platinum oxide in 25 ml. of absolute ethanol and hydrogenated at atmospheric pressure. Three molar equivalents of hydrogen was absorbed in 10 minutes, and 106% of four molar equivalents in 24 hours. The catalyst was separated and the solution was concentrated by fractionation through a semimicro column at atmospheric pressure. Distillation of the residue yielded 0.275 g. (54%) of cycloöctyl ethyl ether, $n^{25}\text{D}$ 1.4570, with an infrared spectrum indicating the presence of about 10% of a carbonyl compound as an impurity. A solution of the ether in 6 ml. of absolute ethanol was heated under reflux for 1 hour with 1.0 g. of Girard's reagent T and 1 ml. of glacial acetic acid. The solution was cooled, poured into 50 ml. of ice-water containing 0.9 g. of sodium carbonate, and extracted with four 15-ml. portions of ether. The extracts were dried over magnesium sulfate and distilled and yielded 0.042 g. of cycloöctyl ethyl ether, $n^{25}\text{D}$ 1.4553, with an infrared spectrum identical with the authentic sample described below except for weak absorption at 5.82 μ due to the presence of a trace of a carbonyl compound as an impurity.

Cycloöctyl Ethyl Ether.—A solution of 2.62 g. of cyclooctanol in 25 ml. of dry benzene was heated under reflux with 1.0 g. of sodium hydride for 12 hours, after which 25 ml. of ethyl iodide was added and heating was continued for an additional period of 20 hours. The mixture was washed with water and concentrated slowly by distillation through a semimicro column under reduced pressure at room temperature. Fractionation of the residue yielded 1.56 g. (41%) of colorless cycloöctyl ethyl ether, b.p. 85–86° (16 mm.), $n^{25}\text{D}$ 1.4540, d^{25}_4 0.888.

Anal. Calcd. for $C_{10}H_{20}O$: C, 76.84; H, 12.90. Found: C, 76.72; H, 12.78.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Cyclic Polyolefins. XXXI. Cycloheptatriene and Bicyclo[4.2.0]octa-2,4-diene Derivatives from Cycloöctatetraene and Mercuric Acetate

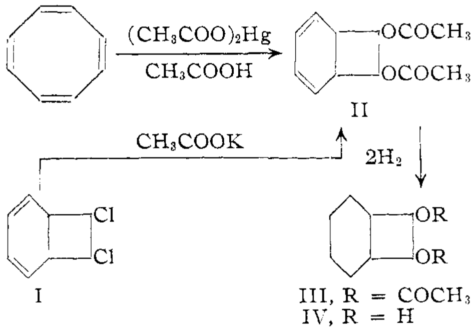
BY ARTHUR C. COPE, NORMAN A. NELSON AND DOUGLAS S. SMITH[1]

RECEIVED OCTOBER 7, 1953

The reaction of cycloöctatetraene with mercuric sulfate (or mercuric acetate) in water forms phenylacetaldehyde as previously reported,[2] but cycloöctatetraene and mercuric acetate in glacial acetic acid form bicyclo[4.2.0]octa-2,4-diene-7,8-diol diacetate (II, 72%) rather than phenylethylidene diacetate, while the same reactants in methanol yield 2,4,6-cycloheptatriene-1-carboxaldehyde dimethyl acetal (V, 88%), instead of phenylacetaldehyde dimethyl acetal. The principal product of the reaction of cycloöctatetraene dichloride (I) and sodium methoxide in methanol also is 2,4,6-cycloheptatriene-1-carboxaldehyde dimethyl acetal (V), rather than the bicyclic isomer XVI as previously formulated.[2]

Reppe, Schlichting, Klager and Toepel[2] have reported the conversion of cycloöctatetraene into phenylacetaldehyde or derivatives of that aldehyde through reaction with mercuric salts in hydroxylic solvents. The products stated to be formed from cycloöctatetraene were phenylacetaldehyde (70%) with mercuric sulfate and water, phenylethylidene diacetate (96%) with mercuric acetate and acetic acid and phenylacetaldehyde dimethyl acetal (78%) with mercuric acetate and methanol. Reinvestigation of these reactions has shown that the products formed in acetic acid and in methanol have structures different from those originally assigned.

The reaction of cycloöctatetraene with mercuric acetate in glacial acetic acid at 70–80° under the conditions previously described[2] yielded 72% of a crystalline compound, $C_{12}H_{14}O_4$, which after recrystallization melted at 61.4–62.5° and undoubtedly is the same product previously obtained from this reaction by Reppe, Schlichting, Klager and Toepel (reported m.p. 64–65°).[2] These authors state that this compound is phenylethylidene diacetate, but that substance as prepared from phenylacetaldehyde and acetic anhydride is a liquid.[3] Another compound with the formula $C_{12}H_{14}O_4$ that was first prepared by Reppe, Schlichting, Klager and Toepel from cycloöctatetraene dichloride (I) and potassium acetate is bicyclo[4.2.0]octa-2,4-dien-7,8-diol diacetate (II), reported as a solid with a melting point of 66°.[2] Proof that the product obtained from cycloöctatetraene and mercuric acetate in acetic acid also has structure II was obtained by quantitative reduction in the presence of a palladium catalyst with the absorption of 102% of two molar equivalents of hydrogen and formation of bicyclo[4.2.0]octane-7,8-diol diacetate (III) (92%), which on hydrolysis yielded *trans*-bicyclo[4.2.0]octane-7,8-diol (IV), m.p. 139.1–140.2°, identical with an authentic sample prepared by hydrogenation of bicyclo[4.2.0]octan-7-ol-8-one.[4]



II

I

III, R = $COCH_3$
IV, R = H

The reaction of cycloöctatetraene with mercuric acetate in methanol formed a liquid product, $C_{10}H_{14}O_2$ (V), in 88% yield. Although Reppe, Schlichting, Klager and Toepel stated that this reaction yielded phenylacetaldehyde dimethyl acetal, the infrared spectrum of the product (Fig. 1) indicated that it was not an aromatic compound, and the ultraviolet spectrum had a broad maximum at 258.5 mμ such as would be expected for a conjugated triene. Quantitative reduction of the

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(1) Atomic Energy Commission Fellow, 1951–1952.

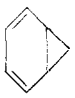
(2) W. Reppe, O. Schlichting, K. Klager and T. Toepel, *Ann.*, **560**, 1 (1948).

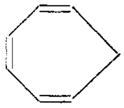
(3) A. Wohl and R. Maag, *Ber.*, **43**, 3293 (1910); E. Späth, *Monatsh.*, **36**, 41 (1915).

(4) A. C. Cope and E. C. Herrick, THIS JOURNAL, **72**, 983 (1950).

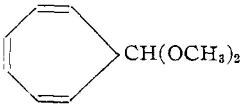
compound in the presence of palladium under conditions that would not result in reduction of an aromatic structure proceeded with the absorption of 101% of three molar equivalents of hydrogen. The reduction product (VI), which was isolated in 77% yield, was a liquid with the empirical formula $C_{10}H_{20}O_2$. The structure of VI was established as cycloheptanecarboxaldehyde dimethyl acetal by conversion to cycloheptanecarboxaldehyde semicarbazone (m.p. 155–156.5°) and 2,4-dinitrophenylhydrazone (m.p. 134.5–135.5°). An authentic sample of the acetal VI was prepared from cycloheptylmagnesium bromide and methyl orthoformate, and had the same properties (including the infrared spectrum) as VI obtained by hydrogenation of V.

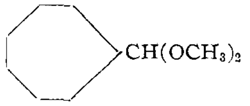
It appeared possible that the unsaturated acetal V could be a derivative of norcaradiene (VII) or cycloheptatriene (VIII), since each could be reduced to a cycloheptane ring with the absorption of three equivalents of hydrogen, with cleavage of the cyclopropane ring accounting for the third equivalent of hydrogen in the case of VII. In the acetal V the $-CH(OCH_3)_2$ side chain might be attached to any of the four different positions in VII or in VIII. Choice between these eight structures proved to be possible by a combination of spectroscopic and chemical evidence.


VII


VIII

The unsaturated acetal V was treated with 2,4-dinitrophenylhydrazine hydrochloride in ethanol at 0°[5] and converted in 93% yield into a 2,4-dinitrophenylhydrazone with an ultraviolet absorption spectrum characteristic of an aldehyde without unsaturation in conjugation with the dinitrophenylhydrazone chromophore (λ_{max_1} 260 mμ, ε 14,900; λ_{max_2} 356 mμ, ε 23,300).[6] This evidence indicates that the $-CH(OCH_3)_2$ side chain is not located on a carbon atom attached to a double bond. It also indicates that the acetal group is not attached to a carbon atom that forms part of the cyclopropane ring in VII, for in such a structure the absorption maximum also would be expected to occur at a wave length longer than 356 mμ.[7] The most probable structure for the unsaturated acetal therefore is 2,4,6-cycloheptatriene-1-carboxaldehyde dimethyl acetal (V).


V


VI

The infrared spectrum of the unsaturated acetal V has two absorption bands at 1000 and 1008 cm.$^{-1}$, a region in which cyclopropane derivatives have an absorption band.[8] Partial hydrogenation of V therefore was investigated, since in a number of compounds containing both an olefin group and a cyclopropane ring it is possible to reduce the ethylenic linkage preferentially.[9] Reduction of V in methanol at 0° in the presence of 1% palladium-on-calcium carbonate resulted in rapid absorption of two molar equivalents of hydrogen, after which the rate of hydrogenation decreased sharply and the reduction was stopped. The partial hydrogenation product that was isolated in 87% yield did not have infrared absorption bands in the region of 1000–1010 cm.$^{-1}$ characteristic of cyclopropane derivatives, but did have bands characteristic of an olefin. Continued hydrogenation of the partial reduction product in the presence of 10% palladium-on-Norit resulted in rapid absorption of 90% of a third molar equivalent of hydrogen, and yielded cycloheptanecarboxaldehyde dimethyl acetal (VI), isolated as cycloheptanecarboxaldehyde 2,4-dinitrophenylhydrazone in 93% yield. The partial reduction product of V probably is a mixture composed principally of IX and X, for it yielded a mixture of 2,4-dinitrophenylhydrazones with a melting point of 139–141°, which was raised to a constant value of 153–153.5° by a series of 14 recrystallizations. Evidence that this pure dinitrophenylhydrazone was derived from IX or X was obtained by boiling it with hydrochloric acid in ethanol briefly; it was recovered unchanged after this treatment, which usually isomerizes β,γ-double bonds to the α,β-position.[5,10]

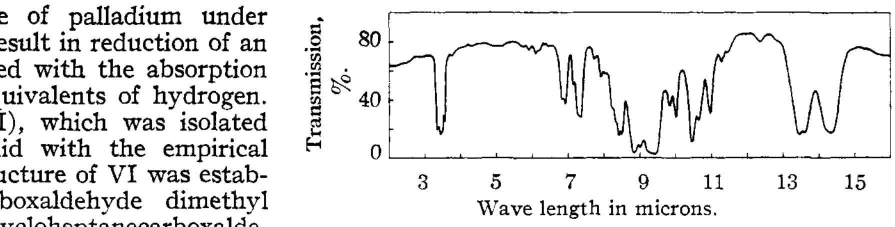
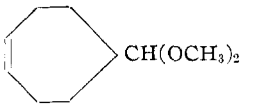
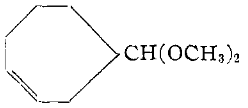


Fig. 1.—Infrared spectrum of 2,4,6-cycloheptatriene-1-carboxaldehyde dimethyl acetal (V) without solvent in a 0.025-mm. cell.


IX


X

It is of interest to consider how the reaction of cycloöctatetraene with mercuric acetate in water, acetic acid and methanol can lead to products with three different ring systems. An addition compound is formed in each solvent, and it seems likely that the reaction paths differ in the decomposition of the addition compound through reaction with the solvents, forming mercury and the organic products. An ion such as XIA could be formed by addition, and XIB by neighboring group participation. The ions XIC and XID could be formed by

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(5) These conditions ordinarily do not cause migration of double bonds from the β,γ- to the α,β-position in ketone 2,4-dinitrophenylhydrazones. For example, see A. J. Birch, *J. Chem. Soc.*, 593 (1946).

(6) E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, 498 (1945).

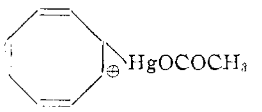
(7) J. D. Roberts and C. Green, THIS JOURNAL, **68**, 214 (1946); E. P. Carr and C. P. Burt, *ibid.*, **40**, 1590 (1918); I. M. Klotz, *ibid.*, **66**, 88 (1944). A sample of cyclopropanecarboxaldehyde 2,4-dinitrophenylhydrazone kindly furnished by Dr. Roberts had a maximum at 365 mμ (ε 23,300) (in chloroform).

(8) J. M. Derfer, E. E. Pickett and C. E. Boord, *ibid.*, **71**, 2482 (1949).

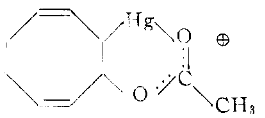
(9) For example see R. Van Volkenburgh, K. W. Greenlee, J. M. Derfer and C. E. Boord, *ibid.*, **71**, 172 (1949).

(10) A. L. Wilds and N. A. Nelson, *ibid.*, **75**, 5360 (1953).

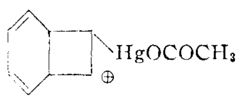
valence tautomerism from XIA and XIB, just as 1,3,5-cycloöctatriene bridges to form bicyclo[4.2.0]octa-2,4-diene.[11] Each of these ions has an equivalent resonance form (not shown) that would be produced by addition of mercuric acetate in the opposite direction to the double bond. Reaction of acetic acid with any of the four ions XIA-D could lead to the formation of II, with cleavage of the carbon–mercury bond and formation of mercury and acetic acid. Bridging by valence tautomerism would follow solvolysis in formation of II from XIA or XIB.



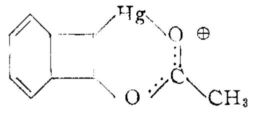
XIA



XIB

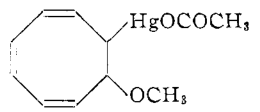


XIC

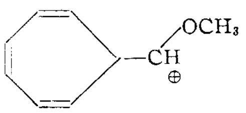


XID

In the reaction of the ionic intermediates with methanol leading to the formation of V, ring contraction could occur through an intermediate such as XII, forming an ion like XIII which would react with methanol to yield V.

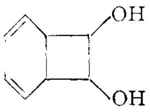


XII

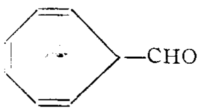


XIII

Both bicyclo[4.2.0]octa-2,4-diene-7,8-diol (XIV) and 2,4,6-cycloheptatriene-1-carboxaldehyde (XV) are possible intermediates in the reaction of cyclooctatetraene with mercuric salts in water forming phenylacetaldehyde, for treatment of both the diacetate II and the acetal V with aqueous acids or treatment of V with ethanolic phosphoric acid yielded phenylacetaldehyde, isolated as the 2,4-dinitrophenylhydrazone in each case.



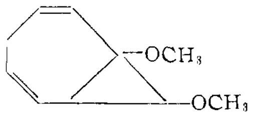
XIV



XV

Electronic displacements can be postulated in intermediate ions produced in the formation of XIV or ions formed by the addition of a proton to an oxygen or double bond of XIV that would lead to phenylacetaldehyde by opening the four-membered ring. Bridging of XV to a norcaradiene aldehyde followed by opening of the three-membered ring might explain the formation of phenylacetaldehyde, although the possibility that XV might be converted to an open chain octadienal that could undergo an intramolecular aldol condensation forming phenylacetaldehyde, or to an intermediate bicyclic system such as XIV which could follow the path to phenylacetaldehyde described above cannot be excluded. These possible interpretations are not presented in detail because there is no experimental evidence bearing on their validity.

Reppe, Schlichting, Klager and Toepel state that the reaction of cycloöctatetraene dichloride (I) with sodium methoxide in methanol forms a product with structure XVI, which on hydrogenation followed by acid hydrolysis yields cycloheptanecarboxaldehyde.[2] The physical constants of their product (with the exception of the refractive index, n^{20}D 1.0588, which appears to be a misprint) were very similar to those observed for 2,4,6-cycloheptatriene-1-carboxaldehyde dimethyl acetal (V) in the present work. Reinvestigation of the reaction of cycloöctatetraene dichloride with sodium methoxide showed that the product, isolated in 69% yield, was the acetal V. This fact was established by comparison of the infrared spectrum of V prepared from I with the pure sample described above, and by conversion to the 2,4-dinitrophenylhydrazone of XV. Hydrogenation of V prepared from I in the presence of palladium-on-Norit formed cycloheptanecarboxaldehyde dimethyl acetal (VI, 72%), with an infrared spectrum identical with the spectrum of an authentic sample.



XVI

The conversion of cycloöctatetraene dichloride into chlorocycloöctatetraene and β-chlorostyrene by treatment with bases and thermal rearrangement has been reported.[12] A yellow forerun in the distillation of V prepared from I that was not investigated further probably contained chlorocyclooctatetraene, while the ultraviolet spectrum of V obtained in this way (λ_{max} 261 mμ, ε 5,010) indicated the presence of a styrene derivative with strong ultraviolet absorption as a contaminant, for pure V has λ_{max} 258.5 mμ (ε 3,630).

Further study of the properties and reactions of 2,4,6-cycloheptatriene-1-carboxaldehyde dimethyl acetal (V) is in progress.

Experimental[13]

Phenylacetaldehyde.—Cycloöctatetraene (26.0 g.) was added to a suspension of 74.5 g. of mercuric sulfate in 190 ml. of water according to the procedure of ref. 2, p. 45. The products that were isolated were 44.7 g. (89%) of mercury and 16.2 g. (54%) of phenylacetaldehyde, b.p. 79° (11 mm.), n^{25}D 1.5232. The phenylacetaldehyde was identified by comparison of its spectrum with the spectrum of an authentic sample, and by conversion in 97% yield into the 2,4-dinitrophenylhydrazone with 2,4-dinitrophenylhydrazine hydrochloride in ethanol (m.p. and mixed m.p. after recrystallization from benzene–ethanol, 125–126°). Phenylacetaldehyde also was obtained by shaking 5.2 g. of cycloöctatetraene with a suspension of 16 g. of mercuric acetate in 100 ml. of water. An exothermic reaction occurred and separation of mercury began at once. The mixture was allowed to stand overnight, after which phenylacetaldehyde (1.11 g. or 19%) was isolated by extraction and distillation, and identified by its infrared spectrum.

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(11) A. C. Cope, A. C. Haven, Jr., F. L. Ramp and E. R. Trumbull, THIS JOURNAL, **74**, 4867 (1952).

(12) A. C. Cope and M. Burg, *ibid.*, **74**, 168 (1952).

(13) Melting points are corrected and boiling points are uncorrected. We are indebted to Dr. S. M. Nagy and his associates for analyses and for the spectra, which were determined with a Cary Ultraviolet Recording Spectrophotometer, model 11 MS, and a Baird Double Beam Infrared Recording Spectrometer, model B, fitted with a sodium chloride prism.

Bicyclo[4.2.0]octa-2,4-diene-7,8-diol Diacetate (II).—Cycloöctatetraene (10.4 g.) was added rapidly to a stirred suspension of 32.0 g. of mercuric acetate in 80 ml. of glacial acetic acid. The white addition compound that formed was decomposed by heating the mixture at 70–80° for 2 hours, after which the mercury that was formed was separated and the filtrate was added to 800 ml. of cold water. The oil that separated solidified after stirring for a short time and was collected on a filter and dried, yielding 15.9 g. (72%) of II, m.p. 55.5–59°. One recrystallization from aqueous acetic acid yielded 11.2 g., m.p. 60–61°. An analytical sample that was recrystallized from 95% ethanol melted at 61.4–62.5° (reported m.p. is 66° in ref. 2, p. 57).

Anal. Calcd. for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 64.67; H, 6.52.

Hydrogenation of a solution of 2.0 g. of II in 25 ml. of methanol in the presence of 1.0 g. of 10% palladium-on-Norit was complete in 2 hours and 102% of two molar equivalents of hydrogen was absorbed. Distillation of the reduction product through a semi-micro column yielded 1.9 g. (92%) of bicyclo[4.2.0]octane-7,8-diol diacetate, b.p. 90.5–92° (0.5 mm.), n^{25}D 1.4653 (reported in ref. 2, p. 57, with b.p. 105° at 0.4 mm., n^{20}D 1.4662).

Anal. Calcd. for $C_{12}H_{18}O_4$: C, 63.70: H, 8.02. Found: C, 63.87; H, 8.20.

A solution of 0.58 g. of the saturated diacetate described above in 2 ml. of methanol containing 3 drops of concentrated hydrochloric acid was warmed slowly while the methyl acetate that was formed and most of the methanol were distilled through a semi-micro column. Crystallization of the residue from benzene yielded 0.26 g. (71%) of *trans*-bicyclo[4.2.0]octane-7,8-diol (III), m.p. 139.1–140.2°. A mixed melting point of III from this source with an authentic sample prepared by hydrogenation of bicyclo[4.2.0]octan-7-ol-8-one[4] was not depressed.

2,4,6-Cycloheptatriene-1-carboxaldehyde Dimethyl Acetal (V).—A suspension of 79.7 g. of mercuric acetate in 400 ml. of methanol was cooled to 10° and stirred in a nitrogen atmosphere, and a solution of 26 g. of cycloöctatetraenen in 100 ml. of methanol was added rapidly. A white addition compound separated quickly, which was decomposed by stirring at room temperature for 2 hours and at 60–64° for 2 hours. The organic layer was separated from the mercury that was formed (49.4 g., 98.5%) by decantation, and concentrated to a volume of about 100 ml. The concentrate was diluted with 400 ml. of ether, washed with dilute sodium hydroxide until the acetic acid formed in the reaction was neutralized, then with water, and dried over sodium sulfate. Distillation through a column with a 15-cm. platinum spiral yielded 36.6 g. (88%) of V, b.p. 90–92° (10 mm.), n^{25}D 1.5004, d^{25}_4 1.006, $\lambda_{\max}$ 258.5 mμ (ϵ 3630) (in cyclohexane). In a preparation in which the addition complex was shaken with methanol for 15 hours at room temperature, the same product was obtained in 82% yield.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.37; H, 8.57.

2,4,6-Cycloheptatriene-1-carboxaldehyde 2,4-dinitrophenylhydrazone was prepared by adding a solution of 1.0 g. of V in 10 ml. of 95% ethanol to a solution of 1.4 g. of 2,4-dinitrophenylhydrazine and 7 ml. of concentrated hydrochloric acid in 85 ml. of 95% ethanol at 0°. The mixture was stirred at 0° for 8 hours, filtered, and the brown solid was washed with cold ethanol, water, 10% sodium carbonate solution and water. The derivative was obtained in a yield of 1.68 g. (93%) after drying, m.p. 139° (dec., introduced at room temperature). Four recrystallizations from benzene–ethanol (containing several drops of pyridine in the first crystallization to prevent acid-catalyzed isomerization of the double bonds[10] gave an analytical sample of 2,4,6-cycloheptatriene-1-carboxaldehyde 2,4-dinitrophenylhydrazone that was orange-brown in color and melted at 137° (dec., inserted at room temperature), or at 149° (dec., inserted at 145–147°), $\lambda_{\max_1}$ 260 mμ (ϵ 14,900), $\lambda_{\max_2}$ 356 mμ (ϵ 23,300) (in chloroform).

Anal. Calcd. for $C_{14}H_{12}N_4O_4$: C, 56.00; H, 4.03. Found: C, 56.24; H, 4.22.

When the unsaturated acetal V was treated with 2,4-dinitrophenylhydrazine and phosphoric acid in ethanol, or hydrolyzed with dilute sulfuric acid and then treated with 2,4-dinitrophenylhydrazine hydrochloride in ethanol, crude mixtures were obtained from which the 2,4-dinitrophenylhydrazone of phenylacetaldehyde was isolated.

Cycloheptanecarboxaldehyde Dimethyl Acetal (VI) (a).—A solution of 2.7 g. of V in 25 ml. of methanol was hydrogenated in the presence of 1.0 g. of 10% palladium-on-Norit. The reduction was complete in 4 hours and 101% of three molar equivalents of hydrogen was absorbed. After separation of the catalyst, distillation through a semi-micro column yielded 2.1 g. (77%) of VI, b.p. 79–80.5° (6 mm.), n^{25}D 1.4499–1.4508. A sample with n^{25}D 1.4499 was analyzed.

Anal. Calcd. for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70. Found: C, 69.93; H, 11.79.

Cycloheptanecarboxaldehyde semicarbazone was prepared by heating a solution of 0.5 g. of VI and 0.75 g. of semicarbazide hydrochloride in 10 ml. of methanol and 4 ml. of water on a steam-bath for 5 minutes, and then for 5 minutes longer after adding 1 ml. of pyridine and 2 ml. of water. The mixture was cooled overnight and then filtered to separate 0.257 g. of cycloheptanecarboxaldehyde semicarbazone as colorless needles, m.p. 156–158°. After two recrystallizations from benzene–petroleum ether the derivative melted at 155–156.5° (reported m.p. 155–156°[2] and 153–154°[14]).

(b).—Cycloheptylmagnesium bromide was prepared from 13.0 g. of cycloheptyl bromide[15] and 1.76 g. of magnesium in 55 ml. of dry ether. Methyl orthoformate[16] (7.5 g.) was added dropwise during 15 minutes to the Grignard reagent. The mixture was stirred under reflux for 6 hours, after which 15 g. of ice and 50 ml. of 10% aqueous ammonium chloride were added. The aqueous layer was extracted with ether, and the combined ethereal solutions were washed with 10% ammonium chloride, water and dried over sodium sulfate. After distillation of the solvent, fractionation of the residue through a semi-micro column yielded 1.13 g. of VI, b.p. 86–88° (10 mm.), n^{25}D 1.4483–1.4490. A redistilled sample with n^{25}D 1.4498 had an infrared spectrum identical with the acetal VI prepared by hydrogenation of V, described under (a) above.

Cycloheptanecarboxaldehyde 2,4-dinitrophenylhydrazone was prepared from both samples of VI described under (a) and (b) above in yields of 80–97% by treatment with a slight excess of 2,4-dinitrophenylhydrazine hydrochloride in ethanol at room temperature for 1 hour, followed by cooling. An analytical sample was recrystallized from benzene–ethanol as long orange-yellow needles, m.p. 134.5–135.5°, $\lambda_{\max}$ 359 mμ (ϵ 21,900) (in chloroform).

Anal. Calcd. for $C_{14}H_{18}N_4O_4$: C, 54.89; H, 5.92. Found: C, 54.87; H, 5.85.

Partial Hydrogenation of V.—A solution of 3.324 g. of V in 35 ml. of methanol was hydrogenated at 0° in the presence of 0.6 g. of 1% palladium-on-calcium carbonate.[17] A sharp break in the rate of hydrogenation occurred just after two molar equivalents of hydrogen had been absorbed (50 minutes), and the reduction was stopped at that point. Distillation of the product through a semi-micro column yielded 0.19 g. of a forerun, b.p. 89–91° (12.5 mm.), n^{25}D 1.4603, followed by 2.98 g. (88%) of a colorless liquid, b.p. 91–92° (12.5 mm.), n^{25}D 1.4593–1.4600. A fraction with nD^{25} 1.4593 was analyzed.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.71; H, 10.62

Evidence that the partial hydrogenation product was not homogeneous and probably contains both IX and X was obtained by its conversion in 98% yield into an orange-yellow mixture of 2,4-dinitrophenylhydrazones, m.p. 139–141°, by treatment with 2,4-dinitrophenylhydrazine hydrochloride in ethanol at 0° for 1 hour. Fourteen recrystallizations from benzene–ethanol raised the melting point gradually to a constant value of 153–153.5°, $\lambda_{\max}$ 359 mμ (ϵ 23,500) (in chloroform).

Anal. Calcd. for $C_{14}H_{16}N_4O_4$: C, 55.25; H, 5.30. Found: C, 55.45; H, 5.63.

Evidence that this derivative is cyclohept-3- or 4-ene-1-carboxaldehyde 2,4-dinitrophenylhydrazone was obtained by heating a solution of the compound in ethanol containing a few drops of concentrated hydrochloric acid on a steam-

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(14) O. Wallach, *Ann.*, **345**, 149 (1906).

(15) A. I. Vogel, *J. Chem. Soc.*, 1323 (1938).

(16) P. P. T. Sah and T. S. Ma, THIS JOURNAL, **54**, 2964 (1932).

(17) M. Busch and H. Stöve, *Ber.*, **49**, 1063 (1916).

bath for 5 minutes. The derivative was recovered unchanged after this treatment, which has been shown in other cases to isomerize β,γ- to α,β-unsaturated dinitrophenylhydrazones.[5,10]

A solution of 0.322 g. of the partially hydrogenated acetal described above in 10 ml. of methanol was reduced in the presence of 0.05 g. of 10% palladium-on-Norit; hydrogen absorption amounted to 90% of one molar equivalent and was complete in 1 hour. Treatment of the reduction product (not isolated) with 2,4-dinitrophenylhydrazine hydrochloride in ethanol gave 0.541 g. (93%) of cycloheptanecarboxaldehyde 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. with an authentic sample 133–134.5°.

Reaction of Cyclooctatetraene Dichloride with Sodium Methoxide in Methanol.—Cycloöctatetraene dichloride[2,12] (42.5 g.) was added with stirring at 0° to a solution of sodium methoxide prepared from 12.0 g. of sodium and 200 ml. of dry methanol. The mixture was stirred at 0° for 2 hours, at room temperature for 1.5 hours, and then was heated under reflux for 3 hours (a mildly exothermic reaction occurred on heating to the reflux temperature). The mixture was allowed to stand at room temperature overnight, filtered to remove sodium chloride and the filtrate was concentrated to a volume of 100 ml. under reduced pressure. The concentrate was diluted with 100 ml. of water and extracted with ether. The extracts were washed with water, dried over sodium sulfate and concentrated. Fractionation of the residue through a semi-micro column separated 0.51 g. of a yellow forerun, b.p. 83–88° (11 mm.), $n^{25}\mathrm{D}$ 1.5388, from 27.7 g. (69%) of crude V as a colorless liquid, b.p. 93–95° (11 mm.), $n^{25}\mathrm{D}$ 1.5064–1.5087. The infrared spectrum of a fraction with $n^{25}\mathrm{D}$ 1.5067 was practically identical with the spectrum of pure V, except for the presence of additional weak bands at 1640 and 780 cm.$^{-1}$ which probably indicate the presence of a small amount of a styrene derivative as an impurity. Observation of stronger absorption in the ultraviolet spectrum ($\lambda_{\max}$ 261 mμ, ϵ 5010 in cyclohexane) for III from this source than for pure III also could be explained by the presence of such an impurity. A fraction was converted into 2,4,6-cycloheptatriene-1-carboxaldehyde 2,4-dinitrophenylhydrazone in 84% yield by the method described above for preparation of this derivative from pure V, and identified by m.p. and mixed m.p. with the analytical sample of the 2,4-dinitrophenylhydrazone prepared from pure V described above.

Hydrogenation of 6.46 g. of V prepared from cycloöctatetraene dichloride under the conditions described above for reduction of pure V resulted in absorption of 94% of three molar equivalents of hydrogen in 1.7 hours. Fractionation of the product separated 0.93 g. of a forerun, b.p. 78–90° (12 mm.), $n^{25}\mathrm{D}$ 1.4577–1.4699, from 4.74 g. (71%) of VI, b.p. 90–91° (12 mm.), $n^{25}\mathrm{D}$ 1.4500–1.4530, identified by its infrared spectrum and by conversion in 77% yield into the 2,4-dinitrophenylhydrazone of VI (m.p. and mixed m.p. with an authentic sample after recrystallization from benzene–ethanol, 134.5–135.5°).

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[CONTRIBUTION FROM THE LEWIS FLIGHT PROPULSION LABORATORY OF THE NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS]

Dicyclic Hydrocarbons. IX. Synthesis and Physical Properties of the Monomethyldiphenylmethanes and Monomethyldicyclohexylmethanes

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Methods of synthesis and purification are described for the 2-, 3- and 4-methyldiphenylmethanes and for both geometrical isomers of the corresponding methyldicyclohexylmethanes. Each of these hydrocarbons has been prepared in a state of purity of 99 mole %, or better. The physical properties presented include melting point, boiling point, refractive index, density, heat of fusion, net heat of combustion and kinematic viscosities at four different temperatures. The methyldicyclohexylmethanes are being reported for the first time and the physical constants for the methyldiphenylmethanes have been improved and extended.

As part of a study of the effect of structure on the properties of dicyclic hydrocarbons the 2-, 3- and 4-methyldiphenylmethanes and corresponding dicyclohexylmethanes were synthesized and purified. The scale of the synthesis was planned so that approximately 500-ml. quantities of each hydrocarbon would be made available in 99 mole % purity for specific test purposes.

None of the methyldicyclohexylmethanes has been mentioned in the literature and the preparation and physical properties of these hydrocarbons are thus described for the first time. The methyldiphenylmethanes have been prepared previously, but only boiling points, indices of refraction and densities are reported and the data from the various sources are not in agreement.

A general method of synthesis was employed for the preparation of the methyldiphenylmethanes and corresponding methyldicyclohexylmethanes. The first step was the preparation of the solid methylbenzhydrol by the Grignard reaction utilizing an appropriate aryl halide and benzaldehyde. The Grignard complex was hydrolyzed by pouring it into an ice-cold acid solution. This hydrolysis procedure, in which the reactants are kept ice-cold, is necessary if good yields are to be obtained. Otherwise intermolecular dehydration probably occurs with the formation of an ether in the same manner as dibenzhydryl ether is formed from benzhydrol by heating with dilute hydrochloric acid at 120–130°.[1] The yield of methylbenzhydrol was improved if less than the theoretical amount (75 to 80%) of benzaldehyde was used for the condensation. This minimized the possibility of oxidation of the reaction product by excess benzaldehyde.[2] Because of differences in solubility and crystal structure, it was necessary to employ various solvents and crystallization techniques for the purification of each methylbenzhydrol.

The methyldiphenylmethanes were prepared by hydrogenolysis of the purified solid methylbenzhydrols. These methyldiphenylmethanes crystallized very readily on cooling and estimates of purity, based on time–temperature melting curves, indicated values over 99.9 mole %. 3-Methyldiphenylmethane exists in two crystalline modifications and time–temperature melting curves were obtained for each form.

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(1) H. Wieland, C. Schopf and W. Hermsen, *Ann.*, **444**, 40 (1925).

(2) J. Marshall, *J. Chem. Soc.*, **107**, 509 (1915).