodide and zinc–copper couple (mole ratio, 10) and 0.1 mole of I gave the trismethylenated product, tetracyclo[12.1.0(*trans*).0^{4,6}(*trans*).0^{9,11}(*cis*)]pentadecane (V), in 54% yield, b.p. 80–84° (1 mm.), n^{20}D 1.4855. This was shown to be homogeneous on gas chromatography; infrared showed absorption (neat) at 1020 cm.$^{-1}$ (cyclopropane ring) and no band due to olefinic linkage.

Anal. Calcd. for $C_{15}H_{24}$: C, 88.16; H, 11.84. Found: C, 88.40; H, 12.09.

No appreciable amount of mono- or diadduct was detected from the reaction product.

***cis*-Bicyclo[10.1.0]tridecane.**—Methylenation of *cis*-cyclododecene[3] (2.5 g., 0.015 mole) with 6.0 g. (0.022 mole) of methylene iodide and 2.0 g. (0.031 g.-atom) of zinc–copper couple in 10 ml. of dry ether gave 2.0 g. (74% yield) of *cis*-bicyclo[10.1.0]tridecane, b.p. 80–82° (3 mm.), n^{20}D 1.4855, infrared absorption (neat) 1020 cm.$^{-1}$ (cyclopropane ring).

Anal. Calcd. for $C_{13}H_{24}$: C, 86.59; H, 13.41. Found: C, 86.82; H, 13.24.

Hydrogenation of *trans*-Bicyclo[10.1.0]trideca-*trans*-4,*cis*-8-diene (II).—Hydrogenation of the bicyclic diene II with 10% palladium-on-charcoal catalyst at ordinary pressure afforded a mixture of methylcyclododecane (VI) and *trans*-bicyclo[10.1.0]-tricane (VII), whose infrared spectrum showed strong bands at 1380 (methyl) and 1020 cm.$^{-1}$ (cyclopropane ring) and whose gas chromatogram consisted of two peaks with relative retention times 1.00 and 1.10, respectively. The latter component was clearly distinguished from the above-mentioned *cis* isomer (retention time 1.29). Exhaustive hydrogenation afforded methylcyclododecane (VI) quantitatively, b.p. 77–79° (3 mm.), n^{20}D 1.4830.

Anal. Calcd. for $C_{13}H_{26}$: C, 85.63; H, 14.37. Found: C, 85.80; H, 14.44.

Hydrogenation of the diadduct or triadduct gave complex mixtures.

Attempted diimide reduction of II by bubbling an air stream into an ethanolic solution of the bicyclic diene II and hydrazine hydrate containing a catalytic amount of cupric acetate for 30 hr. at room temperature resulted in total recovery of the unchanged II.

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(10) Supplied by M. H. Takahasi, Government Industrial Research Institute, Osaka, Japan. The sample contained 97.4% of the *trans,trans,cis* isomer, the rest being all *trans* isomer (2.4%) and other impurities (0.2%).