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 $n^{20}D$ 1.4982.

Upon redistillation VIII showed b.p. 65° (9.1 mm.), $n^{20}D$ 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]

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[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).

at 11.83 or 13.08 μ in the infrared. The required cyclodecylamine was obtained in good yield by lithium aluminum hydride reduction of cyclodecanone oxime.

Thermal Decomposition of Cyclodecyl Esters.—The studies of Alexander and Mudrak[10] and of Hückel, *et al.*,[11] have shown that pyrolysis of 6-membered cyclic alcohol acetates and xanthates results in the preferential elimination of a *cis*-β-hydrogen. In the cyclodecane series this would afford *cis*-cyclodecene. However, examination of the Fisher–Taylor–Hirschfelder models of such 10-membered cyclic esters indicated the greater likelihood of elimination of the *trans*-β-hydrogen, provided the cyclic theory of elimination[10] is correct.

Pyrolysis of cyclodecyl acetate at 500° over carborundum, after removal of a low-boiling dienoid fraction, gave a product comprising 69% *trans*-cyclodecene and 19% *cis*-cyclodecene as indicated by infrared analysis of its spectrum. Correspondingly pyrolytic decomposition of cyclodecyl-S-methyl xanthate gave a product whose infrared spectrum indicated the composition 86% *trans*- and 14% *cis*-cyclodecene.

It would seem probable, on the basis of these results, that the cyclodecane ring, although not strained, is allowed only slight variations in its configuration, movements being such as to maintain in the transition state during pyrolysis *trans*-β-hydrogen atoms in close proximity to the keto-oxygen or sulfur atoms of the ester groups.

Isomerization of *cis*- and *trans*-Cyclodecene.—Three methods for isomerization of *cis*- and *trans*-cyclodecene were applied in an effort to establish the relative stability of the isomers. Two of these, irradiation with ultraviolet light and treatment with silver nitrate, were found to have no effect. The third method, treatment with β-naphthalenesulfonic acid, did bring about isomerization. Such an acid-catalyzed thermal isomerization would be expected to achieve the conversion of the less stable to the more stable isomer.

In the present instance treatment of a mixture of cyclodecenes, containing 80% of the *trans* isomer and 20% of the *cis* isomer, with β-naphthalenesulfonic acid for 22 hr. at 90–100° resulted in the formation of a mixture which contained, as determined by analysis of its infrared spectrum, 16% *trans*-cyclodecene and 82% *cis*-cyclodecene.

In an earlier study[5] *trans*-cyclodecene was isomerized with β-naphthalenesulfonic acid by the method of Ziegler and Wilms.[12] A re-determination of the concentrations of isomers in the product thus obtained indicated the presence of 37% *trans*- and 71% *cis*-cyclodecene.

These results would indicate that in the cyclodecene series the *trans* isomer is less stable than the *cis* isomer. Similar findings have been reported concerning the relative stabilities of the *cis* and *trans* isomers of cycloöctene and cyclononene.[12,13]

Acknowledgment.—The authors are indebted to Professor R. M. Hexter for his aid in obtaining and interpreting the infrared data used in these investigations.

Experimental Part[14]

***cis*-Cyclodecene.**—To a solution of 1.5 g. (0.01 mole) of pure cyclodecyne[5] in 10 ml. of 60–70° petroleum ether was added 0.2 g. of palladium–lead–calcium carbonate catalyst[9] and 0.1 g. of quinoline. The mixture was treated with hydrogen at 1.5 p.s.i. until adsorption ceased. From the filtered mixture impure olefin was obtained on distillation showing b.p. 193–196° (740 mm.). Chromatographing this product through silica gel, without solvent, gave the pure olefin, n^{20}D 1.4851, whose infrared spectrum was identical with that previously reported.[5]

Cyclodecylamine.—To a stirred slurry of 31 g. of lithium aluminum hydride in 750 ml. of anhydrous ether was added slowly a solution of 31 g. (0.18 mole) of cyclodecanone oxime[15,16] in 500 ml. of ether. The mixture was then refluxed for 10 hr., and hydrolyzed by the careful addition of 70 ml. of water. The suspension was filtered and the precipitate washed 3 times with ether. The combined filtrates were concentrated to 500 ml. and extracted with 10% hydrochloric acid. The acid solutions were made basic with 10% sodium hydroxide solution and extracted with ether. The ether extracts were washed with water, dried and evaporated to yield 17 g. (60%) of cyclodecylamine.

Evaporation of the original ether extract gave 4.4 g. of unreacted oxime. Based on the amount of oxime converted, the yield of amine was 72%.

The amine picrate was prepared: m.p. 239–240° dec.; reported by Prelog, *et al.*,[17] m.p. 239° dec.

The amine hydrochloride was prepared: m.p. 176.7–178.8° from methanol; reported by Prelog,[17] m.p. 177–178°.

For use in the preparation of *trans*-cyclodecene the amine was converted to cyclodecyltrimethylammonium iodide following the procedure of Woodward and Doering.[18]

***trans*-Cyclodecene.**—This olefin was obtained by the method previously described. Its properties, including its infrared spectrum, were identical with those reported.[5]

Cyclodecyl Acetate.—A solution of 29 g. (0.19 mole) of cyclodecanol,[5] 50 ml. of glacial acetic acid and 37 ml. of acetic anhydride was refluxed 2 hr. Distillation of the solution gave 32 g. (86.5%) of the acetate: b.p. 90–95° (2.5 mm.), n^{20}D 1.4689. Reported by Kobelt, *et al.*,[19] b.p. 120–121° (11 mm.), n^{20}D 1.4682.

Thermal Decomposition of Cyclodecyl Acetate.—Cyclodecyl acetate (28 g., 0.14 mole) was allowed to drop at the rate of 1 drop every 3 sec. on an 1.8 × 18 cm. column, packed with carborundum chips, maintained at 500°. A stream of dry nitrogen was passed through the column at a rate of *ca.* 3 bubbles/sec. during this operation. After the addition was complete, the column was flushed by the addition of 2 ml. of acetic acid.

Distillation of the thoroughly washed and dried pyrolysate through a 36-inch Podbielniak column at atmospheric pressure (730 mm.) yielded 3 fractions: (1) b.p. 165–169°, n^{20}D 1.4320, 3.2 g.; (2) b.p. 169–196°, n^{20}D 1.4604, 4.1 g.; (3) b.p. 196–196.5°, n^{20}D 1.4808, 4.6 g.

Qualitative catalytic hydrogenation of fraction (1) resulted in the absorption of 99% of 2 molar equivalents of hydrogen; the reduction of fraction 3 resulted in the absorption of 103% of 1 molar equivalent.

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(10) E. R. Alexander and A. Mudrak, THIS JOURNAL, **72**, 1810, 3194 (1950); **73**, 59 (1951).

(11) W. Hückel, W. Tappe and G. Legutke, *Ann.*, **543**, 191 (1940).

(12) K. Ziegler and H. Wilms, *Ann.*, **567**, 1 (1950).

(13) A. T. Blomquist, L. H. Liu and J. C. Bohrer, THIS JOURNAL, **74**, 3643 (1952).

(14) Melting points are corrected and boiling points are uncorrected. The infrared spectra were obtained with a Perkin–Elmer double beam infrared spectrophotometer, model 21, fitted with a sodium chloride prism. Liquid samples, free of solvent, of 0.051 mm. thickness were used; resolution 927; range 9.5–13.5 μ.

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

(16) L. Ruzicka, M. Kobelt, O. Häfliger and V. Prelog, *ibid.*, **32**, 549 (1949).

(17) V. Prelog, M. F. El-Neweihy and O. Häfliger, *ibid.*, **33**, 365 (1950).

(18) R. B. Woodward and W. von E. Doering, THIS JOURNAL, **67**, 860 (1945).

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

The infrared spectrum of fraction (1) was unlike that of any known cyclodecane derivative; that of fraction 3 showed it to be a mixture of *cis*- and *trans*-cyclodecene and that of fraction 2 was a mixture of (1) and (3).

Analysis of the quantitative infrared spectrum of fraction (3), the cyclodecene fraction, indicated the following concentrations of isomers: *cis*, 19%; *trans*, 69%.

Cyclodecyl-S-methyl Xanthate.—The procedure of O'Connor and Nace[20] was adapted for the preparation. To a solution of 20.1 g. (0.13 mole) of cyclodecanol in 450 ml. of reagent grade benzene was added 31 g. of sodium hydride. The mixture was stirred and refluxed for 20 hr. To the cooled solution was then added 254 g. of carbon disulfide, followed by another 20 hr. refluxing. After cooling to room temperature, 455 g. of methyl iodide was added to the mixture. The mixture again was refluxed for 24 hr.

Excess sodium hydride was hydrolyzed by the careful addition of 20 ml. of water after which the reaction mixture was poured into 200 ml. of water. The benzene solution was washed with water, dried and evaporated under reduced pressure to yield 34 g. of crude xanthate.

A small amount of the crude material was chromatographed on alumina (Merck) and eluted with 30–60° petroleum ether. The initial fraction, after removal of the solvent, was a clear, slightly yellow oil, $n^{20}\mathrm{D}$ 1.5577.

Anal. Calcd. for $C_{12}H_{22}S_2O$: C, 58.54; H, 8.94; S, 26.02. Found: C, 58.79; H, 8.77; S, 25.87.

The xanthate decomposed when attempts were made to distil it *in vacuo*.

Thermal Decomposition of Cyclodecyl-S-methyl Xanthate.—The decomposition of the xanthate was carried out by the procedure of Alexander and Mudrak.[10] A sample of crude xanthate (12 g.) was placed in a 100-ml. flask, equipped with a Friedrich condenser and a bubbler, and heated until vigorous bubbling indicated the onset of decomposition (about 130°). The temperature was maintained at 135–140° for 45 min., then raised to 195–205° for 10 min.

The mixture was cooled, transferred to a Claisen flask and distilled under water-pump vacuum, yielding 4.6 g. of a crude yellow mixture of cyclodecenes, b.p. 80–86° (17 mm.).

A 30–60° petroleum ether solution of the distillate was chromatographed on silica gel, removing the yellow contaminant. After removal of the solvent the residue was distilled to yield 1.2 g. (44%) of a mixture of cyclodecenes, b.p. 192–193° (744 mm.), $n^{20}\mathrm{D}$ 1.4820. Analysis of the quantitative infrared spectrum of this mixture showed the presence of the following concentrations of isomeric cyclodecenes: *cis*, 14%; *trans*, 86%.

Isomerization of *cis*- and *trans*-Cyclodecene. (A) By β-Naphthalenesulfonic Acid.—A mixture of cyclodecenes (1.1 g.), which analyzed for 14% *cis* and 77% *trans* was mixed with 50 mg. of β-naphthalenesulfonic acid and 50 mg. of hydroquinone. The flask was flushed with dry nitrogen, tightly stoppered and heated on a steam-bath for 22 hr. After filtration the mixture was distilled from a microdistilling flask to give a colorless liquid, b.p. 180–190° (740 mm.), $n^{20}\mathrm{D}$ 1.4848.

Analysis of the quantitative infrared spectrum indicated the following concentrations of isomers of cyclodecene: *cis*, 82%; *trans*, 16%.

(B) By Silver Nitrate.—A sample of a mixture of cyclodecenes (2.1 g.), which analyzed for 14% *cis* and 77% *trans*, was dissolved in a solution of 95% ethanol which contained 0.5 g. of silver nitrate. The solution was allowed to stand in the dark for 22 hr.

Dilution with water permitted the recovery of the cyclodecene fraction which was then washed with water, dried and distilled; b.p. 191° (740 mm.), $n^{20}\mathrm{D}$ 1.4818.

Analysis of the quantitative infrared spectrum of the distillate indicated the following concentrations of isomeric cyclodecenes: *cis*, 13%; *trans*, 78%.

(C) By Ultraviolet Radiation.—A sample of pure *cis*-cyclodecene, $n^{20}\mathrm{D}$ 1.4851, a sample of pure *trans*-cyclodecene, $n^{20}\mathrm{D}$ 1.4820, and a sample of a mixture of the isomeric cyclodecenes, $n^{20}\mathrm{D}$ 1.4836, which analyzed for 71% *cis* and 36% *trans*, were each placed in small quartz test-tubes. The tubes were flushed with dry nitrogen, tightly stoppered and exposed to ultraviolet light, from four 15-watt General Electric 360 BL fluorescent bulbs arranged in a semi-circular reflector, for 95 hr.

The refractive indices of the resulting samples were: *cis*-cyclodecene, $n^{20}\mathrm{D}$ 1.4851; *trans*-cyclodecene, $n^{20}\mathrm{D}$ 1.4822; mixture of *cis* and *trans*, $n^{20}\mathrm{D}$ 1.4839.

The infrared spectrum of the irradiated sample of the *cis* isomer did not show any absorption characteristic of the *trans* form; that of *trans*-cyclodecene did not show any absorption of the *cis* isomer.

Analysis of the quantitative infrared spectrum of the irradiated sample of the mixture of *cis*- and *trans*-olefins showed the following concentrations of cyclodecene isomers: *cis*, 64%; *trans*, 33%.

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[20] G. L. O'Connor and H. R. Nace, THIS JOURNAL, **74**, 5457 (1952).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF SMITH COLLEGE]

The Synthesis of *dl*-Cryptone

BY MILTON D. SOFFER AND MARGARET A. JEVNIK[1]

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The racemic form of the naturally occurring ketone, cryptone, 4-isopropyl-2-cyclohexenone, has been synthesized *via* Wilds–Nelson–Birch reduction of *p*-isopropylanisole and also by bromination of 4-isopropylcyclohexanone followed by dehydrobromination with collidine. The latter reaction produced a mixture of cryptone and the isomeric β,γ-unsaturated ketone, which were separated by fractionation. The β,γ-isomer also is convertible to cryptone through the α,β-unsaturated semicarbazone.

This paper is a report on two different syntheses of *dl*-cryptone (4-isopropyl-2-cyclohexenone). The first synthesis proceeds through the Birch reduction of *p*-isopropylanisole, which yields the enol ether, 2,5-dihydro-4-isopropylanisole.[2] In initial experiments the crude reduction[3] product was converted[4] directly to cryptone 2,4-dinitrophenylhydrazone in only 27% over-all yield. When, however, the reduction step was carried out with lithium by the new procedure of Wilds and Nelson,[4] similar treatment afforded the same derivative in 84% yield from *p*-isopropylanisole. Similarly, the Wilds–Nelson reduction product gave the pure α,β-unsaturated semicarbazone in good yield on boiling with methanolic semicarbazide hydrochloride. With somewhat

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[1] From the M.A. thesis of Margaret A. Jevnik, Research Fellow, 1952–1954.

[2] This derivative is apparently one of the products obtained recently by similar reduction of *p*-isopropenylanisole. In that case, however, further elaboration of the reduced material through the unsaturated ketone gave as the final product cryptone semicarbazone of somewhat low melting point in only about 7% over-all yield [A. Bhati, *Current Sci. India*, **21**, 314 (1952); *C. A.*, **48**, 1975 (1954)].

[3] A. J. Birch, *J. Chem. Soc.*, 593 (1946).

[4] A. L. Wilds and N. A. Nelson, THIS JOURNAL, **75**, 5361 (1953).