Infrared analysis was compatible with the dioxolane structure but showed no gem-dimethyl splitting. The compound gave a negative silver nitrate test for active halogen.'

Anal. Calcd. for $C_5H_9O_2Br$: C, 33.2; H, 5.0; O, 17.7. Found: C, 33.1; H, 5.1; O, 17.8.

The author is grateful to Mr. C. Mathews for determining the n.m.r. spectra and Mr. M. K. Brandt for the determination of the infrared spectra.

Transannular Interactions. III. Synthesis and Assignment of Configurations in the cis- and trans-5-Cyclodecen-1-yl System[1]

BY HARLAN L. GOERING, WILLIAM D. CLOSSON[2] AND ALFRED C. OLSON[3]

RECEIVED MARCH 20, 1961

trans-5-Cyclodecenol (II, X = OH) was isolated from a mixture of cis- and trans-5-cyclodecenol (85% trans isomer) which was prepared in two steps from 6-ketocyclodecyl p-toluenesulfonate (VI). cis-5-Cyclodecenol (I, X = OH) was obtained from a mixture of the isomeric alcohols (70% cis isomer) prepared by the thermal decomposition of trimethyl-(6-hydroxycyclodecyl)-ammonium hydroxide (III). Structural assignments are based on hydrogenation to cyclodecanol and determination of the position and configuration of the double bond. The isomeric 5-cyclodecenones (VII and VIII) can be prepared by oxidation of the corresponding alcohols.

The isomeric 5-cyclodecenols (I and II, X = OH) were of interest in connection with an investigation of transannular participation by the double bond in the cis- and trans-5-cyclodecen-1-yl systems (I and II). This paper describes the preparation, proof of structure and some reactions of the isomeric alcohols (I and II, X = OH). The kinetics and products of solvolysis (aqueous acetone) of the isomeric p-nitrobenzoate derivatives are described in the following paper.[4]

I   II

Binary mixtures of the isomeric 5-cyclodecenols were prepared from 6-hydroxycyclodecanone(IV)[1b] by three routes. Conversion of IV to the quaternary base III followed by thermal decomposition of the latter gave mixture A. The thermal decomposition of III was first investigated by Cope and co-workers.[5] However, configurations were not assigned—the product was first believed to be the trans isomer[5]—and neither isomer was obtained in pure form. In the preceding paper in this series[1b] it was shown that the product (mixture A) is a mixture in which the cis isomer predominates. Recently it has been found that the composition of this mixture is 70% cis I and 30% trans isomer II (X = OH).[6]

In the earlier work[1b] it was shown that pure cis-5-cyclodecen-1-yl p-toluenesulfonate (I, X = OTs) can be made directly from mixture A (the trans isomer is so reactive that it is completely destroyed prior to isolation). It was also shown[1b] that pure cis-5-cyclodecenol can be isolated from the mixture

by repeated recrystallization of the p-chlorobenzoate derivative followed by saponification. This method, however, is not very satisfactory because a large number of recrystallizations are required to obtain pure material.

In the present work it was found that pure cis-alcohol I (X = OH) can be isolated in excellent yields from mixtures of the isomeric alcohols by conversion to the p-nitrobenzoate derivative, selective solvolysis of the trans-p-nitrobenzoate (II, X = $O_2CC_6H_4NO_2$) in aqueous acetone, and saponification of the unreacted cis-p-nitrobenzoate.[7] As shown in the next paper,[4] in 90% aqueous acetone at 120° the trans-p-nitrobenzoate is 300 times more reactive than the cis isomer. By this method pure cis-alcohol was obtained in good yields from binary mixtures of alcohols containing as little as 15% of the cis isomer.

The purity of the isomeric alcohols was determined by infrared analysis. Intercontamination can be detected readily by this method because the cis isomer has a characteristic strong band at 14.2 μ (disubstituted cis double bond[8]) and the trans isomer has a characteristic strong band at 10.18 μ (disubstituted trans double bond[8]).

Deamination of 6-aminocyclodecanol (V)[9] (probably a mixture of diastereoisomers) gave 5-cyclodecenol in poor yield. This product evidently consisted primarily of the cis-alcohol I (X = OH) because homogeneous derivatives of the cis-alcohol were obtained from it in high yield.

A binary mixture of the isomeric 5-cyclodecenols consisting of 85% of the trans isomer and 15% of the cis isomer (mixture B) was prepared in two steps from 6-ketocyclodecyl p-toluenesulfonate (VI). It has been shown[10] that when VI is heated in diethylaniline a mixture of about 10% bicyclo-[3.2.0]decan-2-one (IX) and 90% 5-cyclodecenone

(1) (a) The first paper in this series is H. L. Goering, A. C. Olson and H. H. Espy, J. Am. Chem. Soc., 78, 5371 (1956); (b) The second paper in this series is H. L. Goering, H. H. Espy and W. D. Closson, ibid., 81, 329 (1959).

(2) Wisconsin Alumni Research Foundation Fellow 1956–1958; National Science Foundation Fellow 1958–1960.

(3) Minnesota Mining and Mfg. Fellow 1952–1953.

(4) H. L. Goering and W. D. Closson, J. Am. Chem. Soc., 83, 3511 (1961).

(5) A. C. Cope. R. J. Cotter and G. G. Roller, ibid., 77, 3594 (1955).

(6) A. C. Cope. private communication.

(7) Attempts to separate binary mixtures of I and II (X = OH) by fractionation with an efficient column were unsuccessful. Fractional crystallization of the p-nitrobenzoate derivative also failed to give complete separation of the isomers.

(8) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1958, Chapt. 3.

(9) A. C. Cope, R. J. Cotter and G. G. Roller, J. Am. Chem. Soc., 77, 3590 (1955).

(10) A. C. Cope and G. Holzman, ibid., 72, 3062 (1950).

(VII and VIII) is formed. Reduction of this mixture with lithium aluminum hydride followed by separation of the unsaturated (monocyclic) alcohols from the saturated (bicyclic) fraction by extraction with aqueous silver nitrate gives mixture B. From the composition of the latter it is clear that the unsaturated ketone fraction is a mixture of *cis* (VIII) and *trans*-5-cyclodecenone (VII). This is also shown by comparison of the infrared spectrum with those of the isomeric ketones.
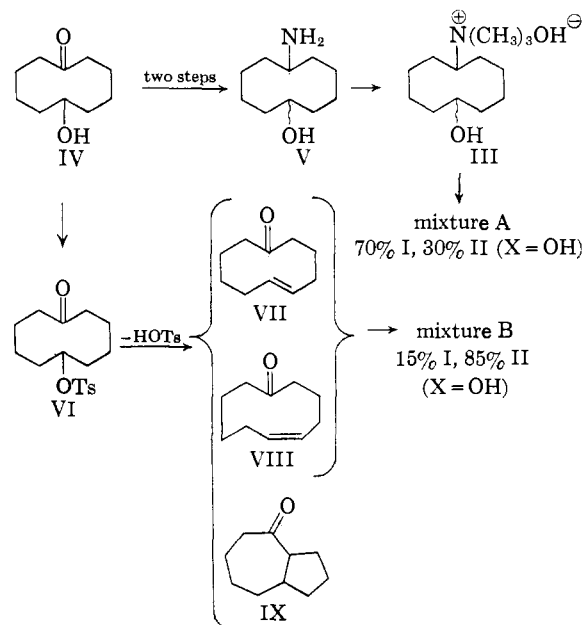
Catalytic hydrogenation (Adams platinum catalyst) of both mixture B, and the mixture of unsaturated ketones from which mixture B was derived, gave cyclodecanol in nearly quantitative yield. Oxidation of the unsaturated ketone fraction with potassium permanganate gave δ-ketosebacic acid. These observations prove that the isomeric ketones VII and VIII and alcohols I and II (X = OH) are 6-cyclodecene derivatives.

Pure *trans*-5-cyclodecenol (II, X = OH) was isolated from mixture B in good yield by liquid–liquid partition chromatography. The stationary phase was aqueous silver nitrate supported on silica gel and petroleum ether–benzene mixtures and benzene–ether mixtures (saturated with aqueous silver nitrate) were used to selectively elute the alcohols. After elution of the *cis*-alcohol and a small amount of the *trans*-alcohol with 35% benzene in petroleum ether the pure *trans*-alcohol was eluted with 50% benzene in ether.[7] This product had a spectrum with a characteristic band at 10.18 μ (there was no absorption at 14.2 μ). Several solid derivatives which appeared to be homogeneous were obtained in good yield. The physical properties of the *trans*-alcohol II (X = OH) were unchanged by conversion to a pure *p*-nitrobenzoate derivative followed by saponification. These findings, together with the fact that kinetic and isotope dilution studies showed the *p*-nitrobenzoate derivative to be homogeneous,[4] indicate that the *trans*-alcohol was pure.

The configuration of the double bond in the *trans*-5-cyclodecenyl system (II) was established by a modification of the method used earlier to determine the configuration of the *cis*-5-cyclodecenyl system (I).[1b] *cis*-Hydroxylation of *trans*-5-cyclodecenyl *p*-nitrobenzoate (II, X = $O_2CC_6H_4NO_2$) with osmium tetroxide gave 5,6-dihydroxycyclodecyl *p*-nitrobenzoate (X) which was converted to the acetonide by treatment with anhydrous copper sulfate in dry acetone. Hydrolysis of the acetonide of X gave the corresponding hydroxyacetonide which was converted to the *p*-toluenesulfonate derivative and reduced with lithium aluminum hydride. The product, isolated in over-all yield of 33%, had an infrared spectrum indistinguishable from the published spectrum[11] of the acetonide of *trans*-1,2-cyclodecanediol. Hydrolysis of the acetonide with acid in aqueous methanol gave the known[11] *trans*-1,2-cyclodecanediol. The formation of the *trans*- rather than the *cis*-glycol establishes that the double bond in II has the *trans* configuration.
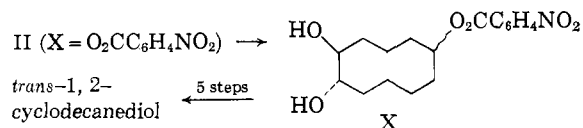
Oxidation of *cis*-5-cyclodecenol (I, X = OH) with chromic acid gave *cis*-5-cyclodecenone (VIII) in good yield. The unsaturated ketone was reconverted to the pure *cis*-alcohol in nearly quantitative yield by reduction with lithium aluminum hydride.

A similar oxidation of *trans*-5-cyclodecenol (II, X = OH) gave a mixture containing about 80% of the *trans*-ketone VII and 20% of at least two unidentified contaminants (the *cis*-ketone was not present). *trans*-Ketone that was over 98% pure was obtained by gas chromatographic separation followed by low temperature recrystallization. The *trans*-ketone VII formed a semicarbazone derivative, but, unlike with the *cis*-ketone, attempts to prepare *p*-nitrophenylhydrazone and 2,4-dinitrophenylhydrazone derivatives were unsuccessful. Reduction of the *trans*-ketone with lithium aluminum hydride gives *trans*-5-cyclodecenol together with at least one other unidentified compound. The anomalous behavior of the *trans*-ketone may be due to transannular interaction of the two functional groups. The chemistry of this compound is being investigated further.

Recently it has been reported[12] that the spectrum of 5-cyclodecenone in ethanol has a band near 260 mμ. The ketone was prepared from 6-ketocyclodecyl *p*-toluenesulfonate (VI) by the method of Cope and Holzman,[10] a method which is now known to give a mixture of the isomeric ketones VII and VIII with the *trans* isomer predominating. This unusual band was attributed to a transannular interaction between the double bond and the carbonyl group in the excited state. In the present work it was found that there is no absorption band near 260 mμ in the spectrum of either *cis*-(VIII) or *trans*-5-cyclodecenone (VII). The spectral properties of

(11) V. Prelog, K. Schenker and H. H. Gunthard, *Helv. Chim. Acta*, **35**, 1598 (1952).

(12) N. J. Leonard and F. H. Owens, *J. Am. Chem. Soc.*, **80**, 6039 (1958).

the isomeric ketones will be described in another paper.

Experimental

6-Ketocyclodecanol (IV).—A solution of 230 g. (1.085 moles) of 11-oxabicyclo[4.4.1]undec-1-yl acetate,[1b,13] m.p. 102–104°, and 100 g. (1.78 moles) of potassium hydroxide in 1400 ml. of 90% aqueous methanol was refluxed for 1 hr. After neutralization with hydrochloric acid and removal of most of the solvent under reduced pressure, the residual material was made alkaline with aqueous sodium hydroxide and extracted with six 100-ml. portions of methylene chloride. The methylene chloride solutions were combined, washed with saturated brine and dried with magnesium sulfate. Removal of the solvent under reduced pressure followed by recrystallization of the residual solid material from ether–petroleum ether gave 175 g. of 6-ketocyclodecanol (IV), m.p. 70.5–71.5° (lit.[10] m.p. 69–70°).

Binary Mixtures of 5-Cyclodecen-1-ol (I and II, X = OH). Mixture A.—The preparation of this mixture of 5-cyclodecenols according to the method of Cope and co-workers[5] was described in the preceding paper in this series.[1b]

A mixture of the isomeric alcohols (I and II, X = OH) was also prepared by nitrous acid deamination of 6-aminocyclodecanol (V)[9] by a method used previously for the deamination of cyclodecylamine.[14] Compound V prepared by this method (reduction of 6-ketocyclodecanoloxime with sodium and n-butyl alcohol)[9] is presumably a mixture of diastereoisomers. From 46 g. of V, 12.0 g. (29% yield) of yellow oil was obtained, b.p. 98–110° (0.6–1.4 mm.), n^{25}D 1.5040. This material gave a phenylurethan derivative, m.p. 110–111°, which was shown to be that of the cis- alcohol by comparison (infrared spectra and melting points of mixtures) with an authentic sample, m.p. 111–112°.[1b] The p-chlorobenzoate derivative, m.p. 65–67° (after several recrystallizations), was also shown to be the derivative of the cis-alcohol by comparison with an authentic sample, m.p. 66–67°.[1b]

Mixture B.—6-Ketocyclodecyl p-toluenesulfonate (VI), m.p. 75–76° (lit.[10] m.p. 71–72°), was prepared from 6-ketocyclodecanol (IV) in 83% yield and converted to a mixture of the isomeric 5-cyclodecenones (VII and VIII) according to the method of Cope and Holzman.[10] From 138 g. of VI, 64 g. (99% yield) of ketone, b.p. 90–105° (17 mm.), was obtained. This product is a mixture of about 10% bicyclo-[5.3.0]decan-2-one (IX) and 90% 5-cyclodecenone (mostly trans isomer). Fractionation with an efficient wire spiral column gave a center fraction (41%), b.p. 98.0–99.0° (9 mm.), n^{25}D 1.4950–1.4951. Hydrogenation of this fraction over Adams platinum oxide in acetic acid resulted in the uptake of 1.82 equivalents of hydrogen. The product was shown to be cyclodecanol by comparison of it and its p-nitrobenzoate derivative, m.p. 114–115° (lit.[15] m.p. 116°), with authentic samples.[15]

The position of the double bond in 5-cyclodecenone (derived from VI and thus a mixture of cis and trans isomers) was established as follows. A solution of 12.5 g. (0.08 mole) of potassium permanganate in 600 ml. of water was added to 3.00 g. (0.02 mole) of the unsaturated ketone. The reaction mixture was stirred at room temperature for 12 hr. and then warmed on a steam-bath for 3 hr. After cooling to room temperature, 17 g. of solid sodium bisulfite and 20 ml. of 6 N sulfuric acid were added and the reaction mixture was stirred until the insoluble manganese salts were decomposed. The solution was neutralized and extracted with five 200-ml. portions of ether to remove neutral components. The aqueous solution was acidified with dilute sulfuric acid, saturated with sodium chloride and extracted with five 200-ml. portions of ethyl acetate. After drying (MgSO₄), the ethyl acetate extracts were concentrated and δ-ketosebacic acid separated. Recrystallization from ethyl acetate gave 0.35 g. of pure δ-ketosebacic acid, m.p. 115.5–116.0°, which was identified by comparison with an authentic sample, m.p. 116°.[16]

Separation of the 5-cyclodecenones from the slightly less volatile saturated bicyclic contaminant(s) IX by fractiona-

(13) H. E. Holmquist, H. S. Rothrock, C. W. Theobald and B. E. Englund, J. Am. Chem. Soc., **78**, 5339 (1956).

(14) V. Prelog, H. J. Urech, A. A. Bothner-By and J. Wursch, Helv. Chim. Acta, **38**, 1095 (1955).

(15) M. Kobelt, P. Barman, V. Prelog and L. Ruzicka, ibid., **32**, 256 (1949).

(16) R. Criegee and R. Kaspar, Ann., **560**, 127 (1948).

tion did not prove satisfactory. It was found more convenient to reduce the ketone fraction and separate the saturated from the unsaturated isomers at the alcohol stage.

Reduction of 64 g. (0.42 mole) of the ketone mixture with 6 g. (0.158 mole) of lithium aluminum hydride in ether in the usual manner gave 47 g. of alcohol. This was mixed with 500 ml. of 10% silver nitrate solution and extracted with 100 ml. of petroleum ether after which the aqueous solution was poured into 500 ml. of ice-cold ammonium hydroxide solution. The resulting emulsion was extracted with five 100-ml. portions of ether, which were washed once with 100 ml. of water and dried with magnesium sulfate. Concentration gave 32 g. of crude material. This when distilled gave 27.7 g. (0.179 mole, 42%) of a binary mixture of cis- and trans-5-cyclodecanol, b.p. 115–118° (16 mm.), n^{25}D 1.5043 (mixture B). The composition of this mixture was estimated to be 85% trans isomer and 15% cis isomer from the infrared spectrum and yields of pure isomers separated from the mixture.

Quantitative hydrogenation of 0.500 g. of this mixture in glacial acetic acid over 0.090 g. of Adams platinum oxide catalyst required 101% of one molar equivalent of hydrogen. Removal of the catalyst and solvent gave 0.498 g. of cyclodecanol, m.p. 38.5–40.5° (lit.[15] m.p. 40–41°). This material was shown to be identical with an authentic sample.

cis-5-Cyclodecen-1-yl p-Nitrobenzoate (I, X = O₂CC₆H₄-NO₂).—A 1.113-g. portion (7.22 mmoles) of a mixture of cis- and trans-5-cyclodecenol (mixture B) was dissolved in 10 ml. of pyridine and stirred at 0° while 1.47 g. (7.93 mmoles) of p-nitrobenzoyl chloride were added slowly. After addition was complete the mixture was stirred at 0° for 3 hr., and then allowed to stand at 5° overnight. The excess acid chloride was destroyed by adding a few drops of water and the mixture was poured into a slurry of ice and hydrochloric acid. The mixture of p-nitrobenzoates was separated by extraction of the acidic mixture with chloroform. The chloroform solution was washed with 3 N hydrochloric acid, water and 3 N sodium carbonate solution. Evaporation of the dry (MgSO₄) chloroform solution gave a solid residue. After one recrystallization from ethyl acetate–petroleum ether, 1.775 g. (81%) of p-nitrobenzoate mixture, m.p. 109.4–111.8°, was obtained. This material was dissolved in 15 ml. of 90% aqueous acetone (9 parts acetone, 1 part water) and heated at 120° for 30 hr. in a sealed ampule. From the rate constants for solvolysis in 90% acetone at 120°[4] it can be determined that these conditions correspond to 11 half-lives (complete destruction) for the trans-p-nitrobenzoate and <3% solvolysis for the cis isomer. The acetone was removed by evaporation under a stream of air and the solid residue was dissolved in 20 ml. of chloroform. The chloroform solution was washed once with 10 ml. of 3 N sodium carbonate solution, once with water and then dried with sodium sulfate. Evaporation of the chloroform followed by two recrystallizations of the residual solid from 10-ml. portions of ethanol at 5° yielded 0.172 g. (0.57 mmole, or about half of the cis isomer in the mixture) of cis-5-cyclodecenyl p-nitrobenzoate (I, X = O₂CC₆H₄NO₂), m.p. 153.4–154.4°. Several recrystallizations from ethyl acetate–ethanol raised the melting point to 154.5–155.0°.

Anal. Calcd. for C₁₇H₂₁NO₄: C, 67.31; H, 6.98. Found: C, 67.68; H, 6.74.

cis-5-Cyclodecen-1-ol (I, X = OH).—A solution of 5.42 g. (17.85 mmoles) of the above cis-p-nitrobenzoate, 5.3 g. (80 mmoles) of potassium hydroxide and 20 ml. of water in 200 ml. of methanol was refluxed for 3 hr. After most of the methanol was removed by distillation at reduced pressure the mixture was diluted with 30 ml. of water and extracted with five 50-ml. portions of ether. The ether solution of the alcohol was washed with 20 ml. of saturated salt solution and dried (MgSO₄). Evaporation of the ether gave 2.67 g. of crude alcohol, m.p. 44.0–46.0°. Two recrystallizations of this product from pentane gave 2.53 g. (92%) of cis-5-cyclodecen-1-ol (I, X = OH), m.p. 44.7–46.2°. Additional recrystallizations did not change the melting point. The infrared spectrum had a strong band at 14.2 μ and medium bands at 9.38, 10.44 and 11.80 μ which are not present in the spectrum of the trans isomer. Bands characteristic of the trans isomer, e.g., 10.18 μ, were completely absent.

Anal. Calcd. for C₁₀H₁₈O: C, 77.86; H, 11.76. Found: C, 77.71; H, 11.49.

The phenylurethan melted at 111.0–111.7° and was identical with that described previously, m.p. 111.5–112.5°.[1b] The α-naphthylurethan, m.p. 138–139°, also was identical with the derivative of cis-5-cyclodecenol described earlier, m.p. 137.8–138.8°.[1b]

trans-5-Cyclodecen-1-ol (II, X = OH).—*trans*-5-Cyclodecenol was separated from mixture B by liquid–liquid partition chromatography. The absorbent was prepared by adding a solution of 10.5 g. of silver nitrate in 50.0 ml. of water slowly and with vigorous shaking to 150 g. of Davison "through 200" silica gel. After addition was complete, the silica gel was shaken vigorously in a closed bottle for several minutes. Approximately 1 g. of the alcohol (mixture B) was placed on a column containing 70 g. of freshly prepared absorbent. Elution with 1 liter of 35% benzene in petroleum ether (previously saturated with 5% aqueous silver nitrate) gave a fraction (0.3 g.) which contained all of the *cis*-alcohol and a little of the *trans* isomer. Elution with 500 ml. of 50% benzene–ether gave a second fraction (0.7 g.) which was *trans*-5-cyclodecen-1-ol (II, X = OH) contaminated with silver nitrate. The average yield of *trans*-alcohol for this separation amounted to about 70% of the amount of mixture B used. Thus the alcohol was isolated from the mixture in about 80% yield.

After distillation, the pure *trans*-5-cyclodecenol (II, X = OH) had b.p. 126° (20 mm.), n^{25}D 1.5028. The infrared spectrum had a strong band at 10.18 μ and weak bands at 9.20 and 10.90 μ which were not present in the spectrum of the *cis* isomer. Bands characteristic of the *cis* isomer were completely absent.

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 77.74; H, 11.67.

The phenylurethan melted at 80.8–81.6° (petroleum ether).

Anal. Calcd. for $C_{17}H_{23}NO_2$: C, 74.69; H, 8.48. Found: C, 74.53; H, 8.73.

The α-naphthylurethan melted at 124.6–125.6° (petroleum ether).

Anal. Calcd. for $C_{21}H_{25}NO_2$: C, 77.98; H, 7.79. Found: C, 78.10; H, 7.77.

trans-5-Cyclodecen-1-yl *p*-Nitrobenzoate (II, X = O₂-$CC_6H_4NO_2$).—A solution of 1.12 g. (7.25 mmoles) of *trans*-5-cyclodecenol (II, X = OH) in 12 ml. of pyridine was cooled at 0°, while 1.48 g. of *p*-nitrobenzoyl chloride (8.00 mmoles) was added slowly with stirring. After addition was complete, stirring was continued at room temperature for 4 hr. and the mixture was placed in a refrigerator overnight. Isolation of the product by the method described above for the mixture of *p*-nitrobenzoates derived from mixture B, followed by two recrystallizations from 60–68° petroleum ether, gave 1.823 g. (83%) of *trans*-5-cyclodecen-1-yl *p*-nitrobenzoate, m.p. 108.4–109.4°.

Anal. Calcd. for $C_{17}H_{21}NO_4$: C, 67.31; H, 6.98. Found: C, 67.23; H, 6.88.

Repeated recrystallizations of the *trans*-*p*-nitrobenzoate from petroleum ether, methanol, ethanol or acetone–water, did not change its melting point.

The *trans*-*p*-nitrobenzoate was reconverted to *trans*-5-cyclodecenol (II, X = OH) as follows. To a solution of 0.3 g. of lithium aluminum hydride (7.8 mmoles) in 30 ml. of ether was added 0.446 g. of the *p*-nitrobenzoate in 20 ml. of ether. The reaction mixture was stirred at room temperature for 45 min. The excess hydride was destroyed with water, the ether decanted, and the residue was triturated with 15 ml. of ether. The ether solution was concentrated to low volume and 10 ml. of pentane was added which precipitated most of the azo compounds. After filtering, the solvent was evaporated and the residual oil was purified by chromatography on 8 g. of Florosil. *trans*-5-Cyclodecenol (II, X = OH) was eluted with 5% ether in petroleum ether. The yield of *trans*-alcohol was 76% (0.173 g.) and its infrared spectrum was identical with that of the original sample of alcohol from which the *p*-nitrobenzoate derivative had been prepared.

Saponification of the *trans*-*p*-nitrobenzoate also regenerated *trans*-5-cyclodecenol in good yield. To a solution of 11.33 g. (37.4 mmoles) of *p*-nitrobenzoate in 400 ml. of methanol was added 21 g. (0.375 mole) of potassium hydroxide and the resulting solution was refluxed for 3 hr. All but about 50 ml. of the methanol was then removed under

reduced pressure. After adding 200 ml. of water the solution was extracted with six 50-ml. portions of ether. The ether extracts were combined, dried (MgSO₄) and concentrated. Distillation gave 5.084 g. (88%) of II (X = OH), b.p. 126–130° (24 mm.), n^{25}D 1.5028–1.5032. This product had an infrared spectrum indistinguishable from that of authentic *trans*-5-cyclodecenol.

Configuration of Double Bond in *trans*-5-Cyclodecen-1-yl *p*-Nitrobenzoate.—The configuration of the double bond in the *trans*-5-cyclodecenyl system (II), was established as follows. To a solution of 1.213 g. (4.00 mmoles) of pure *trans*-5-cyclodecenyl *p*-nitrobenzoate in 20 ml. of dry tetrahydrofuran was added 1.0 g. (3.93 mmoles) of osmium tetroxide in 15 ml. of tetrahydrofuran. The resulting mixture was stirred 18 hr. at room temperature after which the solvent was removed under a stream of dry air and the black complex dissolved in 100 ml. of acetone. Hydrogen sulfide was bubbled into the solution for 15 min., then the solution was boiled for several minutes to remove the excess hydrogen sulfide and coagulate the osmium residues. After filtration, the acetone was removed and the diol was dried under vacuum. The yield of dry product was 1.6 g. This was converted to the corresponding acetonide by stirring with 6 g. of anhydrous copper sulfate in 60 ml. of dry acetone for 13 hr. The solution was filtered and the acetone removed under reduced pressure. After drying under reduced pressure the solid acetonide weighed 1.75 g. This was dissolved in 5 ml. of methanol containing 1 g. of potassium hydroxide and the solution was refluxed for 3 hr. Most of the methanol was removed under reduced pressure. About 50 ml. of water was added, and the solution was extracted with ether for 20 hr. with a continuous extractor. Evaporation of the ether gave 0.80 g. of a mixture of isomeric acetonides of cyclodecane-1,5,6-triols. This material was converted to the corresponding *p*-toluenesulfonate by treatment with 0.85 g. of tosyl chloride (4.45 mmoles) in 10 ml. of pyridine at 0°. After standing overnight at 5°, the excess acid chloride was destroyed with a drop of water and the solution was poured onto 30 g. of ice and extracted with four 10-ml. portions of ether. The ether solution was dried (MgSO₄) and added slowly to a solution of 2 g. of lithium aluminum hydride in 100 ml. of tetrahydrofuran. The solution was refluxed for 3 hr. and then the excess hydride was destroyed by careful addition of a small excess of water and the organic solvent was removed under reduced pressure. The residual material was extracted with ether in a continuous extractor for 18 hr. The product (acetonide) was separated by chromatography on Merck acid-washed alumina. Elution with ether gave the pure acetonide (0.273 g., 33% yield). The infrared spectrum of this material was indistinguishable from the published spectrum of the acetonide of *trans*-1,2-cyclodecanediol.[11] This derivative was converted to *trans*-1,2-cyclodecanediol by hydrolysis with a solution of 2 ml. of water and 4 ml. of methanol containing 2 drops of 70% perchloric acid. After refluxing for 30 min. the solution was made basic, diluted with 10 ml. of water and the organic material was extracted with ether. The ether solution was dried (MgSO₄) and evaporated to dryness. The solid residue was recrystallized twice from pentane and then sublimed at 100° (0.1 mm.). This gave 0.083 g. (12% yield) of *trans*-1,2-cyclodecanediol, m.p. 51.6–53.0° (lit.[11] m.p. 54°). The infrared spectrum (Nujol mull) was almost identical with the published spectrum of the *trans*-glycol.[11]

cis-5-Cyclodecen-1-one (VIII).—A solution of 1.613 g. (10.43 mmoles) of I (X = OH) was dissolved in 100 ml. of acetone and cooled to 5–10° while nitrogen was slowly bubbled through the stirred solution. An 8 N solution of chromic acid in dilute sulfuric acid was added slowly until a permanent orange color was obtained.[17] After stirring for 10 min. (under nitrogen), 0.5 ml. of isopropyl alcohol was added to destroy the excess oxidant. Most of the acetone was evaporated under a stream of nitrogen. Oxygen-free water was added and the solution was extracted with five 10-ml. portions of ether. The ether fraction was washed with 5% sodium bicarbonate solution, dried (MgSO₄), concentrated (under nitrogen) and distilled. Pure *cis*-5-cyclodecen-1-one (VIII) was obtained in 68% yield (1.091 g.), b.p. 100–103° (12 mm.), n^{25}D 1.4943–1.4947. Gas chromatography of this ketone with a 6-ft. column of

(17) A. Bowers, T. G. Halsall, E. R. H. Jones and A. J. Lemin, J. Chem. Soc., 2548 (1953).

10% 1,2,3-tris-(2-cyanoethoxy)-propane on Celite at 170° showed only a single peak.

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.89; H, 10.60. Found: C, 78.87; H, 10.69.

The 2,4-dinitrophenylhydrazone, prepared in the usual manner, melted at 177.5–179.0° dec. (ethyl acetate–petroleum ether).

Anal. Calcd. for $C_{16}H_{20}O_4$: C, 57.82; H, 6.07. Found: C, 58.09; H, 5.79.

The semicarbazone melted at 210–211° dec. (ethanol); $\lambda_{max}^{95\% \ EtOH}$ 229.8 mμ, ϵ_{max} 11,100.

Anal. Calcd. for $C_{11}H_{19}N_3O$: C, 63.13; H, 9.15; N, 20.08. Found: C, 63.32; H, 9.10; N, 20.17.

The oxime melted at 110.0–110.6° (ethanol–water).

Anal. Calcd. for $C_{10}H_{17}NO$: C, 71.81; H, 10.25. Found: C, 71.90; H, 10.12.

cis-5-Cyclodecenone (VIII) was reduced to *cis*-5-cyclodecenol as follows. A solution of 0.53 g. (3.48 mmoles) of VIII in 30 ml. of ether was slowly added to a stirred slurry of 0.3 g. (7.9 mmoles) of lithium aluminum hydride in 35 ml. of ether. When addition was complete, the mixture was stirred for an hour. After the excess hydride was destroyed with saturated aqueous ammonium chloride, the mixture was extracted with ether in a continuous extractor for 18.5 hr. Evaporation of the ether yielded 0.537 g. (3.48 mmoles) of a solid alcohol, m.p. 43–44°. This product had an infrared spectrum (CCl₄ solution) identical with that of authentic *cis*-5-cyclodecenol.

Oxidation of *trans*-5-Cyclodecen-1-ol.—*trans*-5-Cyclodecen-1-ol (II, X = OH) was oxidized by the method described above for the *cis* isomer. A mixture of products (isomers) was obtained in 71% yield, b.p. 99–103° (15 mm.), $n^{25}D$ 1.4918–1.4923.

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.89; H, 10.60. Found: C, 78.50; H, 10.87.

Gas chromatographic analysis of this material with a 6-ft. column of 10% 1,2,3-tris-(2-cyanoethoxy)-propane on Celite (170°) showed it to consist of at least three com-

ponents. The major component comprised about 80% of the total material. This was identified as *trans*-5-cyclodecenone (VII) by its infrared spectrum. A semicarbazone derivative was prepared by treating the crude ketone with semicarbazide hydrochloride and sodium acetate in aqueous ethanol; m.p. 179.5–180.5° (acetonitrile), $\lambda_{max}^{95\% \ EtOH}$ 232.3 mμ, ϵ_{max} 11,000.

Anal. Calcd. for $C_{11}H_{19}N_3O$: C, 63.13; H, 9.15. Found: C, 63.22; H, 8.94.

Attempts to prepare the 2,4-dinitrophenylhydrazone and the *p*-nitrophenylhydrazone failed.

Pure *trans*-5-cyclodecenone (VII) was obtained from the crude ketone (oxidation product) by gas chromatography (1,2,3-tris-(2-cyanoethoxy)-propane on Celite at 170°), followed by low temperature recrystallization from pentane.[18] Capillary gas chromatography (Ucon) showed this material to be over 99% pure. The infrared and ultraviolet spectra also indicated this material was homogeneous.

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.89; H, 10.60. Found: C, 78.80; H, 10.58.

Reduction of 0.521 g. (3.42 mmoles) of the crude ketone with lithium aluminum hydride by the method described for the reduction of the *cis* isomer VIII gave an almost quantitative yield of colorless oil. The infrared spectrum of this material was slightly different from that of *trans*-5-cyclodecenol. The material was dissolved in 15 ml. of olefin-free petroleum ether and shaken with 10 ml. of 10% aqueous silver nitrate. The two phases were separated and the petroleum ether solution evaporated, yielding 0.145 g. of material which was not investigated further. The silver nitrate solution was added to 20 ml. of ice-cold ammonium hydroxide and the resulting emulsion was extracted with ether. The yield of crude unsaturated alcohol was 0.220 g. (42%). This material was converted to 0.289 g. of *p*-nitrobenzoate, m.p. 108.0–109.0°, which was identical with authentic *trans*-5-cyclodecenyl *p*-nitrobenzoate.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF WISCONSIN, MADISON 6, WIS.]

Transannular Interactions. IV. Products and Rates of Solvolysis of *cis*- and *trans*-5-Cyclodecen-1-yl *p*-Nitrobenzoate in Aqueous Acetone[1]

BY HARLAN L. GOERING AND WILLIAM D. CLOSSON[2]

Transannular participation by the double bond is involved in the solvolysis of *cis*- (Ia) and *trans*-5-cyclodecen-1-yl *p*-nitrobenzoate (II) in aqueous acetone. In each case the first-order rate is enhanced (alkyl–oxygen cleavage is involved) and only bicyclic products are formed. At 120° the *trans*-p-nitrobenzoate II is about 300 times more reactive than the *cis* isomer Ia which in turn is more reactive than the saturated analog, cyclodecyl *p*-nitrobenzoate. The *cis* isomer Ia is converted to *cis-cis*-1-decalol (V). Solvolysis of the *trans*-p-nitrobenzoate II is accompanied by an isomeric rearrangement (*ca.* 18%) to an unreactive product. The solvolysis product is *trans-trans*-1-decalol (IV) and the rearrangement product is mainly *trans-cis*-1-decalyl *p*-nitrobenzoate (III). The rearrangement product III formed from carbonyl-O¹⁸-*trans*-p-nitrobenzoate II has two-thirds of the label in the carbonyl position.

An investigation of the solvolysis of *cis*-5-cyclodecen-1-yl *p*-toluenesulfonate (Ib) was reported in an earlier paper.[3] In that work it was found that at 30° the unsaturated *cis-p*-toluenesulfonate Ib ethanolizes ten times faster and acetolyzes seven times faster than the saturated analog cyclodecyl *p*-toluenesulfonate. From the solvolytic behavior and the formation of bicyclic solvolytic and rearrangement products, it was concluded that ionization probably involves "transannular"[4] participation by the double bond.
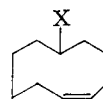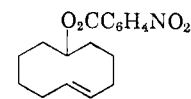
Ia, X = $O_2CC_6H_4NO_2$
b, X = OTs
c, X = OH

II

Transannular interactions involving carbon–carbon double bonds have been observed in other medium-sized ring systems. Pertinent examples