less liquid, b.p. 84–86° (18 mm.), n^{25}D 1.5795. Fractionation through a Piros–Glover micro spinning band column gave colorless $C_{10}H_{10}$ component with b.p. 87.7° (20 mm.) (cor.), n^{25}D 1.5808; reported for *cis*-1-phenyl-1,3-butadiene, b.p. 71° (11 mm.), n^{25}D 1.5822.[4b]

Anal. Calcd. for $C_{10}H_{10}$: C, 92.26; H, 7.74. Found: C, 92.25; H, 7.82.

Hydrogenation of the Orange $C_{10}H_{10}$ Component.—Hydrogenation of 6.5 g. (0.05 mole) of the orange $C_{10}H_{10}$ component in 75 ml. of acetic acid in the presence of 0.1 g. of Adams catalyst was complete in 45 minutes and required exactly five molar equivalents of hydrogen. The product, ethylcycloöctane, was isolated as described above (6.0 g., 86%), b.p. 188.5–189°, n^{25}D 1.4586.

Hydrogenation of the Colorless $C_{10}H_{10}$ Component.—Hydrogenation of 6.9 g. (0.053 mole) of the colorless $C_{10}H_{10}$ component in 75 ml. of methanol in the presence of 0.1 g. of Adams catalyst was complete in 45 minutes and required 99% of two molar equivalents of hydrogen. The product, *n*-butylbenzene, was isolated as above (7.2 g., 100%), b.p. 181–182°, n^{25}D 1.4887. Reported for *n*-butylbenzene,[9a,b] b.p. 183.1°, n^{20}D 1.4899 (see also Component I).

1-Phenyl-1,2,3,4-tetrabromobutane.—To a solution of 1.0 g. (0.0077 mole) of freshly distilled colorless $C_{10}H_{10}$ component was added portionwise a solution of 2.5 g. (0.031 g. atom) of bromine in 10 ml. of carbon disulfide. The resulting solution was heated at reflux for 1 hour, cooled and the solvent removed under reduced pressure. The residue (3.2 g., 93%) was recrystallized from methanol to give clusters of needles which sintered at 135° and melted at 141–142° reported for the tetrabromo derivative of 1-phenyl-1,3-butadiene, m.p. 142°.[10]

Anal. Calcd. for $C_{10}H_{10}Br_4$: C, 26.70; H, 2.24; Br, 71.06. Found: C, 26.87; H, 2.32; Br, 71.15.

1-Phenyl-1,2-dibromobutane.—A 3.0-g. sample (0.023 mole) of freshly distilled $C_{10}H_{10}$ component in 50 ml. of methanol was shaken in the presence of 0.3 g. of 0.5% palladium-on-charcoal under hydrogen until one molar equivalent had been absorbed (15 minutes). The catalyst was removed by filtration and the solvent removed by distillation at reduced pressure. The residue was dissolved in 15 ml. of carbon disulfide and a dilute solution of bromine in carbon disulfide added until the color persisted. The wax-like solid left on removal of solvent was recrystallized twice by freezing out of low boiling petroleum ether, m.p. 68.5–69.5°. Reported for the dibromo derivative of both *trans*- and *cis*-1-phenylbutene, m.p. 70°.[11]

Anal. Calcd. for $C_{10}H_{12}Br_2$: C, 41.13; H, 4.14; Br, 54.73. Found: C, 41.05; H, 4.06; Br, 55.36, 55.32.

Attempted Condensations of the Colorless $C_{10}H_{10}$ Component with Maleic Anhydride.—Solutions of equimolar amounts of the colorless $C_{10}H_{10}$ component and maleic anhydride in both chloroform and benzene were heated at reflux for periods of time ranging from 15 minutes to several hours with no Diels–Alder adduct being formed. When equimolar amounts of the materials were heated to 180° for several minutes, the result was a wax-like solid which appeared to be polymeric in nature. A crystalline adduct of *trans*-1-phenyl-1,3-butadiene and maleic anhydride is reported to be formed in a few minutes in refluxing benzene and ether, m.p. 120–122°.[4a,4b]

***trans*-1-Phenyl-1,3-butadiene.**—1-Phenyl-1,3-butadiene was prepared from cinnamalmalonic acid according to the procedure of Liebermann and Riiber.[12] Distillation of the product gave the colorless oil, b.p. 58–60° (2.0–2.5 mm.), n^{25}D 1.6065. This is the 1-phenyl-1,3-butadiene shown by Grummitt and Christoph[4b] to be the *trans* isomer.

Absorption Spectra.—The ultraviolet absorption spectra were determined in purified isoöctane as a solvent with a Carey recording quartz ultraviolet spectrophotometer. Infrared spectra were determined with a Perkin-Elmer infrared spectrograph.

Acknowledgments.—The authors are indebted to Mr. L. J. Lohr for the distillations carried out in the Podbielniak and spinning band columns, to Dr. S. T. Gross for the measurement and interpretation of the infrared spectra, to Dr. H. Hemmendinger for the measurement and interpretation of the ultraviolet spectra, and to Mr. L. J. Frauenfelder for all analyses.

Summary

The $C_{10}H_{10}$ fraction obtained by polymerization of acetylene in the presence of nickel cyanide was hydrogenated and the hydrogenation products shown to be *n*-butylbenzene, 1-ethylcycloöctene and ethylcycloöctane. The $C_{10}H_{10}$ fraction was separated into two components which were shown to be *cis*-1-phenyl-1,3-butadiene and vinylcycloöctatetraene.

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(9) (a) Timmermans and Martin, *J. chim. phys.*, **25**, 415 (1928); (b) Schmidt, Hopp and Schoeller, *Ber.*, **72**, 1895 (1939).

(10) Liebermann and Riiber, *ibid.*, **33**, 2400 (1900).

(11) Muskat and Knapp, *ibid.*, **64**, 779 (1931).

(12) Liebermann and Riiber, *ibid.*, **35**, 2696 (1902).

EASTON, PENNA. RECEIVED JUNE 19, 1950

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

Cyclic Polyolefins. XII. Isolation of Vinylcycloöctatetraene and *cis*-1-Phenyl-1,3-butadiene from Acetylene Polymers

BY ARTHUR C. COPE AND STUART W. FENTON

Reppe, Schlichting and Meister[1] have described the isolation of several hydrocarbons in addition to benzene and cycloöctatetraene from the products formed by polymerization of acetylene in the presence of nickel cyanide: an orange-yellow hydrocarbon $C_{10}H_{10}$, a light yellow hydrocarbon $C_{10}H_{10}$, a yellow hydrocarbon $C_{12}H_{12}$, naphthalene and azulene. Evidence which they obtained concerning the structure of the $C_{10}H_{10}$ isomers and the $C_{12}H_{12}$ hydrocarbon by hydrogenation, oxidation of the reduction products, and preparation of addition compounds with maleic anhydride failed to elucidate their structures. Patent applications filed by the I. G. Farbenindustrie based on Reppe's work[2] and statements in the monographs written by Reppe[3] and a text based on Reppe's reports[4] indicate that these hydrocarbons were originally considered to be cyclodecapentaene (two stereoisomeric forms) and cyclododecahexaene.

The catalytic polymerization of acetylene to

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(1) Reppe, Schlichting and Meister, *Ann.*, **560**, 93 (1948).

(2) Kammermeyer, "Polymerization of Acetylene to Cycloöctatetraene," revised from FIAT final report 967 (PB-62593), Hobart Publishing Co., Washington, D. C., 1947, pp. 81–85.

(3) (a) Reppe, "Acetylene Chemistry," P. B. Report 18852-S, translated from the German by Charles A. Meyer and Co., New York, N. Y., 1949, pp. 145–148; (b) Reppe, "Neue Entwicklungen auf dem Gebiet der Chemie des Acetylens und Kohlenoxyds," Springer Verlag, Berlin, 1949, pp. 89–90.

(4) Copenhaver and Bigelow, "Acetylene and Carbon Monoxide Chemistry," Reinhold Publishing Corp., New York, N. Y., 1949, pp. 213–219.

cyclooctatetraene which has been conducted in this Laboratory[5] by a procedure similar to the one described by Reppe, Schlichting, Klager and Toepel[6] furnished a mixture of higher boiling hydrocarbons which remained as a residue after distillation of the benzene and cyclooctatetraene fractions. Fractional distillation of this mixture confirmed the observation[1] that the components could not be separated readily by distillation alone. The higher boiling fractions contained naphthalene and azulene which were separated by a method similar to the one described by Reppe, Schlichting and Meister.[1] The intermediate fractions, boiling higher than cyclooctatetraene, varied in color from orange (the lower boiling fractions) to yellow. It was found that the two major components of these fractions could be separated by extraction with aqueous silver nitrate, which is known to form addition compounds with cyclooctatetraene[6,7] and with certain other cyclic polyolefins.[7] The aqueous silver nitrate extracts were bright yellow in color, while the hydrocarbon layer became colorless as the orange component was removed. Addition of ammonium hydroxide to the aqueous silver nitrate extracts decomposed the addition compound which was present and caused separation of an orange hydrocarbon which was extracted with ether, stabilized by addition of hydroquinone, and purified by distillation. It proved to be a single compound with the molecular formula $C_{10}H_{10}$, which was stable when kept under nitrogen in the presence of a trace of hydroquinone, but polymerized rapidly in air forming an orange glass. The orange hydrocarbon $C_{10}H_{10}$ absorbed light strongly in the short wave lengths of the visible spectrum and in the ultraviolet, with a maximum at 230 mμ (Fig. 1). It was reduced readily in the presence of Adams platinum catalyst in acetic acid with the absorption of five molar equivalents of hydrogen, and formed a colorless hydrocarbon $C_{10}H_{20}$. Indications of the probable structures of the orange hydrocarbon $C_{10}H_{10}$ and the reduction product derived from it were obtained from infrared absorption spectra (Fig. 2). The spectrum of the orange hydrocarbon contained a weak absorption band at 3.26 μ, assignable to a terminal methylene group, since the remainder of the spectrum indicated that the compound was not aromatic in nature. The infrared spectrum of the reduction product contained a strong absorption band at 7.25 μ, a wave length

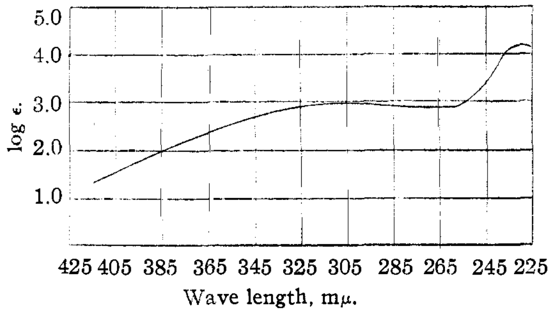

Fig. 1.—Ultraviolet absorption spectrum of vinylcyclooctatetraene (I) in 95% ethanol.

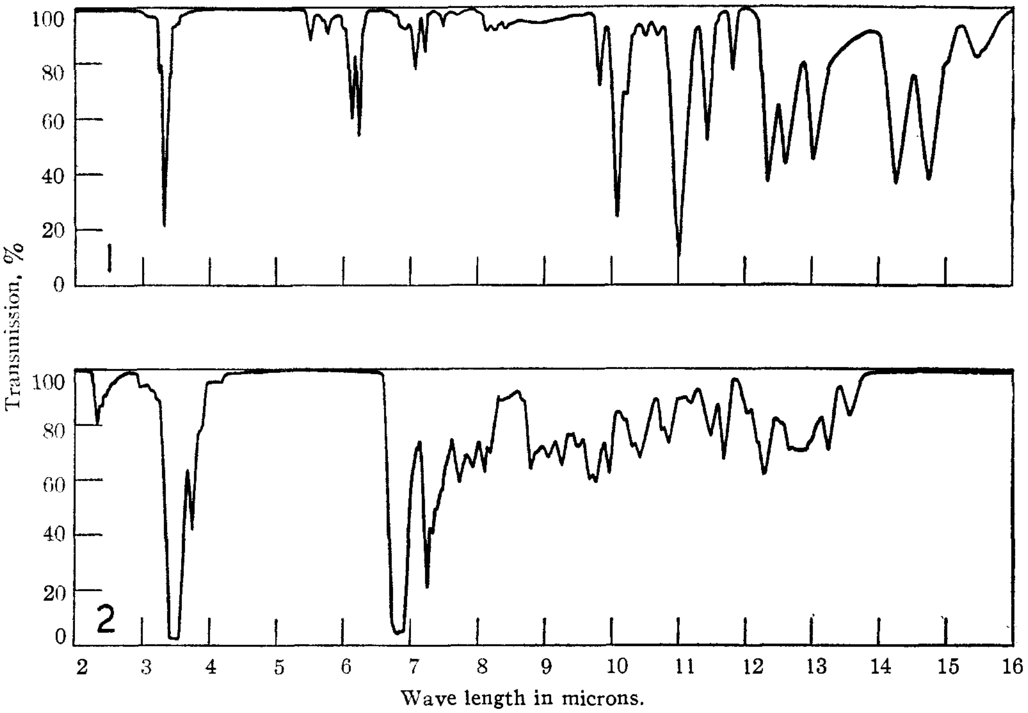

Fig. 2.—Infrared absorption spectra: curve 1, vinylcyclooctatetraene (I), spectrum of a 10% solution in carbon tetrachloride in the regions 2–12 μ and 14–16 μ and of a 10% solution in carbon disulfide in the region 12–14 μ. The cell thickness was 0.1 mm.; curve 2, ethylcyclooctane (II) prepared by hydrogenation of I, spectrum without a solvent with a cell thickness of 0.05 mm.

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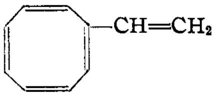
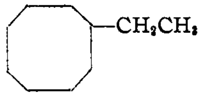
(5) Cope and Estes, THIS JOURNAL, **72**, 1129 (1950).

(6) Reppe, Schlichting, Klager and Toepel, *Ann.*, **560**, 1 (1948).

(7) Cope and Hochstein, THIS JOURNAL, **72**, 2515 (1950).

at which absorption due to the presence of a methyl group is commonly noted. This information indicated that probable structures for the orange hydrocarbon and the saturated hydrocarbon derived from it were vinylcycloöctatetraene (I) and ethylcycloöctane (II), respectively. These structures were confirmed by an independent synthesis of ethylcycloöctane and determination of the properties of the authentic sample. Cyclooctanone was treated with ethylmagnesium iodide and converted to 1-ethylcycloöctan-1-ol, which was converted to an olefin by distillation in the presence of a small amount of iodine. Catalytic hydrogenation of the resulting olefin furnished a known sample of ethylcycloöctane which was identical within experimental error in boiling point, refractive index and infrared spectrum with the sample obtained by reduction of the orange hydrocarbon $C_{10}H_{10}$ (I).


I


II

The colorless hydrocarbon layer remaining after removal of vinylcycloöctatetraene by extraction with silver nitrate yielded an isomeric colorless hydrocarbon $C_{10}H_{10}$ on distillation. Information concerning the structure of this isomer was obtained by hydrogenation, which in the presence of Adams platinum catalyst in acetic acid resulted in the absorption of five molar equivalents of hydrogen, with a decrease in the rate of reduction after two molar equivalents of hydrogen had been absorbed.

Hydrogenation in the presence of palladium-on-carbon resulted in the absorption of two molar equivalents of hydrogen and formed *n*-butylbenzene, which was identified by comparison of the infrared spectrum with the spectrum of an authentic sample and with the published spectrum.[8] This characterization was confirmed by conversion of the reduction product into 1-*n*-butyl-2,4-diacetamidobenzene,[9] which was proved to be identical with a known sample of this solid derivative by melting point and mixed melting point. Additional evidence which established the structure of the colorless hydrocarbon $C_{10}H_{10}$ as *cis*-1-phenyl-1,3-butadiene (III) was furnished by ozonization followed by oxidation, which formed benzoic acid, and by determination of the infrared absorption spectrum, which proved to be identical to the spectrum of *cis*-1-phenyl-1,3-butadiene[10] (made available to us prior to publication through the kindness of Dr. Oliver Grummitt).

Examination of the infrared spectra of the various fractions of the $C_{10}H_{10}$ hydrocarbons and their separation into I and III by extraction with aqueous silver nitrate failed to show the presence of other compounds except cycloöctatetraene itself, which was present as a minor impurity in the lower boiling fractions. Only these same hydrocarbons plus naphthalene and azulene could be found in the higher boiling fractions, which could have contained very little if any of the hydrocarbon $C_{12}H_{12}$ described by Reppe, Schlichting and Meister.[1] Compounds with a much higher boiling point which have not yet been characterized were present in the mixture of acetylene polymers in small amounts, and resinous material which could not be distilled formed the balance of the mixture. Since the mixture originally had been separated from cuprene and resins by steam distillation,[5] the resin must have been formed by partial polymerization on standing prior to (or during) fractional distillation, and any components of the original mixture which polymerized more rapidly than I and III may have escaped detection.

A sample of the high-boiling residues from cycloöctatetraene preparations which was made available to us by the General Aniline and Film Corporation through the kindness of Drs. H. B. Hass and L. E. Craig, was found to contain cycloöctatetraene, vinylcycloöctatetraene, *cis*-1-phenyl-1,3-butadiene, naphthalene, azulene, unidentified higher boiling compounds and a polymeric resin, which were separated and identified by the methods described above. Little if any of the hydrocarbon $C_{12}H_{12}$ described in ref. 1 could have been present in the fractions obtained from this sample by fractional distillation.

From the evidence furnished by the publications by Reppe[1,3] and secondary sources describing the work of his group[2,4] there seems to be little doubt that the orange-yellow hydrocarbon $C_{10}H_{10}$ which they obtained by polymerization of acetylene was vinylcycloöctatetraene (I), while the light yellow isomer was 1-phenyl-1,3-butadiene containing a colored hydrocarbon (probably I) as an impurity.

Experimental[11]

Vinylcycloöctatetraene (I).—A 124-g. sample of the accumulated high-boiling residues from cycloöctatetraene preparations[5] was fractionated through a 20 × 1.8 cm. column packed with glass helices and separated into the following fractions: (1) 32.5 g., b.p. 48–50° (28 mm.), n^{25}_D 1.5346 (cycloöctatetraene); (2) 4.52 g., b.p. 88–90° (28 mm.), n^{25}_D 1.5690; (3) 8.25 g., b.p. 90–92° (28 mm.), n^{25}_D 1.5780; (4) 6.20 g., b.p. 92–95° (28 mm.), n^{25}_D 1.5808; (5) 2.45 g., b.p. 95–105° (28 mm.), n^{25}_D 1.5785; (6) 2.31 g., b.p. 70–80° (0.3 mm.), n^{25}_D 1.5809; (7) 0.95 g. of a blue solid, b.p. 80–90° (0.3 mm.); (8) 58.2 g. of a viscous yellow residue, of which 22 g. was distilled in a short path molecular-type still at 4.0–0.1 mm. and a bath temperature of 60–125°, leaving 36.2 g. of a resinous residue.

A solution of 2.0 g. of fraction (2) in 100 ml. of 30–60° petroleum ether was shaken with eight 20-ml. portions of 20% aqueous silver nitrate. During this process, the yellow color disappeared from the hydrocarbon layer and the aqueous extracts became bright yellow in color. The combined aqueous extracts were cooled in a mixture of ice and salt and concentrated ammonium hydroxide was added until a test portion gave no precipitate on addition of sodium chloride solution. The liquid which separated from the aqueous solution was extracted rapidly with 100 ml. of petroleum ether. The extract was washed with water, dried over sodium sulfate, concentrated and the residue was distilled through a semi-micro column.[12] Vinylcycloöctatetraene was obtained in a yield of 0.94 g., b.p. 92–92.5° (30 mm.), n^{25}_D 1.5664, d^{25}_4 0.9321.

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[8] American Petroleum Institute Research Project 44, Catalog of Infrared Spectrograms Serial No. 468, *n*-butylbenzene, contributed by the U. S. Naval Research Laboratory, Washington, D. C.

[9] Ipatieff and Schmerling, THIS JOURNAL, **59**, 1058 (1937).

[10] Grummitt and Christoph, unpublished.

[11] Melting points are corrected and boiling points are uncorrected. We are indebted to Mr. S. M. Nagy and his associates for analyses and determination of infrared spectra.

[12] Gould, Holzman and Niemann, *Anal. Chem.*, **20**, 361 (1948).

Anal. Calcd. for $C_{10}H_{10}$: C, 92.25; H, 7.75. Found: C, 92.47; H, 7.65.

Vinylcycloöctatetraene was also isolated from fraction (4), in which it was present in smaller amount, and was present in fractions (3) and (5) as shown by examination of infrared spectra of those fractions. Vinylcycloöctatetraene proved to be an orange liquid with a strong, unpleasant, olefin-like odor. It polymerized rapidly in air forming an orange glass, but could be stabilized with a small amount of hydroquinone.

Ethylcycloöctane (II).—A solution of 1.140 g. of vinylcycloöctatetraene in 27 ml. of glacial acetic acid was hydrogenated at atmospheric pressure in the presence of 0.2 g. of prereduced Adams platinum oxide catalyst. The reduction was complete in 1 hour and 101% of five molar equivalents of hydrogen was absorbed, but the mixture was shaken with hydrogen for an additional 2 hours to ensure complete reduction. The catalyst was separated by filtration and the filtrate was made alkaline by addition of 10% aqueous sodium hydroxide. The oil which separated was extracted with two 25-ml. portions of ether and the combined extracts were washed with water, dried over sodium sulfate and concentrated. The ethylcycloöctane formed was purified by fractionation through a semi-micro column[12] and collected as two fractions; weight 0.79 g., b.p. 91–92° (30 mm.), $n^{25}\mathrm{D}$ 1.4566 and 1.4568. The infrared spectrum of II obtained in this manner was identical with the spectrum of an authentic sample of ethylcycloöctane (described below).

Synthesis of Ethylcycloöctane.—Ethylmagnesium iodide was prepared from 7.8 g. of ethyl iodide and 1.1 g. of magnesium in 70 ml. of dry ether in a 200-ml. three-necked flask fitted with a slip-sealed stirrer, dropping funnel and reflux condenser protected from atmospheric moisture. A solution of 4.2 g. of freshly distilled cycloöctanone in 50 ml. of dry ether was added dropwise to the Grignard reagent (at the reflux temperature) during a period of 30 minutes. The mixture was heated at the reflux temperature for 2.5 hours after the addition was completed and then was cooled in ice and treated with 20 ml. of saturated aqueous ammonium chloride solution. The ether layer was separated, washed with water, dried over sodium sulfate and concentrated under reduced pressure. The oily residue failed to crystallize and partial dehydration occurred with the formation of water when an attempt was made to distil it under reduced pressure. Accordingly a small crystal of iodine was added and the liquid was heated at 70° and 30 mm. pressure until no more water was formed. Distillation then yielded 3.35 g. of a crude product containing approximately 30 mole per cent. of cycloöctanone (formed by enolization in the reaction with ethylmagnesium iodide), estimated from the intensity of the carbonyl band at 5.88 μ in the infrared spectrum. A solution of the crude product in 20 ml. of absolute ethanol was treated with 1.0 g. of Girard reagent P and 1.0 g. of glacial acetic acid and heated under reflux for 1 hour. The solution was cooled and poured into 200 ml. of a mixture of ice and water. The mixture was made just neutral to phenolphthalein by addition of 10% aqueous sodium carbonate solution and then was extracted with 50 ml. of ether. The extract was washed with water, dried over sodium sulfate, concentrated, and the residue was fractionated.[12] Ethylcycloöctene was obtained as a colorless liquid in a yield of 2.1 g. (46%), b.p. 84–85° (30 mm.), $n^{25}\mathrm{D}$ 1.4716. No evidence was obtained concerning the location of the double bond in the olefin, which would be expected to be in the 1-position of the cycloöctene ring.

Anal. Calcd. for $C_{10}H_{18}$: C, 86.88; H, 13.12. Found: C, 86.65; H, 13.07.

A solution of 1.691 g. of ethylcycloöctene in 50 ml. of 95% ethanol was hydrogenated at atmospheric pressure in the presence of 0.2 g. of prereduced Adams platinum oxide catalyst. The reduction was complete in 2 hours and 97% of one molar equivalent of hydrogen was absorbed. The catalyst was separated by filtration and 500 ml. of water was added to the filtrate. The hydrocarbon which separated was extracted with two 100-ml. portions of petroleum ether. The extracts were combined, dried over sodium sulfate and concentrated. Fractionation of the residue yielded 1.02 g. (60%) of ethylcycloöctane, b.p. 91.8–92.1° (30 mm.), $n^{25}\mathrm{D}$ 1.4568.

Anal. Calcd. for $C_{10}H_{20}$: C, 85.63; H, 14.37. Found: C, 85.70; H, 14.69.

cis-**1-Phenyl-1,3-butadiene** (III).—The colorless petroleum ether solution of fraction (2) remaining after extraction of the vinylcycloöctatetraene with aqueous silver nitrate solution was washed with water, dried over sodium sulfate and concentrated. The residue was fractionated through a semi-micro column[12] and yielded 0.28 g. of *cis*-1-phenyl-1,3-butadiene, b.p. 84–85° (30 mm.), $n^{25}\mathrm{D}$ 1.5820. These properties are in agreement with the reported[13] constants for III: b.p. 71° (11 mm.), $n^{25}\mathrm{D}$ 1.5822. Moreover, the infrared spectrum of this sample of III was identical within experimental error with the spectrum reported for III by Grummitt and Christoph.[10] Fractions (3), (4) and (5) contained larger amounts of III than fraction (2), the largest amount being present in fraction (5).

Prior to the identification of III through physical properties, in particular the infrared spectrum, structural evidence was obtained by ozonization and by hydrogenation. Ozonization of a sample of III in ethyl acetate solution followed by decomposition of the ozonide by heating with hydrogen peroxide in acetic acid yielded benzoic acid. Hydrogenation of a solution of 1.001 g. of III in 25 ml. of 95% ethanol in the presence of 0.15 g. of 10% palladium on Norit was complete in 40 minutes and 99% of two molar equivalents of hydrogen was absorbed. The catalyst was separated by filtration and the filtrate was diluted with 200 ml. of water. The hydrocarbon which separated was extracted with two 100-ml. portions of 30–60° petroleum ether and the combined extracts were dried over sodium sulfate and concentrated. Distillation of the residue through a semi-micro column[12] yielded 0.78 g. of *n*-butylbenzene, b.p. 84–85° (30 mm.), $n^{25}\mathrm{D}$ 1.4881. The infrared spectrum of this hydrocarbon was identical with the spectrum of a known sample of *n*-butylbenzene. A 0.3-g. sample of *n*-butylbenzene derived from III by hydrogenation was converted into 1-*n*-butyl-2,4-diacetamidobenzene by the procedure of Ipatieff and Schmerling[9]; yield after recrystallization from ethanol and water 0.36 g., m.p. and mixed m.p. with a known sample 215–216.3°.

Naphthalene and Azulene.—Fractions (6) and (7) were combined and freed from traces of vinylcycloöctatetraene by extraction with 20% aqueous silver nitrate. Naphthalene (m.p. 79–80°) and a small quantity of azulene (m.p. 99.4–100°) were isolated from the fraction insoluble in silver nitrate essentially in the manner described by Reppe, Schlichting and Meister.[1]

Absorption Spectra.—The ultraviolet absorption spectrum of vinylcycloöctatetraene (Fig. 1) was determined with a Beckman model DU quartz spectrophotometer. Infrared spectra (Fig. 2) were determined with a Baird double beam infrared recording spectrometer, Model B, fitted with a sodium chloride prism, in cells with sodium chloride windows.

Summary

Vinylcycloöctatetraene and *cis*-1-phenyl-1,3-butadiene have been found to be present in the mixture of hydrocarbons formed in the preparation of cycloöctatetraene from acetylene. They were separated by extraction with 20% aqueous silver nitrate, in which vinylcycloöctatetraene is soluble and *cis*-1-phenyl-1,3-butadiene is insoluble. Vinyl cycloöctatetraene was regenerated from the silver nitrate extracts by the addition of ammonium hydroxide.

CAMBRIDGE, MASSACHUSETTS RECEIVED JUNE 14, 1950

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[13] Grummitt and Oliver, THIS JOURNAL, 71, 4157 (1949).