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CYCLIC POLYOLEFINS. XXXII.,
CIS- AND TRANS-1,3-DIPHENYLCYCLOOCTANE

by

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(Prepared for publication in the
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CYCLIC POLYOLEFINS. XXXII. CIS- AND TRANS-1,3-DIPHENYLCYCLOOCTANE¹.

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By Arthur C. Cope, Mark R. Kinter² and Richard T. Keller

(2) duPont Fellow, 1950-1951.

Received _____

Authentic samples of the two geometric isomers of 1,3-diphenylcyclooctane have been prepared and proved to be identical with the two isomers previously obtained from carbonyl-bridged intermediates. The synthetic route involved Friedel-Crafts addition of benzene to 2-cycloocten-1-one (III), followed by reaction of the resulting 3-phenylcyclooctanone (IV) with phenyllithium, dehydration of the tertiary alcohol, and reduction of the mixture of olefins that was formed. 2-Cycloocten-1-one was prepared by Oppenauer or chromic acid oxidation of 2-cycloocten-1-ol (II), obtained from the acetate (I), which in turn was prepared from 3-bromocyclooctene and silver acetate or cis-cyclooctene and mercuric acetate.

Convenient routes for the synthesis of eight-membered ring compounds from carbonyl-bridged intermediates have been described for the preparation of 2,4-diphenylcycloocta-1,4-diene, 2,4-diphenylcyclooctene and 3,5-

diphenylcyclooctene.³

Evidence for the structure of these compounds was

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- (3) A. C. Cope, F. S. Fawcett and G. Munn, This Journal, 72, 3599 (1950).
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based on ultraviolet absorption spectra, oxidative degradation, analogy with a similar synthesis of 1-phenylcycloocta-1,3-diene,⁴ and reduction to one or

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- (4) A. C. Cope and E. C. Hermann, *ibid.*, 72, 3405 (1950); D. F. Rugen, Ph.D. Thesis, Massachusetts Institute of Technology, 1952.
-

both of two solid hydrocarbons, believed to be the two geometric isomers of 1,3-diphenylcyclooctane.³ The presence of an eight-membered ring in the series of compounds was not definitely proved, but is established by the synthesis of cis- and trans-1,3-diphenylcyclooctane reported in this paper.

3-Bromocyclooctene, prepared from cis-cyclooctene and N-bromosuccinimide,⁵ was treated with silver acetate in glacial acetic acid at

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- (5) A. C. Cope and L. L. Estes, Jr., This Journal, 72, 1129 (1950).
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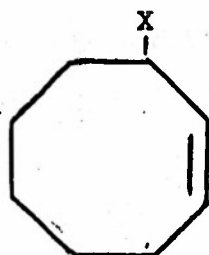
room temperature, and yielded 79% of 2-cycloocten-1-yl acetate (I) and 4% of 1,3-cyclooctadiene. The allylic acetate I also was prepared in 32% yield from cyclooctene and mercuric acetate,⁶ with 34% recovery of the olefin.

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- (6) Preparation of allylic acetates from cyclic olefins and mercuric acetate is described by W. Treibs and H. Bast, Ann., 561, 165 (1949).
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Saponification of the acetate I with potassium hydroxide in aqueous ethanol yielded 2-cycloocten-1-ol (II) (91%), which was characterized as the phenylurethan and by quantitative reduction to cyclooctanol.

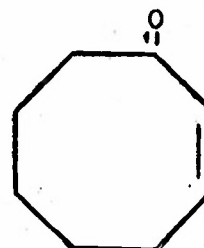
Oxidation of the alcohol II to the pure α,β -unsaturated ketone, 2-cycloocten-1-one (III) was accomplished by two oxidations with chromic acid

in aqueous acetic acid; a third oxidation did not change the intensity of the absorption maximum of III at 230 m μ . This oxidation procedure resulted in a poor yield of the pure ketone III, however, and Oppenauer oxidation with p-benzoquinone and aluminum isopropoxide in benzene was preferable. The latter procedure yielded 66% of the ketone III which was 92% pure according to the extinction coefficient at 230 m μ , and accordingly contained 8% of the alcohol I. The ketone III obtained by this procedure was sufficiently pure for use in the synthesis described below.



I, X = OCOCH₃

II, X = OH



III

Since 2-cyclohexen-1-one can be prepared directly by the oxidation of cyclohexene with chromic acid in acetic acid,⁷ an effort was made

(7) F. C. Whitmore and G. W. Pedlow, Jr., This Journal, 63, 758 (1941).

to prepare the ketone III by oxidation of cis-cyclooctene under similar conditions. The product obtained from cyclooctene, however, was cis-cyclooctene

oxide ⁸ (28%) rather than the ketone ⁹ III.

(8) K. Ziegler and H. Wilms, Ann., 567, 1 (1930); A. C. Cope, S. W. Fenton and C. S. Spencer, This Journal, 74, 5834 (1952).

(9) The oxidation of other (usually hindered) olefins to epoxides with chromic acid has been reported. See W. J. Hickinbottom and D. G. M. Wood, Nature, 168, 33 (1951).

Friedel-Crafts addition of benzene to the carbon-carbon double bond of the ketone III in the presence of aluminum chloride yielded 3-phenylcyclooctanone (IV) (51%). The ketone IV was isolated as a solid, m.p. 61-62.5°, and characterized further as the semicarbazone. The presence of an eight-membered ring in the ketone was established by reduction by a modified Wolff-Kishner method ¹⁰ to phenylcyclooctane, which was identified by

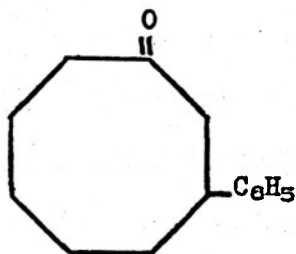
(10) Huang-Minlon, This Journal, 68, 2487 (1946).

comparison with an authentic sample.

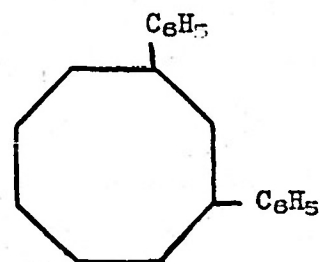
The reaction of phenyllithium with 3-phenylcyclooctanone yielded 1,3-diphenylcyclooctan-1-ol, a viscous, high-boiling liquid that was not isolated, but was dehydrated by heating with iodine in benzene solution. The product, which was isolated in 82% yield, presumably was a mixture of 1,3- and 2,4-diphenylcyclooctene; its ultraviolet spectrum (λ_{max} . 248 m μ , log ϵ 4.13 in cyclohexane) was very similar to the spectra of 2,4-diphenylcyclooctene ³ (λ_{max} . 248.5 m μ , log ϵ 4.00) and 1-phenylcyclooctene ¹¹ (λ_{max} . 248 m μ , log ϵ 4.07).

(11) A. C. Cope and A. A. D'Addieco, ibid., 73, 3419 (1951).

Catalytic hydrogenation of the mixture of 1,3- and 2,4-diphenylcyclooctanones with a palladium catalyst resulted in the absorption of 102% of one molar equivalent of hydrogen and formation of a mixture of the cis and trans forms of 1,3-diphenylcyclooctane (V). Fractional crystallization from methanol yielded the less soluble isomer, m.p. 83.5-85.8°, which was identical (by mixed melting point and comparison of infrared spectra) with the 1,3-diphenylcyclooctane isomer with the same melting point previously prepared from a carbonyl-bridged intermediate.³ The more soluble isomer was isolated from the methanol mother liquors as a slightly impure solid, m.p. 56-60°, which however did not give a melting point depression with the purer sample from the earlier synthesis (m.p. 60.6-61°). The two samples of the low-melting isomer also had infrared spectra that were identical within experimental error.



IV



Va, m.p. 83.5-85.8°

Vb, m.p. 60.6-61.0°

- (12) Melting points are corrected and boiling points are uncorrected. We are indebted to Dr. S. M. Nagy and his associates for analyses.

2-Cycloocten-1-yl Acetate (I). - A suspension of 23.2 g. of silver acetate in 50 ml. of glacial acetic acid was added in portions with stirring and cooling to a solution of 26.7 g. of 3-bromocyclooctene⁵ in 50 ml. of glacial acetic acid. The mixture was allowed to stand overnight and then was filtered to separate the silver bromide, which was washed with 75 ml. of acetic acid. The combined filtrates were concentrated by distillation through a 20 x 1.5-cm. column packed with glass helices to remove acetic acid. The distillate contained 1,3-cyclooctadiene, which was isolated by dissolving it in ether, washing with water and then with 5% aqueous sodium carbonate to remove acetic acid, drying over magnesium sulfate, and distilling through a semimicro column. The yield was 0.62 g. (4%), b.p. 74-76° (86 mm.), n_D^{25} after passing through a small column of silica gel to remove traces of ether 1.4901, λ_{max} 223-230 m μ (ϵ 5740 in cyclohexane) (compare properties in ref. 5). The residue remaining after distillation of the acetic acid was filtered to remove a small amount of solid and distilled through a semimicro column. The yield of 2-cycloocten-1-yl acetate was 18.7 g. (79%), b.p. 55-59° (1 mm.), n_D^{25} 1.4672. A redistilled analytical sample had the following physical properties: b.p. 57° (1 mm.), n_D^{25} 1.4630, d_4^{25} 0.9393.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 71.39; H, 9.59.

Found: C, 71.11; H, 9.49.

2-Cycloocten-1-yl acetate also was prepared by heating a mixture of 10.0 g. of cyclooctene, 29.0 g. of mercuric acetate and 10 ml. of

glacial acetic acid under reflux in an oil bath at 140° for 3 hours. The mixture was cooled, distilled rapidly at 1 mm., and the distillate was fractionated, yielding 4.83 g. (32%) of 2-cycloocten-1-yl acetate, b.p. 116-118° (30 mm.), n_D^{25} 1.4680. By the procedure described above for isolation of 1,5-cyclooctadiene, 3.4 g. (34%) of the cyclooctene was recovered from the acetic acid fraction.

2-Cycloocten-1-ol (II). - 2-Cycloocten-1-yl acetate (7.7 g.) was added to a solution of 5.2 g. of potassium hydroxide in 7 ml. of water and 15 ml. of ethanol, and the solution was allowed to stand for 4 hours with occasional shaking. The solution was diluted with 25 ml. of water and extracted with 50 and 25 ml. portions of ether. The extracts were washed with water, dried over magnesium sulfate, concentrated, and the residue was distilled through a semimicro column. The yield of 2-cycloocten-1-ol was 5.28 g. (91%), b.p. 74° (2 mm.), n_D^{25} 1.4959, d_4^{25} 0.9756.

Anal. Calcd. for $C_8H_{14}O$: C, 76.14; H, 11.18.

Found: C, 76.33; H, 11.18.

2-Cycloocten-1-ol also was prepared by treating 3-bromocyclooctene with silver acetate in acetic acid and adding the solution of the crude acetate to an excess of alcoholic potassium hydroxide. The yield of the alcohol by this procedure was 75%.

2-Cycloocten-1-yl Phenylurethan was prepared by warming 0.28 g. of 2-cycloocten-1-ol with 0.27 g. of phenyl isocyanate briefly and allowing the mixture to stand overnight in a stoppered tube. The solid product was extracted with hot ligroin and crystallized on cooling as colorless needles (0.39 g., 72%), m.p. 92.5-93°. Recrystallization did not change the melting point.

Anal. Calcd. for $C_{15}H_{13}NO_2$: C, 73.43; H, 7.81; N, 5.71.

Found: C, 73.55; H, 7.94; N, 5.70.

Hydrogenation of a solution of 0.415 g. of 2-cycloocten-1-ol in 4 ml. of acetic acid in the presence of 0.4 g. of prereduced platinum oxide was complete in 2 hours and 104% of one molar equivalent of hydrogen was absorbed. Cyclooctanol was isolated as the reduction product in a yield of 0.32 g. (76%) and identified as the phenylurethan by m.p. and mixed m.p.

2-Cycloocten-1-one (III). (a). - A solution of 4.2 g. of chromium trioxide in 2 ml. of water and 9 ml. of acetic acid was added dropwise in a period of 30 minutes with rapid stirring and cooling in an ice bath to a solution of 5.7 g. of 2-cycloocten-1-ol in 10 ml. of glacial acetic acid. The mixture was stirred at room temperature for 2 hours, partially neutralized by addition of a solution of 10.1 g. of potassium hydroxide in 30 ml. of water with cooling, and extracted continuously with ether for 12 hours. The extract was neutralized to phenolphthalein by addition of aqueous potassium hydroxide, and the aqueous layer was extracted with three portions of ether. The combined ethereal solutions were dried over magnesium sulfate, concentrated by distillation through a helix-packed column, and the residue was fractionated through a semimicro column, yielding 3.87 g. (69%) of a mixture of 2-cycloocten-1-one and 2-cycloocten-1-ol, b.p. 94-97° (15 mm.), n_D^{25} 1.4940. A redistilled sample was found to contain 58% of the ketone by comparison of its ultraviolet absorption spectrum with the spectrum of pure 2-cycloocten-1-one. A second oxidation of the mixture by a similar procedure gave the pure ketone, with physical constants that were not changed by a

third oxidation. The 2-cycloocten-1-one isolated after the third oxidation had b.p. 89° (14 mm.), n_D^{25} 1.4953, $\lambda_{\text{max.1}}$ 230 m μ (ϵ 7700), $\lambda_{\text{max.2}}$ 310 m μ (ϵ 80) (in 95% ethanol).

Anal. Calcd. for $C_8H_{12}O$: C, 77.38; H, 9.74. Found:
C, 77.38; H, 10.08.

(b). - 2-Cycloocten-1-one containing a small amount of 2-cycloocten-1-ol as an impurity was obtained conveniently by Oppenauer oxidation of the alcohol. A mixture of 10.1 g. of 2-cycloocten-1-ol, 43.2 g. of pure, dry p-benzoquinone, 16.3 g. of aluminum isopropoxide and 600 ml. of dry benzene was heated under reflux protected from atmospheric moisture for 30 minutes. The mixture was allowed to cool to room temperature and stand for 23 hours, after which it was again heated under reflux for 1 hour. After cooling the mixture with ice, 1 l. of 5% hydrochloric acid was added with shaking, and the benzene layer was combined with an ether extract of the aqueous layer. The solution was washed with three 700-ml. portions of 5% sodium hydroxide, then with water, and dried over magnesium sulfate. Distillation through a semimicro column after removal of the solvent through a helix-packed column yielded 6.48 g. (66%) of 2-cycloocten-1-one, b.p. $88-90^{\circ}$ (12 mm.), n_D^{25} 1.4961, that was 92% pure according to the intensity of the principal absorption maximum at 230 m μ (ϵ 7060 in 95% ethanol, compared to 7700 for the pure ketone).

Oxidation of Cyclooctene with Chromic Acid. - A solution of 15.4 g. of chromium trioxide in 9 ml. of water and 35 ml. of acetic acid was added dropwise with stirring over a period of several hours to a solution of 11.2 g. of cis-cyclooctene in 22 ml. of glacial acetic acid with cooling in ice. The mixture was allowed to stand at room temperature for 2 days, after

which 57 g. of potassium hydroxide in 200 ml. of water was added and the mixture was steam distilled. Ether extraction of the distillate followed by concentration and fractionation separated 0.9 g. of recovered cyclooctene and 3.56 g. (28%) of cyclooctene oxide, which after treatment with Girard's reagent to remove a very small amount of a ketonic impurity had m.p. and mixed m.p. with an authentic sample⁸ of 57-59°.

3-Phenylcyclooctanone (IV). - 2-Cyclooctan-1-one (6.2 g., from procedure b above) was added in one portion to a stirred mixture of 33.3 g. of powdered anhydrous aluminum chloride and 500 ml. of dry benzene. The mixture was stirred and heated under reflux for 3.5 hours, after which it was cooled in ice and shaken with a mixture of 500 ml. of ice water and 100 ml. of concentrated hydrochloric acid. The organic layer was separated, combined with a 250-ml. ether extract of the aqueous layer, washed three times with water, and dried over magnesium sulfate. After removal of the solvent, distillation yielded 7.7 g. of crude 3-phenylcyclooctanone, b.p. 75-134° (0.3 mm.). A mixture of the crude product and 7.63 g. of Girard's reagent "T" in 10 ml. of glacial acetic acid and 100 ml. of absolute ethanol was heated under reflux for 1 hour. The solution was cooled, poured into 400 ml. of ice water containing 8 g. of sodium carbonate, and non-ketonic material was removed by extraction with two 200-ml. portions of ether. Concentrated hydrochloric acid (25 ml.) was added to the aqueous solution, and after 1 hour the product was extracted with two 200-ml. portions of ether. The extracts were washed with water, dried over magnesium sulfate, and concentrated. Distillation through a semimicro column yielded 5.11 g. (51%) of 3-phenylcyclooctanone, b.p. 118-121° (0.5 mm.). The ketone solidified

rapidly, and was recrystallized to a constant melting point of 61-62.5° from 5:1 methanol-water.

Anal. Calcd. for $C_{14}H_{18}O$: C, 85.12; H, 8.97. Found:

C, 85.21; H, 9.04.

3-Phenylcyclooctanone Semicarbazone was prepared by heating 50 mg. of the ketone, 31 mg. of semicarbazide hydrochloride and 25 mg. of sodium acetate in 2 ml. of 50% ethanol. The semicarbazone (52 mg., m.p. 170-171°) was recrystallized from 2:1 ethanol-water as white leaflets, m.p. 173-174°.

Anal. Calcd. for $C_{15}H_{21}N_3O$: C, 69.46; H, 8.16. Found:

C, 69.67; H, 8.29.

3-Phenylcyclooctanone (0.15 g.) was reduced to phenylcyclooctane by heating with 0.5 g. of potassium hydroxide and 1.0 ml. of 85% hydrazine hydrate in 10 ml. of diethylene glycol in a bath at 180° for 1.5 hours, and then at 210° for 3 hours while about 2 ml. of liquid distilled. The solution was cooled, combined with the distillate, and poured into 50 ml. of water, which was extracted with two 25-ml. portions of ether. The extracts were washed with water, dried over magnesium sulfate and concentrated. The residue was distilled through a semimicro column, yielding 90 mg. (64%) of phenylcyclooctane, b.p. approximately 95° (0.3 mm.), n_D^{25} 1.5304, m.p. 5.8-7.5° and mixed m.p. with an authentic sample ¹¹ 6.2-8.0°.

1,3- and 2,4-Diphenylcyclooctenes. - A solution of 2.02 g. of 3-phenylcyclooctanone in 20 ml. of dry ether was added with stirring during a period of 5 minutes in a nitrogen atmosphere to the phenyllithium prepared from 4.72 g. of bromobenzene and 0.46 g. of lithium in 40 ml. of ether. The

mixture was heated under reflux for 0.5 hour, after which 50 ml. of water was added with cooling and stirring. The ether layer was combined with an ethereal extract of the aqueous layer, washed with water, and dried over magnesium sulfate. One-fifth of the solution was reserved for (unsuccessful) attempts to purify the tertiary alcohol, and the remaining four-fifths was concentrated. A solution of the residue in 50 ml. of benzene was heated under reflux with 50 mg. of iodine for 6 hours, with separation of the small amount of water formed in a Dean and Stark separator. The solution was cooled, washed with sodium thiosulfate solution and water, and concentrated. The residue was heated in a short-path still for 2.5 hours at 150° and 0.5 mm. to remove biphenyl, and then was distilled with a heating block temperature of 200-250° (0.5 mm.). A solution of the distillate in 50 ml. of pentane was again washed with sodium thiosulfate solution, water, and concentrated. Slow distillation of the residue in a short-path still at 0.5 mm. with a heating block temperature of 170° yielded 1.71 g. (80%) of a mixture of 1,3- and 2,4-diphenylcyclooctenes as a viscous liquid, n_D^{25} 1.5954.

Anal. Calcd. for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found:
C, 91.23; H, 8.51.

1,3-Diphenylcyclooctane (V). - A solution in 10 ml. of acetic acid of 0.466 g. of the mixture of 1,3- and 2,4-diphenylcyclooctenes described above was hydrogenated at room temperature and atmospheric pressure in the presence of 0.45 g. of 10% palladium on Norit. Reduction was complete

in 45 minutes and resulted in absorption of 102% of one molar equivalent of hydrogen. The catalyst was separated, washed with acetic acid and pentane, and the filtrates were washed with water and sodium carbonate solution to remove acetic acid. Concentration of the pentane solution yielded 0.456 g. of a mixture of cis- and trans-1,3-diphenylcyclooctanes as an oil which solidified, m.p. 54-66°. The mixture was fractionally crystallized from methanol, and after nine crystallizations the least soluble isomer had m.p. 83.5-85.8° and mixed m.p. with a sample prepared by hydrogenation of 2,4-diphenylcycloocta-1,4-diene³ (m.p. 83.6-85.1°) of 83.2-85.8°. Recrystallization of the more soluble isomer obtained from the mother liquors yielded a slightly impure sample, m.p. 56-60° and mixed m.p. with a sample obtained by hydrogenation of 2,4-diphenylcyclooctene³ (m.p. 62.6-61.0°) of 56.5-60°.

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