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The Reactions of *cis, trans, trans*-1, 5, 9-Cyclododecatriene. IV.[1] Selective Reactions with *cis*-Addition Reagents

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The addition reactions of *cis, trans, trans*-1, 5, 9-cyclododecatriene with *cis*-addition reagents, such as osmium tetroxide, potassium permanganate, diimide, and nitrosyl chloride, have been investigated. It has been shown that the first attack of each reagent preferentially takes place at one of the *trans* double bonds. The reactions with osmium tetroxide and potassium permanganate at room temperature afforded *cis*-5, *trans*-9-cyclododecadiene-*trans*-1, 2-diol in 89 and 59% yields respectively. The glycol was then further oxidized with osmium tetroxide into *cis*-9-cyclododecene-1, 2, 5, 6-tetrol in a 60% yield. The reduction of the cyclotriene with diimide, generated in situ by the oxidation of hydrazine, afforded *cis*-cyclododecene in 60—82% yields. The addition of nitrosyl chloride in the presence of hydrochloric acid afforded 2-chlorocyclododecadienone oxime in a quantitative yield; this was then reduced into cyclododecanone oxime, obtained in a quantitative yield, by catalytic reduction with palladium-charcoal.

The discovery of an elegant synthesis of *cis, trans, trans*-1, 5, 9-cyclododecatriene (I) by means of the cyclotrimerization of butadiene with Ziegler catalysts[2,3] has prompted investigations into the reactions of this cyclotriene; the results of these investigations are summarized in Table I. On the basis of our own findings and these previous results, we would like to point out that the competitive reactivities between the *cis* and *trans* double bonds are closely connected with the mode of the addition of reagents.

The oxidation of *cis, trans, trans*-1, 5, 9-cyclododecatriene with osmium tetroxide or potassium permanganate showed a high selectivity and afforded *cis*-5, *trans*-9-cyclododecadiene-*trans*-1, 2-diol; the results are shown in the following scheme:

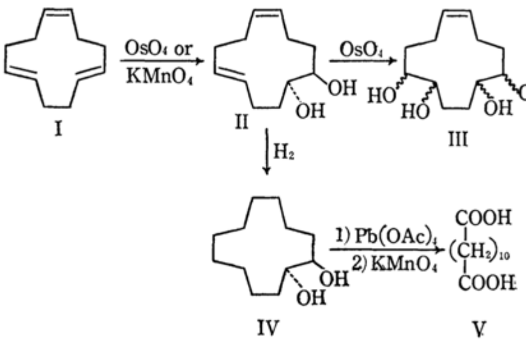

TABLE I. REACTIONS WITH VARIOUS REAGENTS

Reagent	Mole	Product	Addition mechanism	Double bond preferentially attacked	Yield, %	Ref.
Br_2	1	1-Bromocyclododecatriene Tetrabromocyclododecene	*trans*	no selectivity	61 20—30	7
Br_2	2	Tetrabromocyclododecene	*trans*	*cis* and *trans*	20—40	5, 7
Cl_2	1	Dichlorocyclododecadiene	*trans*	no selectivity	70	7
$PhCO_3H$	1	Monoepoxide	*cis*	*trans*	80—90	4, 5a
$PhCO_3H$	2	Diepoxide	*cis*	*trans* and *cis*	80	4, 5a
H_2O_2-HCO_2H	1	Monoepoxide	*cis*	*trans*	76	5b
Et_2BH	3	$(C_{12}H_{21})(BEt_2)_3$	*cis*	*	80	6
$HCl/FeCl_3$	Excess	Mono- and dichlorides	*trans*	no selectivity	20—40	8
$AcOH/BF_3$	Excess	Monoacetate	*trans*	no selectivity	50	8

* It was observed that the *trans* double bond reacted faster than the *cis* one.

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[1] Part III of this series: M. Ohno, M. Okamoto and N. Naruse, *Tetrahedron Letters*, in press (1965). Presented at the 15th Symposium on Organic Reaction Mechanisms of the Chemical Society of Japan, Nagoya, October, 1964.

[2] G. Wilke, *Angew. Chem.*, **69**, 97 (1957).

[3] G. Wilke, ibid., **75**, 10 (1963).

[4] G. Wilke, *J. Polymer Sci.*, **38**, 45 (1959).

[5] a) L. I. Zakharkin and V. V. Korneva, *Dokl. Akad. Nauk S. S. S. R.*, **132**, 1078 (1960); b) H. Takahashi and M. Yamaguchi, This Bulletin, **36**, 1390 (1963).

[6] R. Köster and G. Griaznov, *Angew. Chem.*, **73**, 171 (1961).

[7] H. Takahashi and M. Yamaguchi, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), **83**, 1042 (1962).

[8] L. I. Zakharkin, V. V. Korneva and A. V. Iogansen, *Dokl. Akad. Nauk S. S. S. R.*, **138**, 378 (1961).

cis, trans, trans-1, 5, 9-Cyclododecatriene in aqueous acetone was treated with a one-mole equivalent of potassium permanganate with stirring while being kept at 20°C. A colorless crystalline material, m. p. 168—169°C, was batined in a 59% yield and was proved to be *cis*-5, *trans*-9-cyclododecadiene-*trans*-1, 2-diol (II) by an elemental analysis of it and a study of its infrared spectrum. The infrared spectrum showed that the absorption intensity characteristic of the *trans* double bond at 980 cm^{-1} decreased, while that of the *cis* double bond at 707 cm^{-1} remained unchanged, showing that only one of the *trans* double bonds was subjected to the oxidation. The glycol was quantitatively converted into known cyclododecane-*trans*-1, 2-diol⁹⁾ (IV), m. p. 102—103°C, by catalytic hydrogenation; in turn this was converted into known dodecanedioic acid¹⁰⁾ (V) oxidation with lead tetraacetate and then with potassium permanganate. The same *cis*-5, *trans*-9-cyclododecadiene-*trans*-1, 2-diol was also obtained in a 89% yield from a reaction with a one-mole equivalent of osmium tetroxide at room temperature.

The further oxidation of *cis*-5, *trans*-9-cyclododecadiene-1, 2-diol with osmium tetroxide gave *cis*-9-cyclododecane-1, 2, 5, 6-tetrol (III), m. p. 212—214°C, in a 60% yield. The infrared spectrum showed only an absorption characteristic of the *cis* double bond at 707 cm^{-1}; the catalytic hydrogenation of the unsaturated tetrol yielded cyclododecane-1, 2, 5, 6-tetrol, showing no infrared absorption at 707 cm^{-1}.

Clearly, the first attack by such reagents takes place at one of the *trans* double bonds, and there is difference enough in reactivity between the *cis* and *trans* double bonds to control the product.

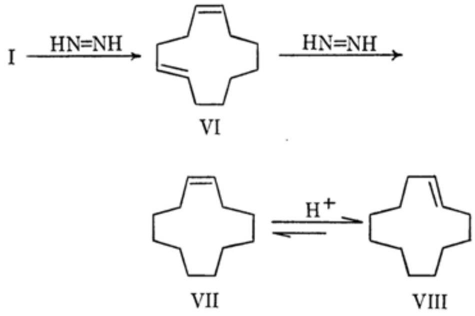
The above oxidation provides a simple method of preparing cyclododecane-*trans*-1, 2-diol, which has previously been obtained by a reaction of *trans*-cyclododecene with osmium tetroxide.⁹⁾

Next, the reduction of *cis, trans, trans*-1, 5, 9-cyclododecatriene with diimide has been investigated in order to clarify which double bond of I is more easily reduced with diimide. As for other olefins, Hünig¹¹⁾ showed that fumaric acid is more rapidly reduced than maleic acid with diimide, although Aylward¹²⁾ showed that elaidic acid is more slowly reduced than oleic acid.

cis, trans, trans-1, 5, 9-Cyclododecatriene dissolved in ethanol was treated with a large excess of hydrazine hydrate in the presence of a catalytic amount of cupric sulfate with a vigorous bubbling-in of air and with vigorous stirring for 24—48 hr. The reaction was found to be highly exothermic. Aliquots of the reaction mixture were subjected to spectroscopic and vapor-phase chromatographic analyses at intervals.

Their infrared spectra showed that only the absorption intensity at 980 cm^{-1} for the *trans* double bond decreased; that at 707 cm^{-1} for the *cis* double bond remained unchanged during the reaction.

Vapor-phase chromatography showed the presence of three components. On the basis of their retention times, two of them were confirmed to be the starting material and *cis*-cyclododecene (VII); another fraction was attributed to *cis, trans*-1, 5-cyclododecadiene (VI). No detectable amount of *trans*-cyclododecene was identified. The reaction was continued until the absorption band at 980 cm^{-1} essentially disappeared, affording a colorless liquid, b. p. 64—65°C/1.0 mmHg, in 60—82% yields from the reaction product. Vapor-phase chromatography using PEG 6000 showed that the liquid was 90—95% *cis*-cyclododecene (VII) and 5—10% cyclododecane. Pure *cis*-cyclododecene was esaily obtained by preparative gas chromatography; its infrared spectrum is completely identical with that of an authentic sample.⁹⁾ The above reactions are shown in the following scheme:



On the other hand, when the cyclododecene was subjected to equlibration by Cope's method,¹³⁾ it afforded a mixture of *trans*-cyclododecene (VIII) and *cis*-cyclododecene (VII) in a ratio of about 2 to 1.

Therefore, the attack by diimide takes palce more easily at the *trans* double bonds, and the reduction presents a simple and valuable method of synthesizing *cis*-cyclododecene, which has previously been prepared by a tedious method.⁹⁾

Finally, the reaction of the cyclododecatriene with nitrosyl chloride was studied. The addition of one mole equivalent of nitrosyl chloride in the presence of hydrochloric acid to *cis, trans, trans*-1, 5, 9-cyclododecatriene (I), in either methylene chloride at −10°C or trichloroethylene at 10°C, was found to be exothermic and to provide 2-chlorocyclododecadienone oxime in nearly quantitative yields. It melted at 110—115°C, even after several recrystallizations from ligroin, and it was easily

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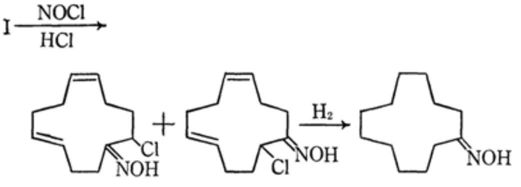
9) V. Prelog and M. Speck, *Helv. Chim. Acta*, **38**, 1786 (1955).
10) J. Walker, *J. Chem. Soc.*, **1940**, 1304.
11) S. Hünig and H. R. Müller, *Angew. Chem.*, **74**, 215 (1962).
12) F. Aylward and M. Sawistowska, *Chem. & Ind.*, **1962**, 484.
13) A. C. Cope, P. T. Moore and W. R. Moore, *J. Am. Chem. Soc.*, **82**, 1744 (1960).

TABLE II. REACTIONS WITH *cis*-ADDITION REAGENTS

Reagent	Mole	Product	Double bond preferentially attacked	Yield, %
OsO_4	1	*cis*-5, *trans*-9-Cyclododecadiene-*trans*-1, 2-diol (II)	*trans*	89
OsO_4	2	*cis*-9-Cyclododecene-1, 2, 5, 6-tetrol (III)	*trans*	60
$KMnO_4$	1	*cis*-5, *trans*-9-Cyclododecadiene-*trans*-1, 2-diol (II)	*trans*	59
HN=NH	Excess	*cis*-Cyclododecene (VII)	*trans*	60—82
NOCl/HCl	1	2-Chlorocyclododecadienone oxime (IXa and IXb)	*trans*	95

hydrogenated to a known cyclododecanone oxime (X) by catalytic reduction. Its infrared spectra showed only that the absorption intensity at 980 cm^{-1} characteristic of the *trans* double bond decreased and that the one at 707 cm^{-1} characteristic of the *cis* double bond remained unchanged. Therefore, the product is probably a mixture of 2-chloro-*cis*-5, *trans*-9-cyclododecadienone oxime (IXa) and 2-chloro-*trans*-5, *cis*-9-cyclododecadienone oxime (IXb).



XIa XIb X

All the results obtained above are summarized in Table II.

Discussion

The results obtained by the present investigation have shown clearly that the first attack by *cis*-addition reagents, such as osmium tetroxide,[14] potassium permanganate, diimide,[15] and nitrosyl chloride,[16-18] takes place at one of the *trans* double bonds of *cis, trans, trans*-1, 5, 9-cyclododecatriene, and that, as far as *cis* addition reagents are concerned, there is difference enough in reactivity between the *cis* and *trans* double bonds to control the product.

Obviously, the selectivity of the reactions of *cis, trans, trans*-1, 5, 9-cyclododecatriene depends on the addition mechanism of the reagents, as is shown in Tables I and II.

A survey of *cis, trans, trans*-1, 5, 9-cyclododecatriene using the Dreiding model shows that there is no considerable difference in steric approach control toward the *cis* and *trans* double bonds, and that the cyclic system is so flexible that no rigid conformation can be considered.

cis, trans, trans-1, 5, 9-Cyclododecatriene is very stable to usual Lewis acids and bases[3]; this suggests that there is no marked difference in the thermodynamic stability of the *cis* and *trans* double bonds.

The reactions of mixture of *cis*- and *trans*-cyclododecene with osmium tetroxide[19] and nitrosyl chloride[3] also show a high selectivity, high enough to control the product; thus, only *trans*-cyclododecene can be converted into addition products. Therefore, it may be reasonable to assume that the reactivity of the *cis* and *trans* double bonds of *cis, trans, trans*-1, 5, 9-cyclododecatriene is very similar to that of a mixture of *cis*- and *trans*-cyclododecene.

On the other hand, Cope[20] has shown that there is a slight predominance of the *trans* isomer at equilibrium for cyclododecene ($\Delta F = 0.49$ kcal./mol.).

More strained acyclic olefins or *cis* olefins react much faster than *trans* olefins with *cis*-addition reagents, as has been demonstrated by Brown[21] in the case of the hydroboration of olefins.

However, the present investigation has disclosed that the more stable *trans* double bond of the 12-membered ring reacts preferentially with *cis*-addition reagents; no satisfactory explanation of this can be obtained from a discussion of the thermodynamic stability of the normal state of the starting material.

Such competitive reactivities might be explained in terms of the conformational stability at four-, five- and six-center transition states or intermediates in the *cis*-addition reactions. The transition states or intermediates for the *trans* double bonds seem to be more stable than those for the *cis* double bond because of the difference in eclipsing effect.[22]

Experimental

All melting points are uncorrected.

The Reaction of *cis, trans, trans*-1, 5, 9-Cyclododecatriene (I) with Potassium Permanganate.—

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[14] E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Company, Inc., New York (1962), p. 358.

[15] E. J. Corey, D. J. Pasto and W. L. Mock, *J. Am. Chem. Soc.*, **83**, 2957 (1961).

[16] J. Meinwald, Y. C. Meinwald and T. N. Baker, III, ibid., **86**, 4074 (1964).

[17] W. J. Serfontein, J. H. Jordaan and J. White, *Tetrahedron Letters*, **1964**, 1909.

[18] R. U. Lemieux, T. L. Nagabhushan and I. K. Oneill, ibid., **1964**, 1909.

[19] M. Ohno, unpublished results. The *trans*-olefin reacts much faster than the *cis* one.

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

[21] H. C. Brown and A. W. Moerikofer, ibid., **83**, 3417 (1961).

[22] D. Y. Curtin and D. B. Kellom, ibid., **75**, 6011 (1953).

The cyclotriene[23] (I, 10 g.), dissolved in 200 ml. of acetone, and 40 ml. of water were placed in a 500-ml. three-necked flask equipped with a stirrer, a thermometer, and a reflux condenser. Potassium permanganate (7 g.) was added into the solution in small portions, and then the mixture was cooled at 20°C for one hour. After the reaction mixture had been stirred for 2 more hr. at room temperature, a solid fraction was removed by filtration and washed with 50 ml. of acetone. After the acetone had been removed under reduced pressure from the filtrate, a colorless solid material (7.6 g., 59%) was separated from the residue by filtration. It melted at 168—169°C after recrystallization from benzene; its infrared spectrum showed absorptions at 980 cm^{-1} for the *trans* double bond and at 707 cm^{-1} for the *cis* double bond. Therefore, the *cis*-5, *trans*-9-cyclododecadiene-*trans*-1, 2-diol (II) structure was assigned.

Found: C, 73.51; H, 10.47. Calcd. for $C_{12}H_{20}C_2$: C, 73.43; H, 10.27%.

The Reaction of *cis, trans, trans*-1, 5, 9-Cyclododecatriene (I) with Osmium Tetroxide.—The cyclotriene (I, 1.27 g.), dissolved in 50 ml. of ether, and pyridine (0.8 g.) were placed in a 100-ml. three-necked flask equipped with a stirrer, a thermometer, and a separatory funnel. An ethereal solution of osmium tetroxide (2.0 g.) was then added into the solution, the reaction temperature was kept at 0°C for over 2 hr. After the reaction mixture had been allowed to stand for 12 hr. at room temperature, it was treated with sodium bisulfite and extracted with chloroform, according to Baran's method.[24] The chloroform solution was dried over sodium sulfate; the removal of the solvent afforded 1.37 g. (89%) of a colorless material. This material melted at 168—169°C after recrystallization from benzene and was proved by a mixed melting point determination and by a study of its infrared spectrum to be identical with the product of permanganate oxidation.

The Hydrogenation of *cis*-5, *trans*-9-Cyclododecadiene-1, 2-diol (II).—The diol (II, 7 g.) dissolved in a mixed solvent of ethanol (50 ml.) and cyclohexane (50 ml.) was hydrogenated with 1 g. of 5% palladium charcoal under atomospheric pressure at room temperature.

It took 12 hr. to absorb 2 mol. equivalents of hydrogen. When, after the reaction, the solvents were removed under reduced pressure, a colorless solid (7 g.) was obtained. It melted at 103—104°C after recrystallization from ether, and its infrared spectrum was identical with that of cyclododecane-*trans*-1, 2-diol.[9]

Found: C, 71.73; H, 11.91. Calcd. for $C_{12}H_{24}O_2$: C, 71.95; H, 12.08%.

The Oxidative Cleavage of Cyclododecane-*trans*-1, 2-diol (IV).—Lead tetraacetate (6.4 g.) was added to a benzene solution of the saturated diol (IV, 3 g.). The reaction mixture was then heated for 40 min. over a steam bath. After the precipitate had been removed by filtration, the benzene solution was washed with water and dried over sodium sulfate. The removal of the solvent left 3.0 g. of a colorless solid. Its infrared spectrum showed the absorptions at 1725 cm^{-1} and 2800 cm^{-1} characteristic of an aldehyde; it was therefore considered to be dodecanedial. It was dissolved in 10% aqueous acetone (100 ml.) and further oxidized with potassium permanganate (6 g.). After the usual treatment, 2.5 g. of a colorless solid was obtained. This solid melted at 125—126°C after recrystallization from aqueous methanol and was proved to be dodecanedioic acid (V) by a study of its infrared spectrum.

Found: C, 62.79; H, 9.63. Calcd. for $C_{12}H_{24}O_4$: C, 62.58; H, 9.63%.

The Reaction of *cis*-5, *trans*-9-Cyclododecadiene-*trans*-1, 2-diol (II) with Osmium Tetroxide.—According to a procedure similar to that described above, the treatment of the unsaturated diol (II, 2.3 g.) with osmium tetroxide (3 g.) afforded 1.7 g. of a colorless solid. It was recrystallized from ether and melted at 212—214°C. Its infrared spectrum showed no absorption 980 cm^{-1} for the *trans* double bond, only an absorption at 707 cm^{-1} for the *cis* double bond; it was therefore considered to be *cis*-9-cyclododecene-1, 2, 5, 6-tetrol (III).

Found: C, 62.45; H, 9.63. Calcd. for $C_{12}H_{22}O_4$: C, 62.58; H, 9.63%.

When the unsaturated tetrol (III) was hydrogenated with palladium-charcoal, a saturated tetrol, m. p. 169—170°C, was obtained in a quantitative yield. Its infrared spectrum showed no absorption at 707 cm^{-1}.

Found: C, 61.83; H, 10.49. Calcd. for $C_{12}H_{24}O_4$: C, 62.04; H, 10.41%.

The Reduction of *cis, trans, trans*-1, 5, 9-Cyclododecatriene (I) with Diimide.—The cyclotriene (I, 60 g.), hydrazine hydrate (300 g.) and cupric sulfate (3 g.) were placed in a one-liter three-necked round-bottom flask equipped with a stirrer, a condenser, and an inlet air tube. Ethanol (200 ml.) was added to the above mixture until the reaction mixture became homogeneous. Air was bubbled into the solution with vigorous stirring. The reaction generated a considerable amount of heat, and the reaction temperature easily rose as high as 50—60°C. It was kept below 50°C by cooling it with ice-water. The reaction mixture gradually turned brown, and the blue color of the cupric ion was deposited on the wall of the reaction vessel in 30—40 hr. It took about 45 hr. for the generation of heat to become negligible. Then the reaction mixture was filtered to remove the catalyst and extracted with ether. The ethereal solution was washed with 2 N hydrochloric acid to remove the excess hydrazine; then it was washed with water and dried over sodium sulfate. The ether was removed under reduced pressure, the residue was distilled in a vacuum. A fraction (42 g.), b. p. 64—65°C/1.0 mmHg, was the main component of the reaction product, which was proved by gas chromatography (PEG 6000) to consist of 91% *cis*-cyclododecene (VII) and 9% cyclododecane. Pure *cis*-cyclododecene was obtained by a preparative gas chromatography, and the compound showed an infrared spectrum identical with that of an authentic sample.[9]

Found: C, 86.48; H, 13.32. Calcd. for $C_{12}H_{22}$: C, 86.66; H, 13.34%.

On the other hand, aliquots of the reaction mixture were subjected to infrared and vapor phase chromatographic analyses at intervals during the reaction. Their infrared spectra showed that only the absorption intensity at 980 cm^{-1} for the *trans* double bond diminished,

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23) Supplied by Hüls Co., Ltd., and the sample contained 98% of *cis, trans, trans*-1, 5, 9-cyclodedecatriene and 1.8% of *trans, trans, trans*-1, 5, 9-cyclododecatriene.

24) J. S. Baran, *J. Org. Chem.*, **25**, 257 (1960).

while that at 707 cm^{-1} for the *cis* double bond remained unchanged during the reaction. Vapor phase chromatography showed the presence of three components. Two of them were confirmed by their retention times to be the starting material and *cis*-cyclododecene (VII), while the other fraction was attributed to *cis, trans*-1, 5-cyclododecadiene (VI). No detectable amount of *trans*-cyclododecene was identified.

At the end of the reaction, a small amount of cyclododecane was observed by vapor phase chromatography, and the ratio of *cis*-cyclododecene to cyclododecane was seen to depend upon the reaction time. Prolonged treatment with diimide caused an increase in the amount of cyclododecane, showing that *cis*-cyclododecene was slowly hydrogenated.

In order to confirm the structure further, the cyclododecene obtained by means of diimide was converted into cyclododecane-*cis*-1, 2-diol in the following way. The cyclododecene (1.32 g.) was dissolved in ether (40 ml.) and treated with pyridine (2 ml.) and osmium tetroxide (2 g.) for 3 days. After the adduct had been decomposed with Baran's reagent,[23] a crude glycol (1.42 g.) was obtained. It melted at 157—158°C after recrystallization from a mixed solvent of benzene and ligroin and was proved by a study of its infrared spectrum to be identical with an authentic sample prepared by Prelog.[9]

Found: C, 72.04; H, 12.05. Calcd. for $C_{12}H_{24}O_2$: C, 71.95; H, 12.08%.

The Reaction of *cis, trans, trans*-1, 5, 9-Cyclododecatriene (I) with Nitrosyl Chloride in the Presence of Hydrochloric Acid.—The cyclododecatriene (I, 200 g.) dissolved in 1 l. of trichloroethylene was placed in two-liter three-necked flask equipped with a stirrer, a condenser, and an inlet tube for nitrosyl chloride. Nitrosyl chloride (81 g.) and hydrogen chloride gas were bubbled into the solution over 3 hr. while the reaction temperature was kept below 12°C. After the addition of nitrosyl chloride, hydrogen chloride was further passed into the solution for 1 hr. After the reaction, the solvent was removed under reduced pressure and a pale yellow crude product (287 g.) was obtained. When this was recrystallized from ligroin, it showed a m. p. of 110—115°C; when it was further recrystallized from aqueous ethanol, it showed a m. p. of 127—129°C.

Found: C, 63.15; H, 7.85; N, 5.85; Cl, 15.99. Calcd. for $C_{12}H_{18}NOCl$: C, 63.3; H, 7.92; N, 6.16; Cl, 15.6%.

Its infrared spectrum showed an absorption at 980 cm^{-1} characteristic of the *trans* double bond and one at 707 cm^{-1} characteristic of the *cis* double bond, showing that one of the *trans* double bond was preferentially attacked by nitrosyl chloride. Besides the above absorptions, a N–OH absorption was observed at 3210 cm^{-1}. No skeletal change or transannular reaction was observed, since its hydrogenation with palladium charcoal afforded cyclododecanone oxime in a quantitative yield. Therefore, the product must be 2-chlorocyclododecadienone oxime (IXa and IXb).

Similar reactions using methylene chloride, chloroform, and carbon tetrachloride showed that there was no essential change in the product; 2-chlorocyclododecadienone oxime was thus afforded in yields of 60—90%.

Summary

Addition reactions of *cis, trans, trans*-1, 5, 9-cyclododecatriene (I) with *cis* addition reagents, such as osmium tetroxide, potassium permanganate, diimide, and nitrosyl chloride, have been investigated. It has been shown that the first attack of each reagent preferentially takes place at one of the *trans* double bonds. From a synthetic point of view, simple methods for preparing cyclododecane-*trans*-1, 2-diol (IV), *cis*-cyclododecene (VII), and cyclododecanone oxime (X) have been presented. An account of such selective reactions has been given in terms of conformational stabilities of the transition states or intermediates in the *cis* manner addition reactions.

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