fonic acid for 20 hours in order to cleave the ketal grouping. Dilution with water, extraction with chloroform, washing with water, drying, evaporating and recrystallizing from acetone–hexane furnished 0.42 g. of the diol VIIa with m.p. 231–234°. The monoacetate VIIb melted at 180–182° and the infrared curves of both products proved to be identical with those of specimens prepared according to (a).

**$\Delta^{16}$-Allopregnene-3$\beta$,11$\alpha$-diol-20-one Acetate** (IVb).—The degradation of the side chain of 22-isoallospirostan-3$\beta$,11$\alpha$-diol (Ib)[14] was carried out exactly as described for the 11-keto analog Ib except that the furosten IIb and the "diosone" IIIb were not isolated. Crystallization from ether–hexane afforded between 43–47% of the $\Delta^{16}$-diacetate IVb with m.p. 156–158°, $[\alpha]^{20}\mathrm{D}$ −10°, $\lambda_{\max}^{\mathrm{EtOH}}$ 237 m$\mu$, log $\epsilon$ 4.12, $\lambda_{\max}^{\mathrm{CHCl_3}}$ 1724 and 1668 cm.$^{-1}$, but no free hydroxyl band.

*Anal.* Calcd. for $C_{25}H_{36}O_5$: C, 72.08; H, 8.71. Found: C, 72.09; H, 8.49.

**Allopregnane-3$\beta$,11$\alpha$-diol-20-one Diacetate** (Vb).—The catalytic hydrogenation of the $\Delta^{16}$-derivative IVb was performed as described for the 11-keto analog IVa and proceeded in 90% yield; m.p. 171–173°, $[\alpha]^{20}\mathrm{D}$ +44°, $\lambda_{\max}^{\mathrm{CHCl_3}}$ 1724 cm.$^{-1}$ (acetate) and 1702 cm.$^{-1}$ (saturated 20-ketone).

*Anal.* Calcd. for $C_{25}H_{38}O_5$: C, 71.74; H, 9.15. Found: C, 71.97; H, 9.19.

**Allopregnane-3$\beta$,11$\alpha$,17$\alpha$-triol-20-one 3,11-Diacetate** (VIII).—The above diacetate Vb was converted into its enol acetate and treated with peracid exactly as described for allopregnan-3$\beta$-ol-20-one[15] except that monoperphthalic acid[18] rather than perbenzoic acid[15] was used. The crude product from the alkaline saponification of the epoxide was directly acetylated with pyridine–acetic anhydride and after recrystallization from hexane–acetone afforded in 65–73% yield the diacetate VIII with m.p. 180–182°, $[\alpha]^{20}\mathrm{D}$ −28°, $\lambda_{\max}^{\mathrm{CHCl_3}}$ 1726, 1704 cm.$^{-1}$ and free hydroxyl band.

*Anal.* Calcd. for $C_{25}H_{38}O_6$: C, 69.09; H, 8.81. Found: C, 69.34; H, 8.87.

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[18] G. Rosenkranz, J. Pataki, St. Kaufmann, J. Berlin and C. Djerassi, This Journal, **72**, 4081 (1950).

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[Contribution from the Baker Laboratory of Chemistry at Cornell University]

# Many-Membered Carbon Rings. V. Cyclodecyne, *cis*- and *trans*-Cyclodecene and Related Compounds[1]

By A. T. Blomquist, Robert E. Burge, Jr.,[2] and Arthur C. Sucsy[2]

Received December 26, 1951

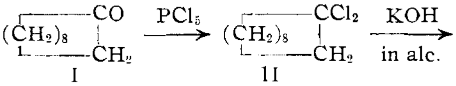
The synthesis of the ten-membered cyclic hydrocarbons cyclodecyne, *cis*-cyclodecene and *trans*-cyclodecene has been achieved. Cyclodecyne was obtained by the oxidative decomposition of 1,2-cyclodecanedione dihydrazone with yellow mercuric oxide. Hydrogenation of cyclodecyne in the presence of a palladium catalyst led to *cis*-cyclodecene which was also obtained by dechlorination of 1-chlorocyclodecene using sodium in liquid ammonia. *trans*-Cyclodecene was produced by dehydration of cyclodecanol, by the action of zinc on 2-bromocyclodecanol acetate, and by the thermal decomposition of cyclodecyltrimethylammonium hydroxide. Certain physical properties of these cyclic hydrocarbons and many of their cyclic intermediates have been determined. The infrared spectra of these compounds show that there is a close correspondence in characteristic absorptions for various atomic groupings in acyclic and $C_{10}$-carbocyclic compounds. A comparison of the properties of the isomeric cyclodecenes indicates that both forms are probably strainless with *trans*-cyclodecene being the more stable thermally.

The development of the acyloin condensation as a useful method for the synthesis of carbocyclic compounds[3,4,5] has encouraged a study of the chemistry of simple functional derivatives of many-membered carbon rings in the intermediate range, *i.e.*, carbocycles having 9 to 12 members. The extensive work of Ruzicka and others has shown that derivatives of carbocycles containing 15 or more ring members may be obtained by transformations applicable to open-chain molecules of comparable size and, further, the properties of such compounds are also similar to those of analogous acyclic molecules. However, in the intermediate range of carbocycles methods of synthesis as well as chemical and physical properties appear not to correspond closely to acyclic analogs.

The present article describes observations pertaining to certain unsaturated hydrocarbons having a ten-membered carbon ring. The considerable interest in corresponding derivatives of the eight-membered carbocycle stimulated these particular studies.[6,7]

Sebacoin, obtained in improved yield (55%) by certain modifications of methods previously described,[3,4,5] was used as the starting material for all syntheses. Since the application of infrared spectrophotometry proved to be of great value in following the purification of many of the ten-membered ring compounds and in their ultimate characterization, infrared absorption curves for some of the compounds studied are presented. No data up to the present time have been published on the infrared spectra of carbocycles containing more than eight members.

**Cyclodecyne.**—In view of Domnin's report of a successful synthesis of cyclooctyne[8] it seemed reasonable to apply his method to the synthesis of cyclodecyne (V) from cyclodecanone (I) as outlined in the following diagram.



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[1] For the preceding paper in this series see A. T. Blomquist, *et al.*, This Journal, **73**, 5510 (1951).

[2] Abstracted from the dissertations presented by Arthur C. Sucsy in February, 1949, and Robert E. Burge, Jr., in February, 1952, to the Graduate Faculty of Cornell University 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).

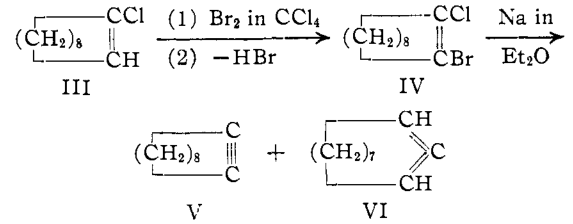
[4] V. Prelog, L. Frenkiel, M. Kobelt and P. Barman, *Helv. Chim. Acta*, **30**, 1741 (1947).

[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).

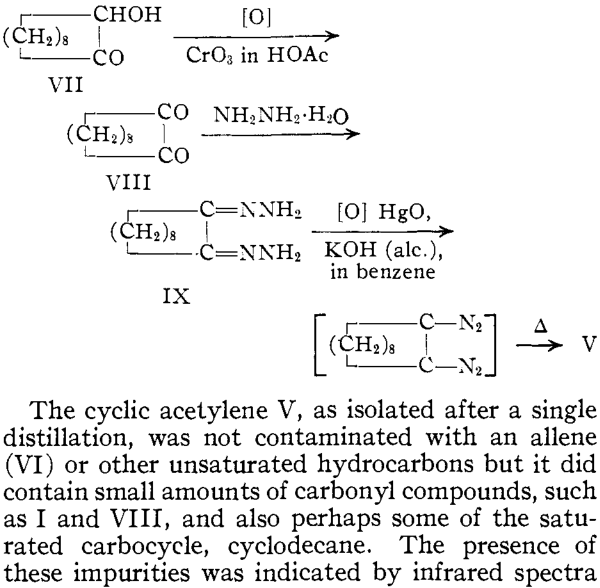
[7] L. E. Craig, *Chem. Revs.*, **49**, 103 (1951).

[8] N. A. Domnin, *J. Gen. Chem.* (*U. S. S. R.*), **8**, 851 (1938); *C. A.*, **33**, 1282 (1939).



However, it was observed that pure V could not be obtained by Domnin's method and that the product of dehalogenation of 1-bromo-2-chlorocyclodecene (IV) was largely 1,2-cyclodecadiene (VI) containing some V. The infrared spectrum of this product, a mixture of V and VI, showed a very weak absorption at 4.53 $\mu$ (C≡C stretching) and a much stronger absorption at 5.16 $\mu$ (C=C=C stretching) (Fig. 1). Ozonolysis of this product gave a mixture of azelaic and sebacic acids in about a 3 to 1 ratio. The molecular refractivity was found to be intermediate between the values calculated for V and VI.

Through application of a synthetic method developed by Curtius for diaryl acetylenes[9] pure V was synthesized from sebacoin (VII).



The cyclic acetylene V, as isolated after a single distillation, was not contaminated with an allene (VI) or other unsaturated hydrocarbons but it did contain small amounts of carbonyl compounds, such as I and VIII, and also perhaps some of the saturated carbocycle, cyclodecane. The presence of these impurities was indicated by infrared spectra and by quantitative catalytic hydrogenation experiments. Removal of the impurities to obtain pure V was achieved by chromatographing through silica gel. The sample of V thus obtained required 99–100% of two molar equivalents of hydrogen upon quantitative reduction in acetic acid using Adams catalyst and gave pure cyclodecane. Only sebacic acid was formed on ozonolysis. Hydration of V gave cyclodecanone. The infrared spectrum of pure V (*cf*. ref. 1) showed characteristic absorption for C≡C at 4.53 $\mu$ and no absorption characteristic for other carbon–carbon multiple bonds.

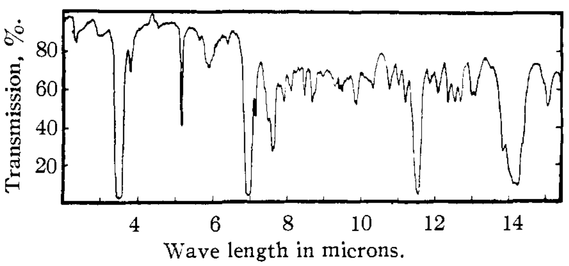


Fig. 1.—Infrared spectrum of product of dehalogenation of IV.

***cis*-Cyclodecene.**—The phenomenon of *cis-trans* isomerism about the carbon–carbon double bond in carbocyclic compounds was first demonstrated by Stoll, Hulstkamp and Rouve[10] in civetone (cycloheptadecen-10-one). The *cis* and *trans* isomers of this unsaturated carbocyclic ketone were separated by fractional crystallization of a mixture of the ethylene ketals. Natural civetone was found to have the *cis* configuration. More recently Ziegler and Wilms have shown that the two known cyclooctenes are *cis–trans* isomers.[6] The *trans* modification, obtained by the pyrolysis of cycloöctyltrimethylammonium hydroxide, is the labile, strained form. It is readily isomerized to the *cis* form, is easily polymerized, and is the isomer which is the more reactive toward phenyl azide.

Examination of Fisher–Hirschfelder–Taylor models of *cis*- and *trans*-cyclodecene indicated that both forms should be strainless. Accordingly, a study of the synthesis and properties of the isomeric cyclodecenes was made.

Hydrogenation of V in ethyl acetate using prereduced palladium catalyst supported on barium carbonate gave a cyclodecene to which is assigned the *cis* configuration. Quantitative reduction of this cyclodecene in acetic acid using Adams catalyst required 99% of one molar equivalent of hydrogen and ozonolysis gave only sebacic acid. The infrared spectrum of the olefin (Fig. 2) showed absorption at 6.09 $\mu$ which is characteristic of olefins in general, showed no absorption in the region 10.2–10.3 $\mu$ characteristic of a *trans* C=C, but showed a very strong absorption at 14.17 $\mu$ which falls in the region 14.0–14.4 $\mu$ characteristic of a *cis* C=C. It was observed that the ten-membered carbocyclic hydrocarbons (cyclodecane, *cis*- and *trans*-cyclodecene and cyclodecyne) all showed general absorption in the infrared region of 14.0 to 14.25 $\mu$. However, the absorption of *cis*-cyclodecene in the latter region is markedly stronger than any of the other hydrocarbons and there is no absorption at 10.22 $\mu$, which has been found to be characteristic of *trans*-cyclodecene. Thus the partial catalytic hydrogenation of cyclic acetylenes with palladium appears to afford *cis*-cycloölefins just as acyclic *cis*-olefins are produced by catalytic hydrogenation of corresponding acetylenes.[11]

*cis*-Cyclodecene (b.p. 194–195° (740 mm.), $n^{20}_{D}$ 1.4858, $d^{20}_{4}$ 0.8760) was also obtained by the dechlorination of III with sodium in liquid ammonia. The infrared spectrum of this sample of *cis*-cyclodecene was in excellent agreement with the spectrum for the sample of *cis*-olefin produced by cat-

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[9] T. Curtius, *Ber.*, **22**, 2161 (1889); T. Curtius and K. Thun, *J. prakt. Chem.*, [2] **44**, 168 (1891).

[10] M. Stoll, J. Hulstkamp and A. Rouve, *Helv. Chim. Acta*, **31**, 543 (1948).

[11] (a) K. N. Campbell and B. K. Campbell, *Chem. Revs.*, **31**, 77 (1942); (b) K. N. Campbell and L. T. Eby, THIS JOURNAL, **63**, 2683 (1941); (c) K. N. Campbell and M. J. O'Connor, *ibid.*, **61**, 2897 (1939); (d) K. N. Campbell and L. T. Eby, *ibid.*, **63**, 216 (1941); (e) L. Crombie and S. H. Harper, *J. Chem. Soc.*, 873, 1707 (1950); (f) F. Sondheimer, *ibid.*, 877 (1950).

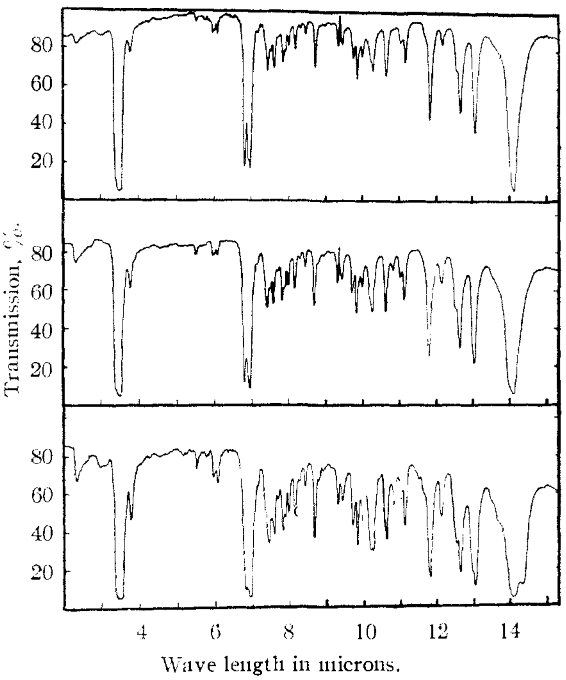


Fig. 2.—Infrared spectra of samples of *cis*-cyclodecene: upper curve, specimen from hydrogenation of V; middle curve, specimen obtained as accessory product in formation of cyclodecyl bromide; lower curve, specimen from dechlorination of III.

alytic reduction of V (Fig. 2). Since it has been shown by Hoff, Greenlee and Boord that dechlorination of chloroölefins such as 3-chloro-*cis*-3-hexene using sodium in liquid ammonia to replace chlorine atoms with hydrogen atoms proceeds with the over-all steric effect of retention of configuration,[12] the configuration of III is probably *cis*. Treatment of cyclodecanol in acetic acid with anhydrous hydrogen bromide to produce cyclodecyl bromide gave as a lower boiling accessory product (b.p. 73–78° (12.5 mm.), $n^{20}$D 1.4823) a mixture of cyclodecane and *cis*-cyclodecene. An intermediate fraction (b.p. 65° (100 mm.), $n^{20}$D 1.4811) collected on redistillation was chromatographed twice through silica gel and the resulting sample, $n^{20}$D 1.4837, was calculated to contain 87.5% *cis*-cyclodecene and 12.5% cyclodecane. Upon quantitative hydrogenation this mixture absorbed 89% of one molar equivalent of hydrogen. The infrared spectrum of this product was almost identical with that of *cis*-cyclodecene obtained from V; see Fig. 2.

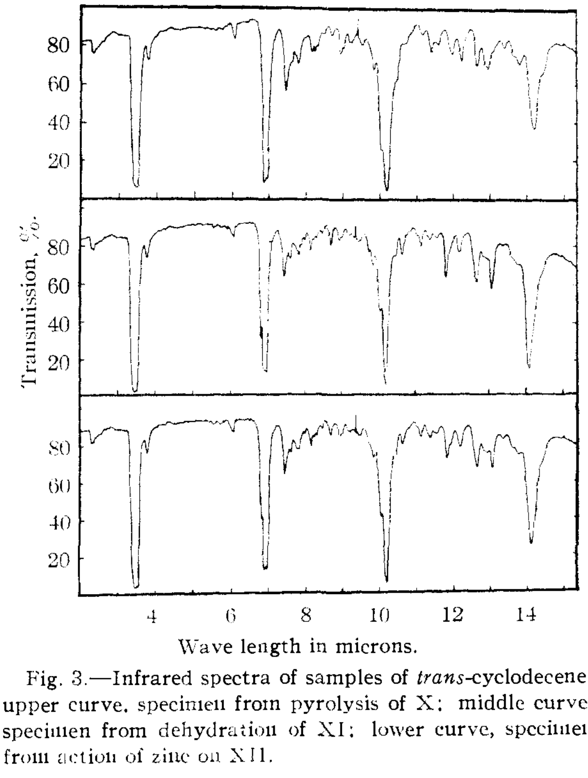
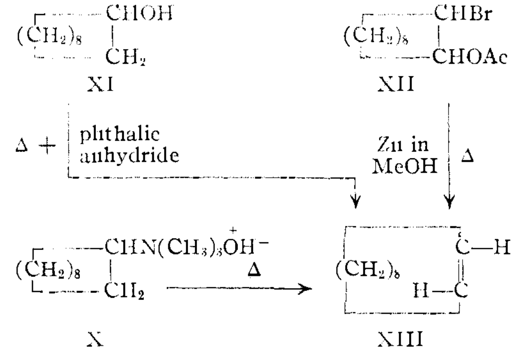


Fig. 3.—Infrared spectra of samples of *trans*-cyclodecene: upper curve, specimen from pyrolysis of X; middle curve, specimen from dehydration of XI; lower curve, specimen from action of zinc on XII.

*trans*-**Cyclodecene (XIII)**.—This hydrocarbon has been obtained following three different routes as outlined in the diagram below.



The properties of the three specimens of *trans*-cyclodecene (XIII) thus prepared were practically identical: b.p. 194–195° (740 mm.), $n^{20}$D 1.4820–1.4822, $d^{20}_4$ 0.8672–0.8676. The infrared spectra shown in Fig. 3 are also in excellent agreement. They all show weak absorption at 6.08 μ, characteristic of olefins in general, and very strong absorption at 10.22–10.23 μ indicative of a *trans* configuration about the C=C. The three samples of XIII absorbed one molar equivalent of hydrogen on quantitative reduction. Ozonolysis of XIII, obtained by dehydration of XI, gave only sebacic acid.

The only instance in which a mixture of *cis*- and *trans*-cyclodecene was obtained appeared to be in the dehydrobromination of cyclodecyl bromide with collidine. This is shown by inspection of the infrared absorption spectrum of the product (Fig. 4). Continued fractionation of this mixture of *cis*- and *trans*-cyclodecene by chromatographing

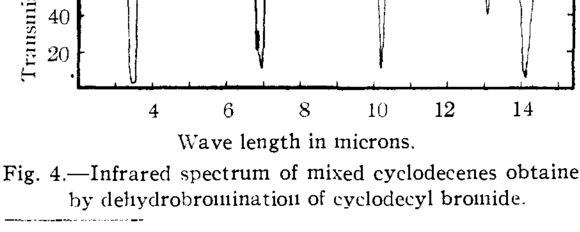


Fig. 4.—Infrared spectrum of mixed cyclodecenes obtained by dehydrobromination of cyclodecyl bromide.

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[12] M. C. Hoff, K. W. Greenlee and C. E. Boord, This Journal, **73**, 3329 (1951).

through silica gel indicated that a partial separation of the isomers could be made. The *trans* isomer appeared to be adsorbed less strongly than the *cis* form.

A comparison of certain physical properties of eight- and ten-membered cyclic hydrocarbons,[6,8] and of ten-membered cyclic hydrocarbons with open chain $C_{10}$-hydrocarbons[13] is of interest. In the open-chain series and in the strainless ten-membered carbocyclic series there is a decrease in refractive index and density as one proceeds from acetylene to *cis*-olefin to *trans*-olefin to saturated hydrocarbon. In the eight-membered carbocyclic series however the refractive index and density of the *trans*-olefin, which is strained, are higher than they are for the less strained *cis*-olefin.

Comparison of the properties of *cis*- and *trans*-cyclodecene with *cis*- and *trans*-cycloöctene with respect to isomerization and reactivity toward phenyl azide has also been made. Both *cis*- and *trans*-cyclodecene when heated at 170–180° for 1.5 hours in the presence of a small amount of $\beta$-naphthalenesulfonic acid gave a mixture of the *cis* and *trans* forms. Refractive index measurements and infrared spectra of the mixtures indicate that *trans*-cyclodecene is less easily isomerized than the *cis* isomer. The opposite was found to be true with the cycloöctenes.[6]

Both *cis*- and *trans*-cyclodecene appeared to be unreactive toward phenyl azide, no observable reaction occurring over a period of three weeks. This result also indicates that both *cis*- and *trans*-cyclodecene are probably strainless.

The characteristic infrared absorptions for certain atomic groups in ten-membered carbocyclic compounds are found in ranges which correspond to those encountered in acyclic compounds.

## Experimental Part[14]

**Sebacoin (2-Hydroxycyclodecanone) (VII).**—Modification of the procedure described by Prelog[4] and by Stoll[5] made it possible to obtain VII in substantially improved yield (55% instead of *ca.* 43%) and to double the ratio of reactants per unit volume of solvent (1.0 mole of dimethyl sebacate per liter of xylene). The important modifications which were made in the earlier procedures were: (1) Linde high-purity nitrogen was used to blanket the reaction mixture; (2) the entire reaction system was kept under nitrogen not only during the period of condensation but also during the hydrolysis of the condensation product; and (3) during the hydrolysis the temperature of the reaction mixture was never permitted to rise above 25–30°.

The infrared spectrum for VII, b.p. 113–114° (6 mm.), is shown in Fig. 5.

Treatment of VII with acetic anhydride afforded the acetate, 2-acetoxycyclodecanone; b.p. 116–117° (4 mm.), $n^{20}_{D}$ 1.4780, $d^{20}_{4}$ 1.0604.

*Anal.* Calcd. for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 67.75; H, 9.42.

**Cyclodecanone (I).**—This ketone was prepared by a slight modification of the method described by Prelog.[4] The reduction of VII on a 0.7 mole scale gave 80% yields of I consistently; b.p. 103–105° (12 mm.). The infrared spectrum of a sample of the ketone purified through its semicarbazone, m.p. 203.5–205.5° (cor.), is given in Fig. 5.

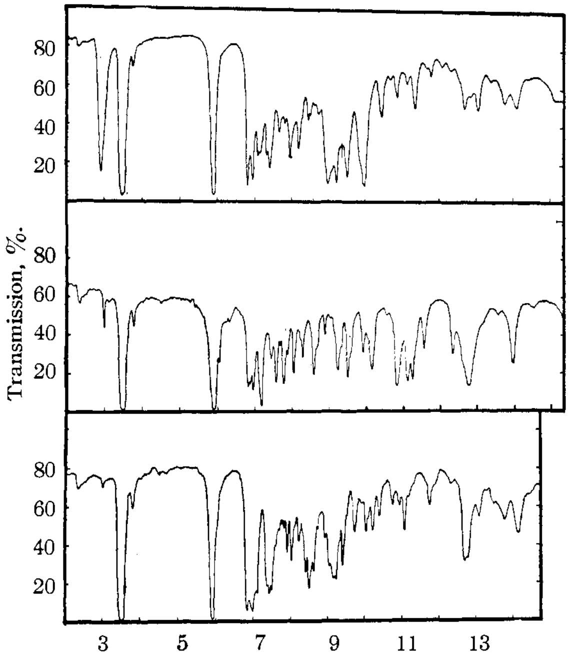

Fig. 5.—Infrared spectra: upper curve, sebacoin; middle curve, sebacil; lower curve, cyclodecanone.

**1-Chlorocyclodecene (III).**—To 340 g. (1.63 moles) of phosphorus pentachloride contained in a 1-l. flask there was added 241 g. (1.57 moles) of I slowly over a period of 1.5 hours. The brownish reaction mixture gave fumes of hydrogen chloride. After the mixture, protected from the moisture of the air, had stood at room temperature for four days it was subjected to vacuum distillation to remove phosphorus oxychloride (177 g., 75%). The residue was distilled under reduced pressure and there was obtained 187 g. (70%) of crude III, b.p. 100–140° (30 mm.), contaminated with I and II.

The crude III was then chromatographed several times through silica gel until I was removed. The removal of the ketone impurity was followed by determining the infrared spectrum for successive fractions. The fractions which showed no carbonyl absorption (5.90–5.92 $\mu$) were combined and redistilled. In this manner there was obtained 92 g. (34.2%) of III: b.p. 121–124° (29 mm.), $n^{20}_{D}$ 1.5038, $d^{20}_{4}$ 1.0165.

*Anal.* Calcd. for $C_{10}H_{17}Cl$: C, 69.54; H, 9.93. Found: C, 69.45; H, 9.98.

Quantitative reduction in acetic acid using Adams catalyst required 96.4–98% of two molar equivalents of hydrogen.

**1-Bromo-2-chlorocyclodecene (IV).**—A solution of 16 g. (0.1 mole) of bromine in 25 ml. of chloroform was added slowly with shaking at 0° to 17.3 g. (0.1 mole) of III dissolved in 25 ml. of chloroform. At about the midpoint of addition the liberation of hydrogen bromide was appreciable. The mixture, which was allowed to stand 30 minutes after the addition of bromine, was washed with two portions of sodium bisulfite solution and with water. Solvent was removed from the dried chloroform solution and the resulting residue dissolved in 25 ml. of ethanol was added slowly to a cooled solution of 11.2 g. (0.2 mole) of potassium hydroxide in 60 ml. of ethanol. The initial reaction was vigorous but controllable with a large amount of solid precipitating. After refluxing for 1.5 hours the mixture was poured into 500 ml. of cold water and extracted with ether. The ether solution was washed once with saturated salt solution, twice with dilute hydrochloric acid, again with saturated salt solution and dried over anhydrous magnesium sulfate. After removal of the ether and distillation under reduced pressure there was obtained 6.5 g. (26%) of IV: b.p. 125–129° (1.5 mm.), $n^{20}_{D}$ 1.5450, $d^{20}_{4}$ 1.372.

*Anal.* Calcd. for $C_{10}H_{16}BrCl$: C, 47.73; H, 6.41. Found: C, 48.25, 48.28; H, 6.46, 6.52.

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[13] K. N. Campbell and L. T. Eby, THIS JOURNAL, **63**, 216 (1941); G. Egloff, "Physical Constants of Hydrocarbons," Reinhold Publishing Corp., New York, N. Y., 1939, Vol. I, p. 67.

[14] Melting points and boiling points are uncorrected except where indicated. The infrared spectra were determined with a Perkin–Elmer Double Beam Infrared Spectrophotometer, Model 21, using a sodium chloride prism. Pure liquid samples, *i.e.*, free of solvents, of varying thickness (up to 0.002 in.) were used in the determinations.

**Dehalogenation of IV.**—A solution of 3.75 g. (0.015 mole) of IV in 35 ml. of absolute ether to which there had been added 1 g. (0.045 g. atom) of fine sodium wire cut into 1-cm. lengths was sealed in a glass vessel under nitrogen. This reaction mixture was allowed to stand at room temperature for ten days with occasional shaking. After filtering, the reaction mixture was washed once with saturated salt solution, twice with dilute hydrochloric acid, again with salt solution and dried over anhydrous magnesium sulfate. From the ether solution there was obtained 1.0 g. (49%) of a colorless liquid hydrocarbon whose infrared absorption spectrum (Fig. 1) indicated the presence of an acetylene and an allene: b.p. 72–75° (13 mm.), $n^{20}\text{D}$ 1.5024, $d^{20}_4$ 0.897. $M\text{D}$ calcd. for $C_{10}H_{16}$ with one triple bond: 44.20; calcd. for $C_{10}H_{16}$ with two double bonds: 45.26. Found: $M\text{D}$ 44.85.

Ozonolysis of the material (0.8 g.) dissolved in ethyl acetate was carried out using a stream of ozonized oxygen for 1.5 hours. The ozonide was decomposed using 30% hydrogen peroxide and acetic acid. In working up the products of ozonolysis three solid acidic fractions were obtained from water: Fraction I, 0.1 g., m.p. 110–115°; Fraction II, 0.2 g., m.p. 96–100°; Fraction III, 0.15 g., m.p. 95–100°.

Fraction I recrystallized from water showed m.p. 124–128°. A mixed m.p. determination with an authentic sample of sebacic acid, m.p. determination with an authentic sample of sebacic acid, m.p. 130–132°, gave a m.p. 127.5–130°. The bis-*p*-toluidide of the ozonolysis product showed a m.p. 197–200° (cor.). A mixed m.p. determination with an authentic sample of the bis-*p*-toluidide of sebacic acid (m.p. 198–200° (cor.)) showed no depression.

Recrystallization of Fractions II and III gave an acid melting at 99–101°. A mixed m.p. determination with an authentic sample of azelaic acid (m.p. 101–104°) showed no depression. The m.p. of the bis-*p*-toluidide of the acid was 197–199° (cor.), while that of an authentic sample was 199–200° (cor.). The mixture melted at 197–199° (cor.).

**Sebacil (1,2-Cyclodecanedione) (VIII).**—To a solution of 160 g. (1.6 moles) of chromium trioxide in 200 ml. of water there was added 800 ml. of acetic acid. To this solution, cooled by an ice–salt-bath, 360 g. (2.12 moles) of VII dissolved in 600 ml. of acetic acid was added slowly with stirring. The temperature of the mixture was kept below 20° and stirring was continued overnight. The mixture was then poured into 1500 ml. of saturated salt solution. This mixture was then extracted with ether, the ether extracts washed with salt solution, dilute sodium carbonate, and finally with salt solution. The residue obtained after removal of the ether from the solution dried over anhydrous magnesium sulfate was distilled under reduced pressure using a modified Claisen flask. There was obtained 260 g. (73.2%) of VIII; b.p. 99–109° (8.5 mm.). A sample was redistilled for analysis; b.p. 104–105° (10 mm.), m.p. 40–41°.

*Anal.* Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.49, 71.54; H, 9.40, 9.50.

The infrared spectrum for VIII is shown in Fig. 5.

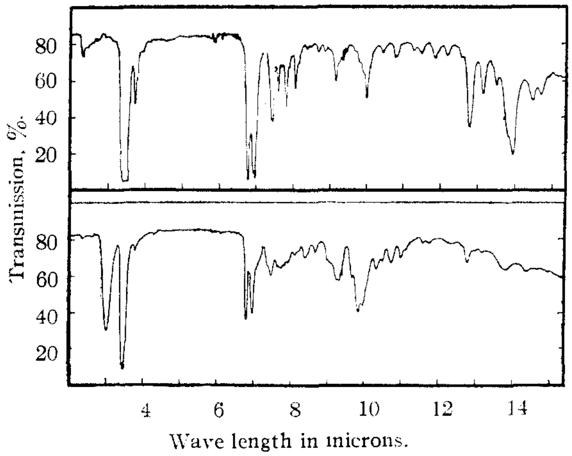

Fig. 6.—Infrared spectra: upper curve, cyclodecane; lower curve, cyclodecanol.

Sebacil dihydrazone was prepared in quantity by adding to a chilled solution of 534 g. (3.18 moles) of VIII in 2.5 l. of absolute ethanol a total of 400 g. (6.78 moles) of 85% hydrazine hydrate. The mixture was stirred during the addition and the temperature was kept below 20°. After stirring for one hour following the addition of the hydrazine most of the alcohol was removed by distillation. The crude dihydrazone which separated was recrystallized from 95% ethanol: yield 409 g. (65.5%), m.p. 121–123° (dec.).

*Anal.* Calcd. for $C_{10}H_{20}N_4$: C, 61.2; H, 10.27; N, 28.54. Found: C, 62.02, 61.83; H, 10.16, 10.24; N, 28.64, 28.28.

**Cyclodecyne (V).**—In a 2-l. three-necked flask fitted with a mercury-sealed Hershburg stirrer and reflux condenser closed by a benzene trap were placed 204 g. (1.04 moles) of sebacil dihydrazone and one liter of dry benzene. The stirred mixture was brought to reflux by heating with a steam-bath and 50 g. of yellow mercuric oxide was added. No reaction occurred until 80 g. of anhydrous sodium sulfate and 2 ml. of a saturated solution of potassium hydroxide in 95% ethanol had been added. Then the reaction mixture changed in color from bright orange to black almost immediately with a vigorous evolution of nitrogen. After the initial vigorous reaction had subsided somewhat further additions of mercuric oxide and alcoholic potassium hydroxide were made until 563 g. (2.6 moles) of mercuric oxide and 20 ml. of the alkali solution had been added. Throughout the entire period of reaction, *ca.* 70 hours, the mixture was stirred and refluxed continuously.

After filtering, benzene was removed from the reaction mixture by distillation *in vacuo* at the water-pump. The residue was then distilled at 5–6 mm. and the principal fraction boiling at 59–60° was collected: yield 51.5 g. (36.3%). The infrared spectrum of this fraction indicated that it contained a small amount of a carbonyl compound.

The distillate was chromatographed without the use of a solvent through a column (56 cm. × 1.6 cm.) packed with silica gel (Davison No. 922-08-08-226 through 200). A yellow band, probably the carbonyl compound, was formed which aided in following the separation. The column was eluted with 95% ethanol. Quantitative hydrogenation of the first chromatographed fraction indicated that it probably contained a small amount of the saturated hydrocarbon, formed perhaps by a Wolff–Kishner type reduction.

Fractional distillation of the intermediate chromatographed fractions free from carbonyl compounds gave V: b.p. 203–204° (740 mm.), $n^{20}\text{D}$ 1.4903, $d^{20}_4$ 0.8975.

*Anal.* Calcd. for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.30, 88.06; H, 11.78, 11.98.

Quantitative reduction in acetic acid using Adams catalyst required 99–100% of two molar equivalents of hydrogen. From 2.71 g. (0.02 mole) of V there was obtained after distillation 1.97 g. (71.4%) of cyclodecane: b.p. 199–200° (740 mm.), $n^{23}\text{D}$ 1.4716, $d^{20}_4$ 0.8575. Plattner and Hulstkamp[15] reported $n^{20}\text{D}$ 1.4715; $d^{20}_4$ 0.8577. The infrared spectrum of cyclodecane is shown in Fig. 6.

*Anal.* Calcd. for $C_{10}H_{20}$: C, 85.63; H, 14.37. Found: C, 85.81; H, 14.29.

A solution of 0.7 g. of V in 25 ml. of ethyl acetate was treated with ozonized oxygen for 1.5 hours. The ozonide was decomposed with glacial acetic acid and 30% hydrogen peroxide giving 0.4 g. (37.3%) of a solid acid; m.p. 126–129° from water. A mixed m.p. with an authentic sample of sebacic acid (m.p. 129–131°) was 126–129°. The bis-*p*-toluidide of the ozonolysis product was prepared; m.p. 198–200° (cor.) from ethanol. A mixed m.p. with an authentic sample of the bis-*p*-toluidide of sebacic acid (m.p. 198–200° (cor.)) was 198–200° (cor.).

Following the procedure described by Thomas, Campbell and Hennion[16] 0.7 g. of V was hydrated by treatment with a mixture of 80% acetic acid, sulfuric acid and mercuric sulfate. The resulting crude hydration product was converted to a semicarbazone by the usual procedure; m.p. 203.5–205.5° (cor.) from aqueous methanol. A mixed m.p. with an authentic sample of cyclodecanone semicarbazone (m.p. 203.5–205.5° (cor.)) was 203.5–205.5° (cor.).

*cis*-**Cyclodecene. A. From Cyclodecyne (V).**—A solution of 4.0 g. of V in 4 ml. of ethyl acetate was introduced

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[15] P. A. Plattner and J. Hulstkamp, *Helv. Chim. Acta*, **27**, 220 (1944).

[16] R. J. Thomas, K. N. Campbell and G. F. Hennion, THIS JOURNAL, **60**, 718 (1938).

into a quantitative hydrogen apparatus[17] which contained 1.0 g. of prereduced palladium catalyst supported on barium carbonate. The solution absorbed 98.9% of one molar equivalent of hydrogen. After removing the catalyst by filtration the mixture was distilled and gave 2.8 g. (70%) of *cis*-cyclodecene: b.p. 194–195° (740 mm.), $n^{20}{}_D$ 1.4854, $d^{20}{}_4$ 0.8770. The infrared spectrum for this sample of *cis*-cyclodecene is shown in Fig. 2.

*Anal.* Calcd. for $C_{10}H_{18}$: C, 86.88; H, 13.12. Found: C, 86.87, 86.95, 86.77; H, 12.97, 12.80, 12.98.

Quantitative reduction in acetic acid using Adams catalyst required 99.3–99.8% of one molar equivalent of hydrogen.

Ozonolysis of *cis*-cyclodecene was carried out following essentially the procedure described for cyclodecyne. From 0.8 g. of cyclodecene there was obtained 0.6 g. of crude acidic ozonolysis product; m.p. 113–123°. After recrystallization from water it showed m.p. 126.5–128.5°. A mixed m.p. with an authentic specimen of sebacic acid (m.p. 130–132.5°) was 127–131°. The bis-*p*-toluidide of the ozonolysis product gave a m.p. of 197–200° (cor.). The mixed m.p. with an authentic sample of the bis-*p*-toluidide of sebacic acid (m.p. 198–200° (cor.)) was 198–200° (cor.).

**B. From 1-Chlorocyclodecene (III).**—In a 1-l., three-necked flask fitted with a Dry Ice condenser, stirrer and addition funnel there was placed 300 ml. of redistilled liquid ammonia. To the liquid ammonia, cooled by a bath of Dry Ice–trichloroethylene, there was added with stirring a solution of 7.35 g. (0.043 mole) of III in 50 ml. of anhydrous ether. Then 2.15 g. of clean sodium in small pieces was added gradually and stirring was continued for two hours after addition was complete. Ammonium chloride was then added until the blue color was discharged, 100 ml. of water was added and the mixture allowed to come to room temperature overnight. The aqueous mixture was extracted with ether; the combined ether extracts washed with dilute hydrochloric acid, water and dried. From the ether solution there was obtained 2.5 g. (50.4%) of a colorless liquid which gave a slight positive Beilstein test for halogen; b.p. 195–205° (740 mm.).

The distillate was chromatographed three times through silica gel and redistilled: b.p. 194–195° (740 mm.); $n^{20}{}_D$ 1.4858; $d^{20}{}_4$ 0.8760. The infrared spectrum of this sample of cyclodecene is shown in Fig. 2.

**C. In the Preparation of Cyclodecyl Bromide.**—Into a solution of 106 g. (0.67 mole) of XI in 150 ml. of acetic acid contained in a 500-ml. flask anhydrous gaseous hydrogen bromide was introduced at a moderate rate while stirring and heating at reflux temperature. After five hours the introduction of hydrogen bromide was stopped and the reaction mixture cooled. The upper layer of cyclodecyl bromide was separated and the lower layer after being diluted with water was extracted with ether. The bromide layer and ether extracts were combined, washed with saturated salt solution, sodium carbonate solution, finally with salt solution and dried over magnesium sulfate.

Distillation *in vacuo* through a 30-cm. electrically-heated Vigreux column gave the following fractions: No. 1, 20 g., b.p. 73–78° (12.5 mm.), $n^{20}{}_D$ 1.4823; No. 2, 10 g., b.p. 78° (12.5 mm.) –118° (11 mm.), $n^{20}{}_D$ 1.4919; No. 3, 103 g. (70.7%), b.p. 119–121° (11 mm.), $n^{20}{}_D$ 1.5125. Analysis of fraction 3 indicated that it was the desired cyclodecyl bromide.

*Anal.* Calcd. for $C_{10}H_{19}Br$: C, 54.80; H, 8.74. Found: C, 54.95; H, 8.69.

Redistillation of fraction 1 gave a center cut having b.p. 65° (10 mm.) and $n^{20}{}_D$ 1.4811. The infrared spectrum of this sample was almost identical with that of *cis*-cyclodecene. On the assumption that it was a mixture of cyclodecane and *cis*-cyclodecene it was calculated from its refractive index to be 69% *cis*-cyclodecene. On quantitative hydrogenation it absorbed 70% of one molar equivalent of hydrogen. This mixture was then chromatographed twice through silica gel and gave a product ($n^{20}{}_D$ 1.4837) which was calculated to contain 87.5% *cis*-cyclodecene. It absorbed 89% of one molar equivalent of hydrogen. The infrared spectrum of this sample is shown in Fig. 2.

**Cyclodecanol (XI).**—In a 3-l. flask was placed 850 ml. of anhydrous ether and 11.4 g. (0.3 mole) of lithium aluminum hydride. After the mixture had been refluxed with stirring for half an hour, 154 g. (1.0 mole) of I was added at a rate which maintained gentle refluxing of the ether. Stirring of the mixture was continued for half an hour after the addition was complete whereupon water was added cautiously until there was no further reaction. The mixture was then poured into 650 ml. of 10% sulfuric acid, the ether layer separated and the aqueous layer washed twice with ether. The combined ether solutions were dried with potassium carbonate and distilled. There was obtained 146 g. (93.6%) of XI: b.p. 118–119° (10.5 mm.); $n^{20}{}_D$ 1.4926; $d^{20}{}_4$ 0.9626; m.p. 40–41°. Kobelt, *et al.*,[18] reported $n^{20}{}_D$ 1.4926; $d^{20}{}_4$ 0.9606; m.p. 40–41°.

*Anal.* Calcd. for $C_{10}H_{20}O$: C, 76.86; H, 12.90. Found: C, 76.84; H, 12.85.

The infrared spectrum for cyclodecanol is shown in Fig. 6.

**1,2-Cyclodecanediol.**—This glycol was prepared by the reduction of VII using three different methods. Aluminum isopropoxide reduction of 27 g. of VII gave 12.6 g. (47%) of crude glycol which after recrystallization from benzene showed a melting point of 135–136°. Reduction using lithium aluminum hydride produced the crude glycol in 52% yield; m.p. 135–138° from benzene. Catalytic reduction of VII in absolute ethanol using Adams catalyst gave the glycol in 75% yield; m.p. 135–138° from benzene. Prelog, *et al.*,[4] reported m.p. 141.5° while Stoll[5] reported 139–141°.

The bis-*p*-nitrobenzoate of the glycol was prepared: m.p. 164–165° (cor.).

*Anal.* Calcd. for $C_{24}H_{26}O_8N_2$: C, 61.25; H, 5.57. Found: C, 61.32, 61.37; H, 5.87, 5.77.

The diacetate was obtained by treating the glycol with acetic anhydride: b.p. 150–151° (5 mm.), $n^{20}{}_D$ 1.4667, $d^{20}{}_4$ 1.0550.

*Anal.* Calcd. for $C_{14}H_{24}O_4$: C, 65.57; H, 9.44. Found: C, 65.57; H, 9.47.

**2-Bromocyclodecanol Acetate (XII).**—In a 500-ml. flask fitted with a gas inlet tube leading to the bottom of the flask, a stirrer and reflux condenser was placed 16.8 g. (0.098 mole) of 1,2-cyclodecanediol dissolved in 200 ml. of acetic acid. Anhydrous gaseous hydrogen bromide was added rapidly to the stirred solution heated by an oil-bath (130–135°) over a period of 3.5 hours. During the last two hours of heating the rate of introduction of hydrogen bromide was decreased somewhat.

After removing the acetic acid by distillation *in vacuo* the residue was taken up in ether and the ether solution washed with saturated salt solution, dilute sodium carbonate solution and finally with salt solution. The dried ether solution was distilled and gave 17.4 g. (64.5%) of XII: b.p. 112–116° (0.65 mm.); $n^{20}{}_D$ 1.5098; $d^{20}{}_4$ 1.285.

*Anal.* Calcd. for $C_{12}H_{21}O_2Br$: C, 51.98; H, 7.64. Found: C, 51.98; H, 7.62.

**3-Bromocyclodecene.**—A mixture of 28 g. (0.115 mole) of N-bromosuccinimide and 21.5 g. (0.155 mole) of XIII, $n^{20}{}_D$ 1.4822, in 50 ml. of carbon tetrachloride was refluxed, after an initial vigorous reaction, for 1.5 hours. After filtering, the reaction mixture was distilled *in vacuo*. From an intermediate fraction, b.p. 92–100° (4 mm.), there was obtained on redistillation 19 g. (56.5%) of 3-bromocyclodecene: b.p. 86–87° (3 mm.); $n^{20}{}_D$ 1.5319; $d^{20}{}_4$ 1.2483.

*Anal.* Calcd. for $C_{10}H_{17}Br$: C, 55.31; H, 7.88. Found: C, 55.40; H, 7.88.

**3-Dimethylaminocyclodecene.**—A solution of 10.5 g. (0.0485 mole) of 3-bromocyclodecene in 25 ml. of benzene was added to a cooled solution of 8.5 g. (0.19 mole) of dimethylamine in 100 ml. of benzene. After standing at room temperature for three days the mixture was refluxed 3 hours, cooled, and filtered. From the mixture 4.9 g. (81%) of dimethylamine hydrobromide was obtained. The filtrate was extracted with dilute hydrochloric acid and the combined acid extracts made alkaline with 20% sodium hydroxide. The aqueous alkaline mixture was then extracted with ether. Distillation of the dried ether extracts gave 6.15 g. (70%) of 3-dimethylaminocyclodecene: b.p. 95–100° (8 mm.), $n^{20}{}_D$ 1.4896. A redistilled sample (b.p. 98° (8 mm.), $n^{20}{}_D$ 1.4892) was used for analysis.

*Anal.* Calcd. for $C_{12}H_{23}N$: C, 79.49; H, 12.78; N, 7.73. Found: C, 79.53; H, 12.91; N, 7.58.

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[17] R. W. Holley, Ph.D. Thesis, Cornell University, Ithaca, N. Y., 1947.

[18] M. Kobelt, P. Barman, V. Prelog and L. Ruzicka, *Helv. Chim. Acta*, **32**, 256 (1949).

The methiodide of the dimethylaminocyclodecene was prepared by a standard method: m.p. 195–197° (dec.).

*Anal.* Calcd. for $C_{13}H_{26}NI$: C, 48.30; H, 8.11; N, 4.33. Found: C, 48.36; H, 8.20; N, 4.25.

**Cyclodecyltrimethylammonium Iodide.**—A solution of 5.41 g. (0.03 mole) of 3-dimethylaminocyclodecene in 5 ml. of absolute ethanol was hydrogenated in the presence of 1.0 g. of prereduced platinum oxide. Over a period of seven hours 101.3% of one molar equivalent of hydrogen was absorbed. After removal of the catalyst the ethanolic solution of the saturated amine was treated with 10.7 g. of methyl iodide. The mixture was refluxed for one hour. To the cooled solution 10 ml. of isopropyl ether was added, precipitating the methiodide. After filtering, washing with isopropyl ether and drying there was obtained 8.57 g. (87.8%) of cyclodecyltrimethylammonium iodide; m.p. 261–262°. On recrystallization from a mixture of 95% ethanol and isopropyl ether it showed a m.p. of 265–265.5° (dec.).

*Anal.* Calcd. for $C_{13}H_{28}NI$: C, 48.00; H, 8.68; N, 4.31. Found: C, 47.98, 48.20; H, 8.62, 8.59; N, 4.39, 4.27.

***trans*-Cyclodecene (XIII) (A) From XI.**—In a 250-ml. flask fitted with a dropping funnel and an insulated, carborundum-packed, Hempel column arranged for distillation 75 g. of phthalic anhydride was brought to boiling by heating with a Woods metal bath (295°). Cyclodecanol (38 g., 0.24 mole) was added in portions to the boiling phthalic anhydride. Toward the end of the addition the temperature of the heating bath was increased to 340°. The mixture of phthalic anhydride, water and cyclodecene, which collected in the receiver was worked up to remove anhydride and water. There was obtained 26.2 g. (80%) of XIII: b.p. 68–70° (10 mm.), $n^{20}{}_D$ 1.4822, $d^{20}{}_4$ 0.8672. The infrared spectrum is shown in Fig. 3.

*Anal.* Calcd. for $C_{10}H_{18}$: C, 86.87; H, 13.13. Found: C, 87.78, 87.71; H, 13.16, 13.12.

Quantitative reduction in acetic acid using Adams catalyst required 100.3–100.6% of one molar equivalent of hydrogen.

Ozonolysis of this *trans*-cyclodecene was carried out following the procedure used with V. From 0.66 g. of the olefin there was obtained 0.6 g. (62%) of an acid showing m.p. 127–129° (cor.), which on recrystallization from water melted at 129–130.5° (cor.). A mixed m.p. determination with an authentic sample of sebacic acid was 129–130.5° (cor.). The identity of the acid was confirmed by preparation of the bis-*p*-toluidide, m.p. 199–200.5° (cor.), which did not depress the m.p of an authentic specimen of the bis-*p*-toluidide of sebacic acid.

**(B) From XII.**—A mixture of 9 g. of zinc dust and 0.5 g. of zinc chloride in 75 ml. of absolute methanol was refluxed with stirring while 10 g. (0.036 mole) of XII was added portionwise. After the mixture had refluxed for 7 hours it was filtered to give a cloudy filtrate. Methanol was then removed from the filtrate by distillation through a column and the residue, taken up in ether, was washed with dilute hydrochloric acid and with water. From the dried ether solution after distillation and chromatographing through silica gel there was obtained 3.38 g. (68%) of XIII: b.p. 194° (740 mm.), $n^{20}{}_D$ 1.4820, $d^{20}{}_4$ 0.8676.

The infrared spectrum of this sample of XIII is shown in Fig. 3.

*Anal.* Calcd. for $C_{10}H_{18}$: C, 86.87; H, 13.13. Found: C, 87.03; H, 13.20.

Quantitative reduction in acetic acid using Adams catalyst required 99.2–100% of one molar equivalent of hydrogen.

**(C) From X.**—Freshly prepared silver oxide obtained from 8.5 g. of silver nitrate was added to a solution of 8.13 g. (0.025 mole) of cyclodecyltrimethylammonium iodide in 100 ml. of water. After the mixture had been stirred for 3 hours it was filtered and the filtrate concentrated to a sirup by distillation at the water-pump. The sirupy residue was then decomposed by heating in a Claisen flask at 20 mm. pressure, the distillate being collected in a receiver cooled with a Dry Ice–trichloroethylene bath. The crude distillate was neutralized with dilute sulfuric acid and extracted with ether. The combined ether extracts were washed with saturated salt solution, dried and distilled. There was obtained 2.12 g. (64%) of XIII: b.p. 194° (740 mm.), $n^{20}{}_D$ 1.4820, $d^{20}{}_4$ 0.8674. The infrared spectrum of this sample of XIII is shown in Fig. 3.

*Anal.* Calcd. for $C_{10}H_{18}$: C, 86.87; H, 13.13. Found: C, 86.98; H, 13.05.

Quantitative reduction in acetic acid using Adams catalyst required 104.3–104.5% of one molar equivalent of hydrogen.

**Dehydrobromination of Cyclodecyl Bromide.**—A solution of 46.2 g. (0.21 mole) of cyclodecyl bromide in 100 ml. of collidine was refluxed for 2 hours. The cooled mixture was filtered, an additional 50 ml. of collidine added to the filtrate which was refluxed for another 3 hours. Collidine hydrobromide was again removed by filtration, the combined precipitates weighing 30 g. (75%). The filtrate from the reaction mixture, after dilution with ether, was extracted with dilute hydrochloric acid until free of collidine. From the washed and dried ethereal solution there was obtained 17.5 g. (60%) of impure cyclodecene on distillation; b.p. 65–75° (9 mm.). This product contained traces of cyclodecyl bromide which was removed by chromatographing through silica gel. The infrared spectra of the chromatographed fractions showed that they were mixtures of *cis*- and *trans*-cyclodecene. The *trans* isomer appeared to be less strongly adsorbed and a partial separation of the *cis*–*trans* isomers was effected.

**Thermal Isomerization of *cis*- and *trans*-Cyclodecene.**—Small samples of *cis*-cyclodecene (2.39 g.) and *trans*-cyclodecene (3.0 g.) were sealed under nitrogen in glass tubes containing 50 mg. each of hydroquinone and β-naphthalenesulfonic acid. The two sealed tubes were heated at 170–180° for 1.5 hours, opened and the contents distilled. From *cis*-cyclodecene the distilled product (b.p. 59–60° (7 mm.)) showed $n^{20}{}_D$ 1.4838. From *trans*-cyclodecene the distilled product (b.p. 59–60° (7 mm.)) showed $n^{20}{}_D$ 1.4832. The infrared spectra of the two isomerized products indicated that they were mixtures of *cis*- and *trans*-cyclodecene. The product derived from heating the *trans* isomer showed more pronounced absorption at 10.23 μ than the product obtained on heating *cis*-cyclodecene.

**Behavior of *cis*- and *trans*-Cyclodecene Toward Phenyl Azide.**—Following the procedure described by Ziegler,[6] 0.5-g. samples of *cis*- and *trans*-cyclodecene were each treated with 0.7 g. of phenylazide. No observable reaction occurred in either case after standing at room temperature for a period of three weeks.

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