2,5-Bis-(aminomethyl)-tetrahydrofuran dipicrate was prepared from the diamine and picric acid in ethanol and recrystallized from ethanol to a constant melting point of 211.5–212.5° dec.

Anal. Calcd. for $C_{18}H_{20}N_8O_{15}$: C, 36.74; H, 3.43; N, 19.04. Found: C, 36.55; H, 3.49; N, 18.62.

2,5-Bis-(dimethylaminomethyl)-tetrahydrofuran (VI).—A mixture of 0.70 g. of 2,5-bis-(aminomethyl)-tetrahydrofuran (V), 5 ml. of 87% formic acid and 3.0 g. of 37% formalin was heated under reflux for 24 hours. After addition of 5 ml. of concentrated hydrochloric acid, the solution was concentrated to a small volume under reduced pressure, made basic with 25 ml. of 6 *N* sodium hydroxide, and extracted continuously with ether for 18 hours. The extract was dried over sodium sulfate, concentrated, and the residue was distilled by heating in a short-path still at 1 mm. The diamine VI was obtained in a yield of 0.45 g. (44%), n^{25}D 1.4500; it formed a dipicrate melting at 214.1–214.8° which was identical by mixed m.p. with the dipicrate of VI described above, prepared from I and dimethylamine.

2,5-Bis-(dimethylaminomethyl)-tetrahydrofuran dimethiodide was prepared by heating a solution of 0.45 g. of VI (prepared from V by the route described above) and 2 ml. of methyl iodide in 60 ml. of dry methanol under reflux for 2 hours. The dimethiodide that separated on cooling amounted to 0.82 g. (72%). An analytical sample that was recrystallized from methanol melted at 317.5–318.5° dec.

Anal. Calcd. for $C_{12}H_{28}I_2N_2O$: C, 30.61; H, 5.99; I, 53.91. Found: C, 30.46; H, 5.93; I, 54.19.

A sample of the dimethiodide prepared in 88% yield from the diamine VI obtained from the ditosylate I and dimethylamine had the same melting point and a mixed melting point with the sample described above was not depressed.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

Many-membered Carbon Rings. VIII. *cis-trans* Isomers of 1,3-Cyclodecadiene[1]

BY A. T. BLOMQUIST AND ALBERT GOLDSTEIN[2]

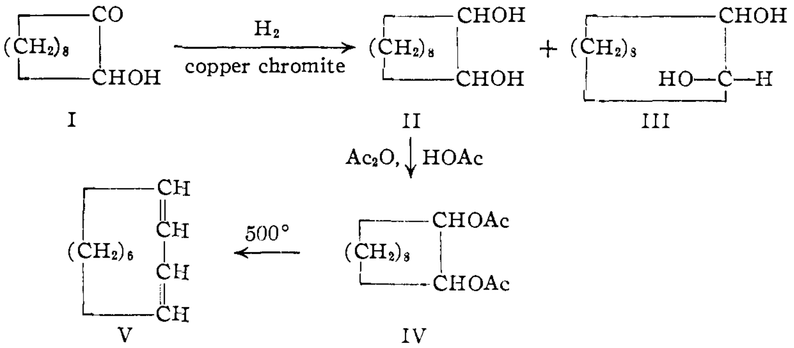
RECEIVED JULY 23, 1954

The ten-membered carbocycles *cis–cis*-1,3-cyclodecadiene and *cis–trans*-1,3-cyclodecadiene have been synthesized. Pyrolysis of *cis*-1,2-cyclodecanediol diacetate, obtained from 2-hydroxycyclodecanone, gave *cis–cis*-1,3-cyclodecadiene. Treatment of *cis*-1,2-cyclodecanediol with phosphorus tribromide afforded 3-bromo-*cis*-cyclodecene. Aminolysis of the latter with trimethylamine followed by a Hofmann degradation of the base derived from the resulting quaternary ammonium bromide produced *cis–trans*-1,3-cyclodecadiene. Chemical and physical properties, including infrared and ultraviolet spectra, of these isomeric hydrocarbons indicate that they possess a fairly rigid structure. The *cis–trans* isomer appears to be strained.

The development of the acyloin condensation for the formation of carbocyclic compounds[3,4a,5] has greatly facilitated study of the chemistry of many-membered carbon rings of intermediate size. As part of the general study, much of the work reported by Prelog,[4] Ziegler,[6] Cope[7] and this Laboratory[8] has been concerned with investigating the effect of ring size on various properties of 8-, 9- and 10-membered carbocycles.

In an effort to gain further insight into the behavior of these systems, study of the *cis–trans* isomers of 1,3-cyclodecadiene was undertaken. For this the cyclic acyloin sebacoin, 2-hydroxycyclodecanone (I), was used as the starting material.[4a,8b]

***cis–cis*-1,3-Cyclodecadiene** (V).—Synthesis of this diene V from I was achieved as indicated in the diagram which follows.



Sebacoin (I) was reduced to a separable mixture of *cis-* and *trans*-1,2-cyclodecanediol (II and III) by high pressure hydrogenation using a copper chromite catalyst. Pyrolysis of the *cis*-diacetate IV, derived from II, at 500° gave the diene V in 27–40% yield, m.p. 19–22°, b.p. 190.3–191.2° (744 mm.), n^{20}D 1.4928. This diene showed no marked tendency to polymerize on distillation or on standing.

Upon quantitative catalytic hydrogenation, V absorbed 100% of 2 molar equivalents of hydrogen and gave cyclodecane. Oxidation of the hydrocarbon with aqueous potassium permanganate gave a 57% yield of suberic acid. The isolable products obtained upon ozonolysis of V were

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[1] For the preceding paper in this series see A. T. Blomquist and L. H. Liu, THIS JOURNAL, **75**, 2153 (1953).

[2] Taken from the dissertation of A. Goldstein presented to the Graduate School of Cornell University in September, 1954, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] V. L. Hansley, U. S. Patent 2,228,268, Jan., 1941; *C. A.*, **35**, 2534 (1941).

[4] (a) V. Prelog, K. Schenker and H. H. Günthard, *Helv. Chim. Acta*, **35**, 1598 (1952); (b) V. Prelog and K. Schenker, *ibid.*, **35**, 2044 (1952); (c) V. Prelog, K. Schenker and W. Küng, *ibid.*, **36**, 471 (1953).

[5] M. Stoll and J. Hulstkamp, *ibid.*, **30**, 1815 (1947); M. Stoll and A. Rouve, *ibid.*, **30**, 1822 (1947).

[6] K. Ziegler and H. Wilms, *Ann.*, **567**, 1 (1950).

[7] (a) A. C. Cope, H. R. Nace and L. L. Estes, Jr., THIS JOURNAL, **72**, 1123 (1950); (b) A. C. Cope and L. L. Estes, Jr., *ibid.*, **72**, 1128 (1950); (c) A. C. Cope, C. L. Stevens and F. A. Hochstein, *ibid.*, **72**, 2510 (1950); (d) A. C. Cope, S. W. Fenton and C. F. Spencer, *ibid.*, **74**, 5884 (1952); (e) A. C. Cope, R. A. Pike and C. F. Spencer, *ibid.*, **75**, 3212 (1953).

[8] (a) A. T. Blomquist, *et al.*, *ibid.*, **73**, 5510 (1951); (b) A. T. Blomquist, R. E. Burge, Jr., and A. C. Sucsy, *ibid.*, **74**, 3636 (1952); (c) A. T. Blomquist, L. H. Liu and J. C. Bohrer, *ibid.*, **74**, 3643 (1952); (d) A. T. Blomquist and L. H. Liu, *ibid.*, **75**, 2153 (1953).

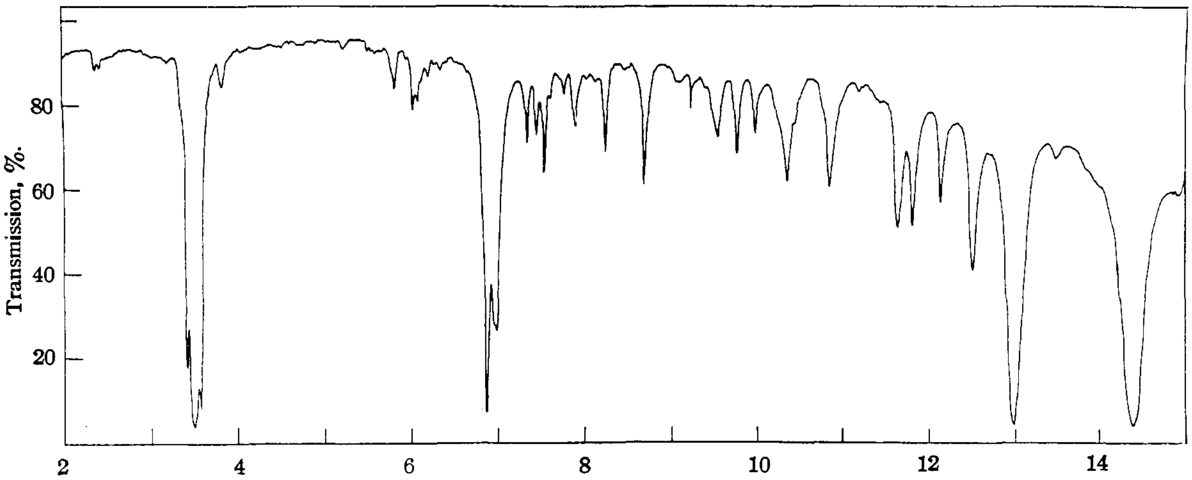


Fig. 1.—Infrared spectrum of *cis–cis*-1,3-cyclodecadiene.

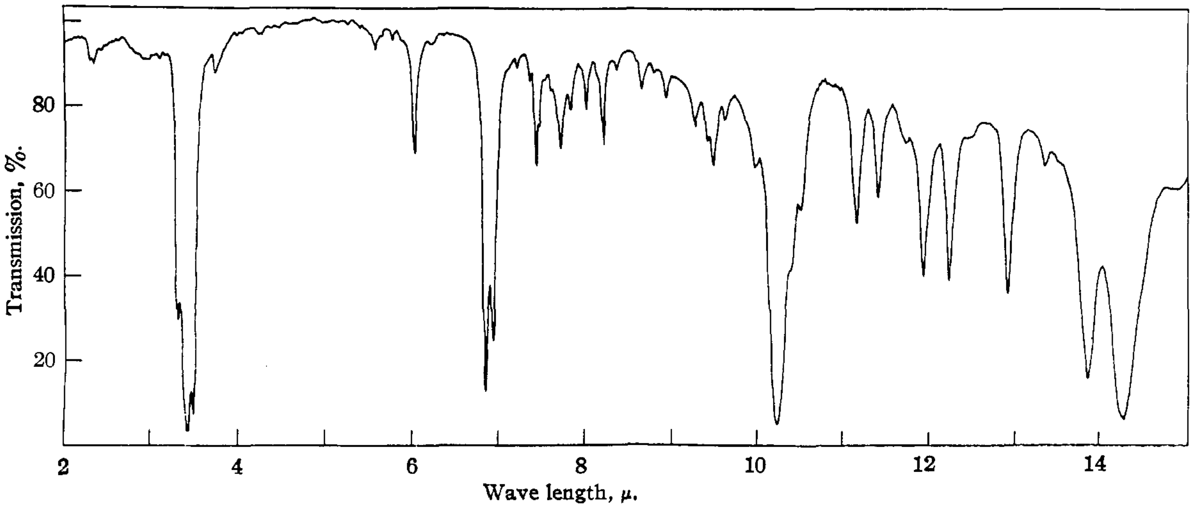


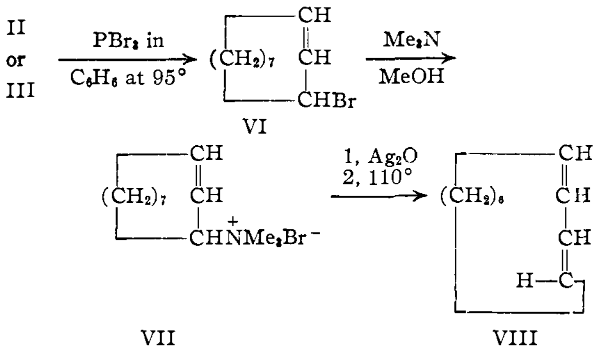
Fig. 2.—Infrared spectrum of *cis–trans*-1,3-cyclodecadiene.

acetone, succinic acid and polymeric substances.[9]

The diene V failed to react with maleic anhydride and N-phenylmaleimide.

The infrared spectrum of V (see Fig. 1) showed no absorption at 10.2–10.3 μ, the *trans* double bond region, nor at 4.53 or 5.16 μ, the acetylene and allene regions, respectively. The ultraviolet spectrum of V showed only increased general absorption at the shorter wave lengths, no maximum being observed in the region 215–230 mμ, as would be expected for a conjugated diene.

***cis–trans*-1,3-Cyclodecadiene (VIII).**—The synthesis of this diene VIII from II or III was carried out as indicated.



Treatment of either *cis*- or *trans*-1,2-cyclodecanediol (II or III) with phosphorus tribromide gave 3-bromo-*cis*-cyclodecene (VI); no 1,2-dibromocyclodecane was isolated. The infrared spectrum of this preparation of VI was identical with that of VI obtained earlier by treatment of *trans*-cyclodecene with N-bromosuccinimide.[8b] Assignment of the *cis* configuration to VI was based on its infrared spectrum, which showed no absorption in the *trans* double bond region, 10.2–10.3 μ, but did show maxima at 11.96, 12.31 and 13.19 μ. The latter correspond closely to those observed for *cis*-cyclodecene.[8b]

Heating VI with trimethylamine in methanol

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[9] Similar failures to obtain useful degradation products *via* ozonolysis have been reported for azulene: Y. Asahina and S. Nakanishi, *J. Pharm. Soc. Japan*, **52**, 1 (1932); K. S. Birell, THIS JOURNAL, **57**, 893 (1935); J. Melville, *ibid.*, **55**, 3288 (1933); L. Ruzicka and A. J. Haagen-Smit, *Helv. Chim. Acta*, **14**, 1104 (1931); A. St. Pfau and P. Plattner, *ibid.*, **19**, 858 (1936). Also, Cope, *et al.*, report polymerization and extensive degradation in the ozonolysis of bicyclo[4.2.0]octa-2,4-diene: A. C. Cope, A. C. Haven, F. L. Ramp and E. R. Trumbull, THIS JOURNAL, **74**, 4867 (1952).

gave 3-*cis*-cyclodecyltrimethylammonium bromide (VII). Treatment of VII with moist silver oxide followed by thermal decomposition at 110° *in vacuo* gave the diene VIII in *ca.* 20% yield, b.p. 65° (9.1 mm.), $n^{20}\mathrm{D}$ 1.4990. This diene polymerized on standing and when distilled at atmospheric pressure.

VIII absorbed 99.2% of 2 molar equivalents of hydrogen on quantitative catalytic hydrogenation and gave a 65% yield of suberic acid when oxidized with aqueous potassium permanganate. When VIII was treated with maleic anhydride, polymerization occurred and no simple adduct could be isolated.

The infrared spectrum of VIII (see Fig. 2) showed strong absorption at 10.25 μ, indicative of a *trans* double bond, and weaker absorption at 11.96, 12.27 and 12.95 μ, indicating the probable presence of a *cis*-olefinic link. The ultraviolet spectrum of VIII possessed a broad maximum at $\lambda 222$ mμ, log ϵ 3.86.

Discussion.—The observations noted in the foregoing with respect to the properties of the isomeric 1,3-cyclodecadienes are consistent with the notion that these molecules have a rather rigid structure and that the *cis–trans* diene VIII is somewhat strained. The *cis–cis* isomer V seems to be sufficiently rigid that its two double bonds are unable to assume a coplanar arrangement. This would account for the absence of evidence of resonance as indicated by its infrared and ultraviolet spectra.

On the other hand, the ultraviolet spectrum of the *cis–trans*-diene VIII indicates that this diene is capable of attaining a configuration in which resonance between the double bonds is possible. However, strain in the molecule is indicated by the fact that its absorption maximum is shifted to a position some 6–8 mμ lower than the maxima observed for similar compounds.

The failure of these dienes to form Diels–Alder adducts is also not surprising in view of the difficulty of attaining coplanar configuration of the double bonds. Further, inspection of molecular models of the *cis–cis* diene V shows that this diene is restricted from assuming the requisite cisoid configuration to form an adduct.

In general the properties of these dienes are in good agreement with what one might expect from a consideration of their structure as indicated by molecular models. Further, models indicate that the possibility of forming the third isomer, *trans–trans*-1,3-cyclodecadiene, is slight indeed. If obtained, it would show evidence of great strain.

Experimental Part[10]

2-Hydroxycyclodecanone (Sebacoin) (I).—This acyloin was prepared from dimethyl sebacate by the procedure described[8b] previously, but using dilute aqueous acetic acid instead of dilute sulfuric acid to hydrolyze the reaction mixture.

***cis-* and *trans*-1,2-Cyclodecanediol (II and III).**—Using 50 g. of copper chromite catalyst (Harshaw; CU-0202P; 556-002) 140 g. (0.81 mole) of I dissolved in 230 ml. of 95% ethanol was hydrogenated at 150° and 2000 p.s.i. After addition of sufficient hot ethanol to effect solution of the solid glycol, which separated from the cooled hydrogenated mixture, the catalyst was removed by filtering through Celite. Subsequently, ethanol was removed from the filtrate by distillation and the solid residue redissolved in hot benzene–ethanol (1:1). The *cis*-glycol crystallized upon cooling and was separated. Concentration of the filtrate gave an additional quantity of II. Finally, complete removal of the solvent gave the *trans*-glycol III. There was obtained 68 g. (47.3%) of II, m.p. 136–138°, and 37 g. (25.2%) of III, m.p. 54°.

Treatment of the glycols with acetic anhydride and acetic acid gave the corresponding diacetates: *cis*-1,2-diacetoxycyclodecane (IV), b.p. 108–109° (0.6 mm.), $n^{20}\mathrm{D}$ 1.4672, and *trans*-1,2-diacetoxycyclodecane, b.p. 118–119° (1.2 mm.), $n^{20}\mathrm{D}$ 1.4680; previously reported for IV: b.p. 150–151° (5 mm.), $n^{20}\mathrm{D}$ 1.4667, d^{20}_4 1.0550.[8b]

***cis–cis*-1,3-Cyclodecadiene (V).**—In a vertically arranged carborundum chip-packed column, 1.8 × 30 cm., maintained at 500 ± 5°, 167 g. (0.65 mole) of IV was pyrolyzed by adding IV at the rate of one drop every 3 seconds. Dry nitrogen, at the rate of *ca.* 3 bubbles per sec., was passed through the apparatus throughout the pyrolysis. The pyrolysate, collected at ice temperature, was diluted with 30–60° petroleum ether and thoroughly washed with water and 5% sodium bicarbonate solution. Distillation of the dried solution through a 36-inch Podbielniak column gave 24.9 g. (28%) of V, b.p. 190.3–191.2° (744 mm.), $n^{20}\mathrm{D}$ 1.4928.

After five recrystallizations from 30–60° petroleum ether V showed m.p. 19–22°, $n^{25}\mathrm{D}$ 1.4911, d^{25}_4 0.8797. The infrared spectrum of this sample of V is shown in Fig. 1. The ultraviolet spectrum of V showed only increased general absorption at the shorter wave lengths, no maximum being observed in the 215–230 mμ region.

Anal. Calcd. for $C_{10}H_{16}$: C, 88.24; H, 11.76. Found: C, 87.95, 88.08; H, 11.90, 11.96.

Quantitative reduction of V in 95% ethanol with Adams catalyst required 100% of 2 molar equivalents of hydrogen. The infrared spectrum of the reduction product was identical with that previously reported for cyclodecane.[8b]

To a stirred mixture of 2.5 g. (0.018 mole) of V and 250 ml. of water, maintained below 37°, 38 g. of potassium permanganate was added in *ca.* 4-g. portions. The reaction mixture was then filtered through Celite, extracted with ether, acidified and finally steam distilled. The distillation residue was extracted with ether and evaporation of the ether extracts gave 1.8 g. (57%) of a solid acid which after recrystallization from benzene–ethanol showed m.p. 137.8–140.9°. A mixed m.p. with an authentic sample of suberic acid, m.p. 138.6–141.5°, was 138.0–141.2°. The observed neut. equiv. of the acid was 87.95; calcd. neut. equiv. for suberic acid, 87.09. The *p*-bromophenacyl ester of the oxidation product showed m.p. 144.8–150.9° after recrystallization from ethanol–benzene. A mixed m.p. with authentic di-*p*-bromophenacyl suberate, m.p. 144.8–150.9°, was 144.8–150.9°.[11]

3-Bromo-*cis*-cyclodecene (VI).—To a stirred suspension of 50 g. (0.29 mole) of II in 200 ml. of thiophene-free benzene, maintained at 20°, 57 ml. (0.60 mole) of phosphorus tribromide was added gradually during one hour. Subsequently, the mixture was refluxed 41 hr., cooled, and hydrolyzed with 150 ml. of water. The benzene solution was then washed with saturated salt solution, 3% sodium bicarbonate solution and finally with saturated salt solution. After drying and distilling there was obtained 15.7 g. (25%) of VI, b.p. 67–68° (0.55 mm.), $n^{20}\mathrm{D}$ 1.5280. An earlier preparation of VI showed $n^{20}\mathrm{D}$ 1.5319, d^{20}_4 1.2483.[8b] However, the infrared spectra of the two preparations of VI were identical. VI was obtained similarly in the same yield by starting with III.

***cis–trans*-1,3-Cyclodecadiene (VIII).**—A solution of 15.7 g. (0.07 mole) of VI and 12.8 ml. (0.14 mole) of trimethylamine

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(10) Melting points are corrected and boiling points are uncorrected. Infrared spectra were obtained of the pure liquids, thickness 0.05 mm., using a Perkin–Elmer double beam infrared spectrophotometer, model 21, fitted with a sodium chloride prism.

(11) The broad melting point ranges reported here may be due to a polymorphic transformation. The authentic sample of *p*-bromophenacyl ester and the one derived from the acidic oxidation product both started to melt at 144.8°, resolidified at a slightly higher indeterminate temperature, resumed melting at 149.5°, and were completely melted at 150.9°. T. L. Kelly and P. A. Kleff, THIS JOURNAL, 54, 4444 (1932), report m.p. 144.2° for di-*p*-bromophenacyl suberate recrystallized from acetone.

in 30 ml. of methanol was heated in a glass bomb at 40–45° for 40 hr. The reaction mixture was evaporated to dryness at 40°, the resulting solid residue VII washed with ether and finally dried. An aqueous solution of this VII was then stirred for 2 hr. with a fresh preparation of silver oxide, obtained from 25 g. of silver nitrate and 9 g. of potassium hydroxide. Filtration followed by removal of water *in vacuo* at 35–40° gave the quaternary base as a brown oil. The latter was decomposed by heating under reduced pressure, 20 mm., at temperatures up to 110°. The pyrolysate, collected in a Dry Ice trap, was treated with concentrated hydrochloric acid and the mixture extracted with 30–60° petroleum ether. Distillation of the thoroughly washed and dried extracts gave 1.97 g. (20%) of VIII showing $n^{20}\text{D}$ 1.4982.

Upon redistillation VIII showed b.p. 65° (9.1 mm.), $n^{20}\text{D}$ 1.4990, $d^{20}{}_4$ 0.8872. The infrared spectrum of this sample of VIII is shown in Fig. 2. The ultraviolet spectrum of VIII showed a single broad maximum at λ 222 mμ, log ϵ 3.86.

Anal. Calcd. for $C_{10}H_{16}$: C, 88.24; H, 11.76. Found: C, 88.09, 88.04; H, 11.95, 11.80.

VIII polymerized when its distillation was attempted at atmospheric pressure and also when it stood under nitrogen either at room temperature or normal refrigerator temperatures.

VIII absorbed 99.2% of 2 molar equivalents of hydrogen when reduced quantitatively in ethanol using Adams catalyst.

Oxidation of 1.0 g. (0.0074 mole) of VIII with aqueous potassium permanganate using the procedure described for V gave 0.84 g. (65%) of a solid acid which, after recrystallization from ethanol–ether, showed m.p. 136.8–140.3°. A mixed m.p. with authentic suberic acid, m.p. 138.6–141.5°, was 136.8–141.4°. The *p*-bromophenacyl ester of the oxidation product showed m.p. 144.1–150.9° after crystallization from ethanol–benzene. A mixed m.p. with authentic di-*p*-bromophenacyl suberate, m.p. 144.8–150.9°, was 144.4–150.9°.[11]

ITHACA, N. Y.

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

Many-membered Carbon Rings. IX. *trans*-Elimination in Thermal Decomposition of Cyclodecyl Esters[1]

BY A. T. BLOMQUIST AND ALBERT GOLDSTEIN[2]

RECEIVED JULY 23, 1954

Using pure samples of known *cis*-cyclodecene and *trans*-cyclodecene as standards of reference for quantitative infrared analysis of mixtures of *cis*- and *trans*-cyclodecene, it was observed that pyrolytic decomposition of cyclodecyl acetate and cyclodecyl S-methyl xanthate afforded principally *trans*-cyclodecene (69–86%). Isomerization of a mixture of isomeric cyclodecenes (80% *trans*) with β-naphthalenesulfonic acid afforded a mixture of cyclodecenes in which the *cis* isomer predominated (71%).

Reported studies of the 8-, 9- and 10-membered carbocycles have shown that a number of their reactions are anomalous with respect to the corresponding reactions in classical open-chain and cyclic systems. The most striking of these are the so-called "transannular" reactions involving cyclooctene, cyclononene and cyclodecene.[3,4] Dehydrobromination of cyclodecyl bromide has been shown to yield a mixture of *cis*- and *trans*-cyclodecene in almost equal amounts,[5] although the reaction, on the basis of previous work on elimination reactions, would be expected to yield predominantly the *trans* isomer.[6]

The present article gives additional information on the formation and relative stability of the *cis* and *trans* isomers of cyclodecene.

Relative concentrations of *cis*- and *trans*-cyclodecene formed in various ways were estimated by analysis of the infrared spectrum of the product in the 9.5–13.5 μ region. The method of "base line density,"[7] based on the spectra of pure *cis*- and pure *trans*-cyclodecene,[5] was used, the results obtained being accurate to about 5%. Thus, for example, infrared analysis of a known synthetic mixture comprising 53% *cis*- and 47% *trans*-cyclodecene indicated the composition 57% *cis*- and 45% *trans*-cyclodecene. Calculation of the amount of *trans*-cyclodecene present was based on the intensities of the peak at 10.19 μ and the shoulder at 10.45 μ, the "base line" for these measurements being drawn from the curve at 10.83 μ. Calculation of the concentration of *cis*-cyclodecene was based on the intensities of the peaks at 11.83 and 13.08 μ, the "base line" being drawn from the curve at 12.30 μ.

As previously reported pure *cis*-cyclodecene is best obtained by selective catalytic hydrogenation of cyclodecyne.[5,8] *cis*-Cyclodecene thus prepared using Lindlar catalyst, palladium-on-calcium carbonate poisoned by lead acetate and quinoline,[9] showed no absorption at 10.19 μ in the infrared. Its final purification was achieved by chromatographing on silica gel.

Pure *trans*-cyclodecene was prepared *via* the Hofmann degradation of cyclodecyltrimethylammonium hydroxide[5,8] with final purification realized by chromatographing on silica gel. This sample of the hydrocarbon showed essentially no absorption

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(1) For the preceding paper in this series see A. T. Blomquist and A. Goldstein, THIS JOURNAL, **77**, 998 (1955).

(2) Abstracted from part of the dissertation presented by Albert Goldstein in September, 1954, to the Graduate School of Cornell University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) A. C. Cope, S. W. Fenton and C. F. Spencer, THIS JOURNAL, **74**, 5884 (1952).

(4) V. Prelog and K. Schenker, *Helv. Chim. Acta*, **35**, 2044 (1952); V. Prelog, K. Schenker and W. Küng, *ibid.*, **36**, 471 (1953).

(5) A. T. Blomquist, R. E. Burge, Jr., and A. C. Sucsy, THIS JOURNAL, **74**, 3636 (1952).

(6) (a) C. C. Price and J. V. Karabinos, *ibid.*, **62**, 1159 (1940); (b) S. Winstein, D. Pressman and W. G. Young, *ibid.*, **61**, 1645 (1939); (c) A. Michael, *J. prakt. Chem.*, **52**, 208 (1895).

(7) J. J. Heigl, M. F. Bell and J. U. White, *Anal. Chem.*, **19**, 298 (1947).

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

(9) H. Lindlar, *ibid.*, **35**, 446 (1952).