

[CONTRIBUTION FROM THE CENTRAL RESEARCH LABORATORIES, GENERAL ANILINE AND FILM CORPORATION]

Eight-membered Carbocycles. Identification of the C₁₀H₁₀ Fraction from Cyclooctatetraene Preparations

BY L. E. CRAIG AND CLIFFORD E. LARRABEE

From the higher-boiling hydrocarbons produced in the preparation of cyclooctatetraene by cyclic polymerization of acetylene, Reppe and co-workers¹ isolated naphthalene, a small amount of azulene, and hydrocarbons having the empirical formulas C₁₀H₁₀ and C₁₂H₁₂. The German workers obtained what they believed to be two different C₁₀H₁₀ hydrocarbons, one orange-yellow, the other, bright yellow. From a series of hydrogenation studies, no conclusive evidence was obtained as to their structures, although the German workers expressed the belief that they were pure compounds, probably stereoisomeric cyclodecapentaenes. The possibility that the C₁₀H₁₀ was vinylcyclooctatetraene was recognized (Ref. 1a, No. 1288) but apparently not given much consideration. This paper reports the identification of hydrogenation products of the C₁₀H₁₀ fraction, the separation of the C₁₀H₁₀ fraction into two components and the identification of these components.

The C₁₀H₁₀ fraction used in this investigation was isolated by fractional distillation from high-boiling fractions from several cyclooctatetraene preparations carried out at 90°. Its properties were in good agreement with those reported by Reppe and co-workers¹ for the orange-yellow C₁₀H₁₀. Examination of the infrared absorption spectrum (Fig. 4) of the C₁₀H₁₀ fraction showed absorptions attributable to a substituted benzene ring (14.3, 13.2, 9.25, 6.72 and 6.25 μ) and an absorption attributable to non-benzenoid conjugated double bonds (6.17 μ). These facts indicated that the C₁₀H₁₀ fraction was a mixture containing at least one substituted benzene and, since it was highly colored, probably at least one cyclic polyolefin. The absorptions at 5.62 and 8.56 μ are probably due to oxygenated compounds, as the material was found to absorb oxygen rapidly from the air.

A series of hydrogenations under varying conditions gave hydrogen absorptions which were not integral numbers of molar equivalents, and ultraviolet absorption spectra of the hydrogenation products showed the selective absorption typical of a monoalkyl benzene. Hydrogenation of a large amount of the C₁₀H₁₀ fraction was carried out under conditions in which the benzene ring was not hydrogenated, that is, at room temperature and at low pressure with Adams catalyst and methanol as the solvent. Distillation of the hydrogenation product through a very efficient column gave three materials (Fig. 1) which were shown by elementary

(1) (a) See the following P. B. Reports: No. 1288, pp. 14-16; No. 18852-S, pp. 145-150; No. 62593, pp. 10-12, 17-18; and No. 99207, pp. 82-87. (b) For an excellent summary of the work described in these P. B. reports, see Copenhaver and Bigelow, "Acetylene and Carbon Monoxide Chemistry," Reinhold Publishing Corp., New York, N. Y., 1949, pp. 213-219. (c) Reppe, Schlichting and Meister, *Ann.*, **560**, 93 (1948).

analysis to be C₁₀H₁₄ (Component I), C₁₀H₁₈ (Component II) and C₁₀H₂₀ (Component III).

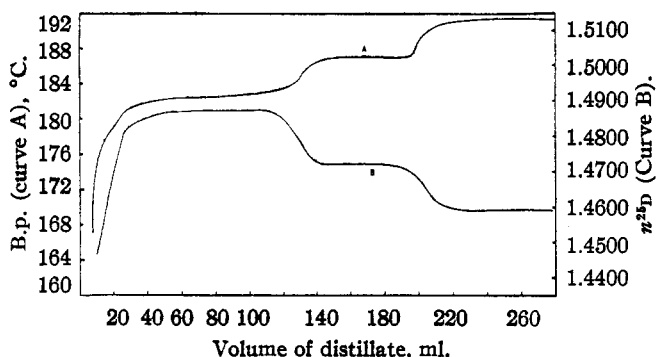


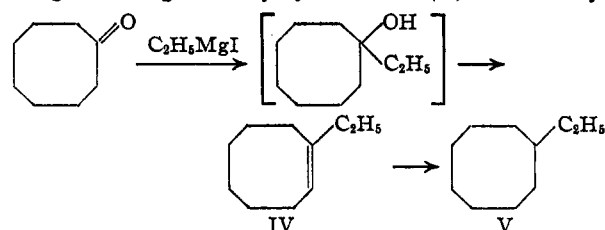
Fig. 1.—Distillation curve of hydrogenated C₁₀H₁₀: first plateau, component I; second plateau, component II; and third plateau, component III.

Component I was shown to be *n*-butylbenzene by comparison of physical constants and infrared absorption spectra (Fig. 2) with those reported for *n*-butylbenzene. A diacetylamino derivative was prepared and shown by means of a mixed melting point determination to be identical with 2,4-diacetylamino-*n*-butylbenzene prepared from an authentic sample of *n*-butylbenzene.

Component II was shown to have one double bond by its infrared absorption spectrum and by the uptake of one molar equivalent of hydrogen on quantitative hydrogenation. Furthermore, the hydrogenated Component II was identical with Component III as shown by its boiling point, refractive index and infrared absorption spectrum.

A saturated hydrocarbon of empirical structure C₁₀H₂₀ must have a cyclic structure. Of the three most likely compounds, butylcyclohexane, cyclodecane and ethylcyclooctane, only ethylcyclooctane was unknown. Since the physical constants of Component III were not in good agreement with those reported for butylcyclohexane and for cyclodecane, ethylcyclooctane was prepared for comparison with the unknown material.

By treatment of cyclooctanone with ethylmagnesium iodide and dehydration of the resulting carbinol, 1-ethylcyclooctene (IV) was obtained. Hydrogenation gave ethylcyclooctane (V). Not only



was V shown to be identical with Component III by comparison of their physical constants and infra-

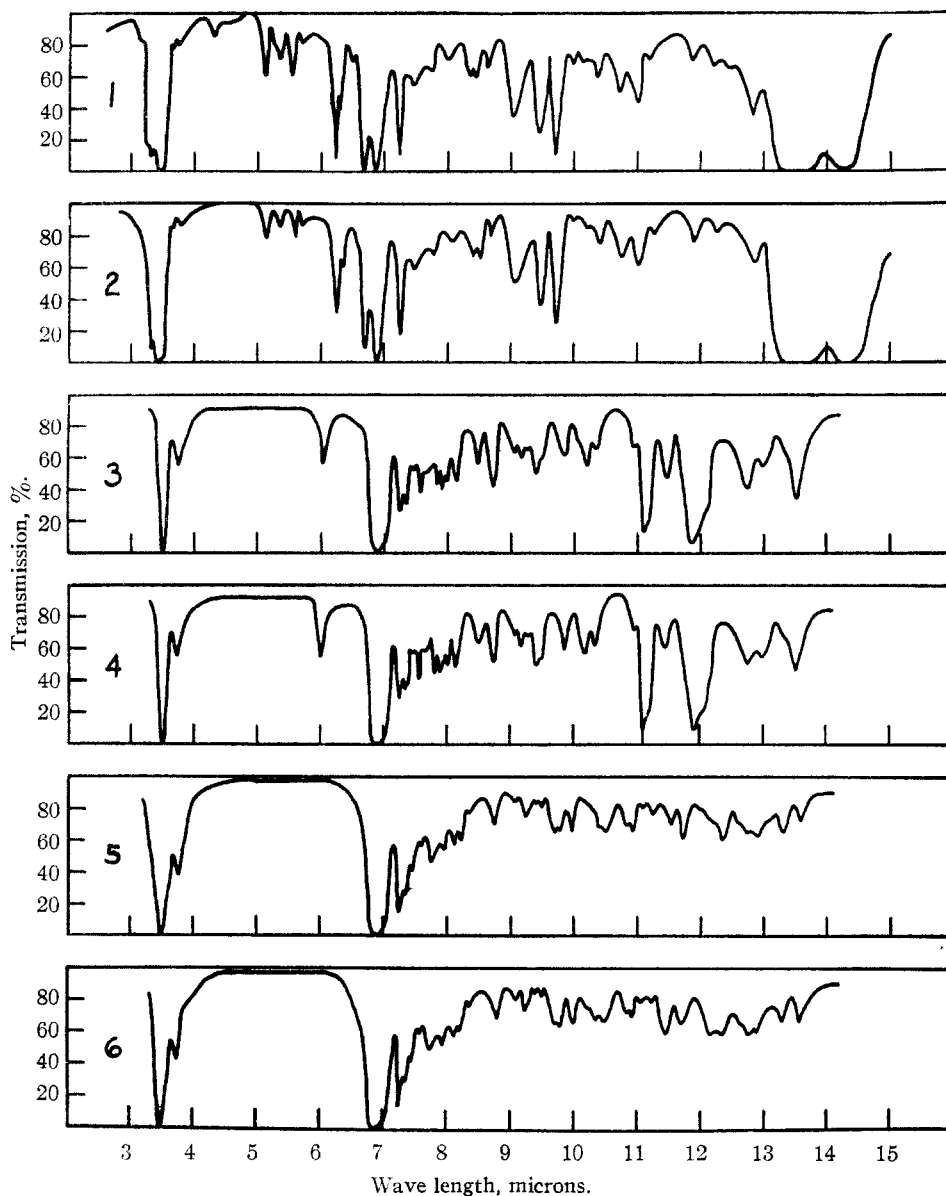


Fig. 2.—Infrared spectra: curve 1, component I; curve 2, *n*-butylbenzene; curve 3, component II; curve 4, 1-ethylcyclooctene; curve 5, component III; and curve 6, ethylcyclooctane.

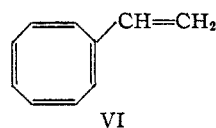
red absorption spectra, but also IV was found to be identical with Component II.

Since both Components II and III could have been produced from the same material on hydrogenation and the butylbenzene was probably produced from a single material, it seemed likely that the original $C_{10}H_{10}$ fraction was a mixture of two materials, both of empirical formula $C_{10}H_{10}$. In an attempt to produce a solid derivative of one or both of the highly unsaturated materials, the $C_{10}H_{10}$ was shaken with aqueous silver nitrate.² Rather than a solid derivative being formed, it was found that the orange-yellow color went into the aqueous solution and an essentially colorless oil remained. Extraction of this mixture with petroleum ether and concentration of the extracts gave a colorless $C_{10}H_{10}$ component. An orange $C_{10}H_{10}$ component was ob-

(2) Reppe (Ref. 5, p. 11) reported the preparation of a crystalline cyclooctatetraene-silver nitrate adduct.

tained by the addition of sodium chloride followed by steam distillation.

On careful distillation, the orange component was found to be one material of empirical formula, $C_{10}H_{10}$. It absorbed five molar equivalents of hydrogen on quantitative hydrogenation in acetic acid over Adams catalyst to give V. The most likely structure for the orange $C_{10}H_{10}$ seemed to be vinylcyclooctatetraene (VI).



The ultraviolet (Fig. 3) and infrared (Fig. 4) absorption spectra are in agreement with the vinylcyclooctatetraene structure (VI). The absorptions at 6.26 and 6.15 μ are indicative of double bonds more

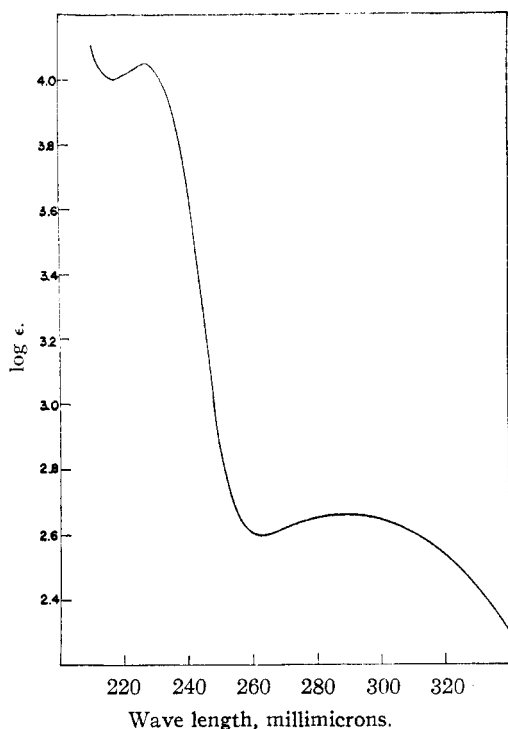


Fig. 3.—Ultraviolet spectra of orange $C_{10}H_{10}$ component.

The vinyl group of VI could be in a plane with one of the double bonds of the cyclooctatetraene ring and thus allow for conjugation which cannot exist in the non-planar cyclooctatetraene itself.

Distillation of the colorless $C_{10}H_{10}$ component also showed it to be essentially one material. It absorbed two molar equivalents of hydrogen in methanol over Adams catalyst to give *n*-butylbenzene. Of the possible $C_{10}H_{10}$ hydrocarbons which could give butylbenzene on hydrogenation, the most likely appeared to be 1-phenyl-1,3-butadiene on the basis of the infrared absorption spectrum (Fig. 4). The absorptions in the region of 6.27–6.38 μ are attributable to double bonds conjugated with a benzene ring. The colorless $C_{10}H_{10}$ was identified as 1-phenyl-1,3-butadiene by preparation of two known bromine addition products. Its physical constants agreed closely with those reported for *cis*-1-phenyl-1,3-butadiene. The facts that it failed to give a Diels-Alder adduct with maleic anhydride and that, after irradiation with ultraviolet light, its ultraviolet absorption spectrum was in good agreement with that of an authentic sample of *trans*-1-phenyl-1,3-butadiene indicated that the colorless $C_{10}H_{10}$ was *cis*-1-phenyl-1,3-butadiene.⁴

In view of the separation of the $C_{10}H_{10}$ fraction into two components, the orange VI and the colorless 1-phenyl-1,3-butadiene, it seems probable that

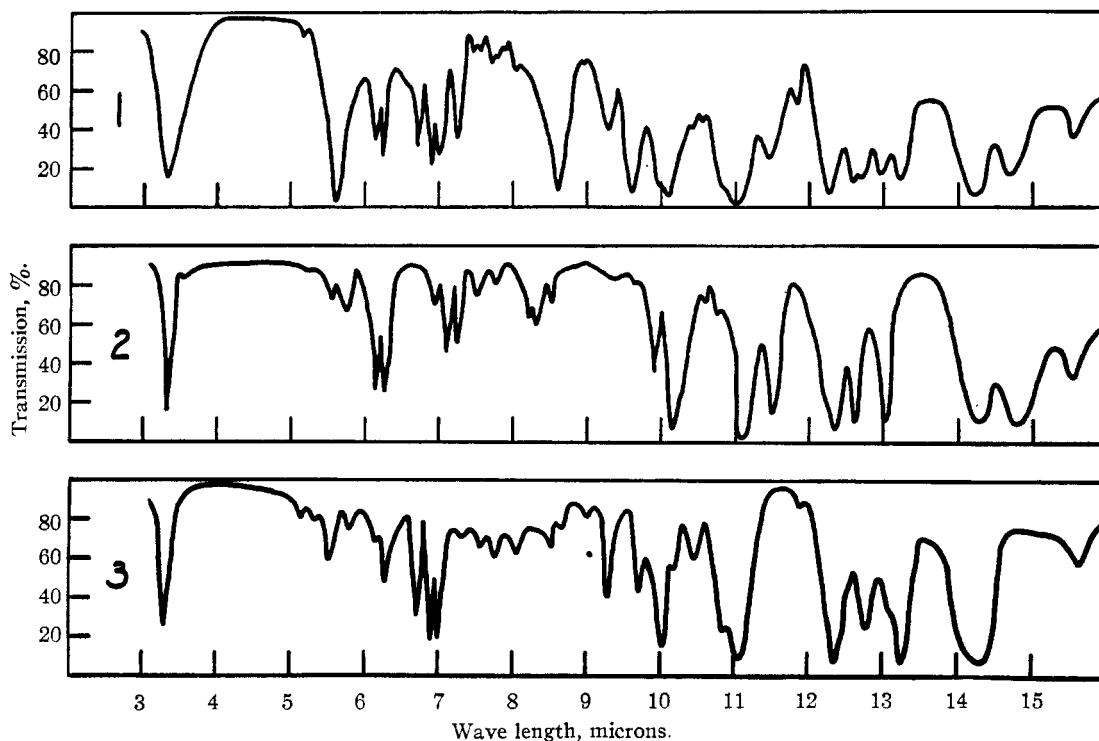


Fig. 4.—Infrared spectra: curve 1, $C_{10}H_{10}$ fraction; curve 2, orange $C_{10}H_{10}$ component; and curve 3, colorless $C_{10}H_{10}$ component.

highly conjugated than those of cyclooctatetraene, which shows a double bond absorption at 6.11 μ .³ Also the absorption maxima in the ultraviolet at 228 and 292 $m\mu$ are indicative of more conjugation than is shown in cyclooctatetraene, which shows no absorption maximum in the ultraviolet region.³

(3) A. P. I. Research Project 44, Infrared Spectrum No. 595, Ultraviolet Spectrum No. 180 and 181.

the two supposedly different $C_{10}H_{10}$ hydrocarbons

(4) (a) Alder, Vagt and Vogt, *Ann.*, **565**, 135 (1949), reported that *trans*-1-phenyl-1,3-butadiene underwent the Diels-Alder reaction with maleic anhydride very readily. (b) Crummitt and Christoph, *This Journal*, **71**, 4157 (1949), cleared up the confusion that has existed in the literature concerning *cis*- and *trans*-1-phenyl-1,3-butadiene. They prepared both isomers and measured their physical constants, which differed widely, and reported that isomerization could be brought about by irradiation with ultraviolet light.

obtained by the German workers were actually mixtures containing varying ratios of the two components. The bright yellow $C_{10}H_{10}$, obtained when the acetylene polymerization was carried out at higher temperatures, probably contained a larger ratio of the 1-phenyl-1,3-butadiene. This would explain the higher refractive index and lower hydrogen uptake as compared to the orange-yellow $C_{10}H_{10}$, which probably contained a higher ratio of VI.

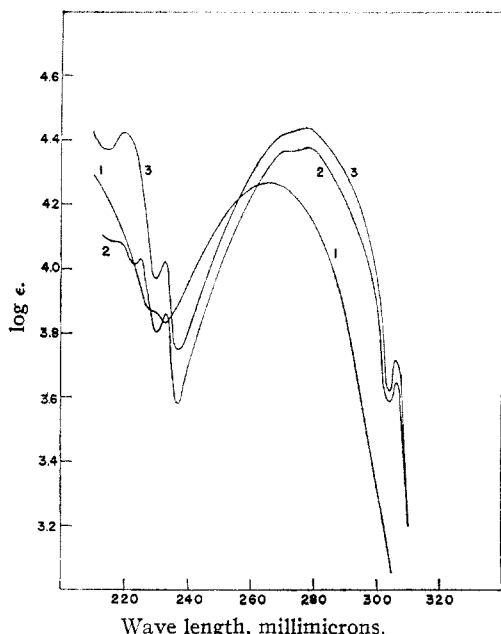


Fig. 5.—Ultraviolet spectra: curve 1, colorless $C_{10}H_{10}$ component; curve 2, colorless $C_{10}H_{10}$ component after ultraviolet irradiation; and curve 3, *trans*-1-phenyl-1,3-butadiene.

Experimental⁵

$C_{10}H_{10}$ Fractions from Cyclooctatetraene Preparations.—Cyclooctatetraene preparations were carried out in a 1-gallon Blaw-Knox stirred autoclave at 90° by the procedure of Reppe, Schlichting, Klager and Toepel.⁶ The products were isolated by crude distillation and arbitrarily divided into two fractions, the first (300–400 g., mostly cyclooctatetraene) having a boiling point range of about 40 – 60° (20 mm.) and the second (60–100 g.) having a boiling point range of about 60° (40 mm.) to 120° (1 mm.). A 968-g. sample of the higher boiling fraction, accumulated from several of the above preparations, was fractionated through a glass helix-packed column to give 211 g. of cyclooctatetraene, b.p. 52 – 54° (29 mm.), n_D^{25} 1.5341–1.5351; 283 g. of orange-yellow liquid, b.p. 70 – 75° (10 mm.), n_D^{25} 1.574–1.577; and 97 g. of greenish material, b.p. 55 – 85° (2 mm.), containing at least 25 g. of naphthalene. The orange-yellow fraction ($C_{10}H_{10}$) amounted to about 30% of the crude high-boiling fraction from the cyclooctatetraene preparations.

Anal. Calcd. for $C_{10}H_{10}$: C, 92.26; H, 7.74. Found: C, 92.16; H, 7.96.

Reppe and co-workers^{1b,10} reported the following constants for the $C_{10}H_{10}$ hydrocarbons: orange-yellow $C_{10}H_{10}$ prepared at 60 – 70° , b.p. 48 – 50° (2 mm.), 75 – 76° (12 mm.), n_D^{25} 1.5783; orange-yellow $C_{10}H_{10}$ prepared at 90 – 100° , b.p. 47 – 50° (2 mm.), n_D^{25} 1.5755; and bright yellow $C_{10}H_{10}$ prepared at 120 – 130° , b.p. 35 – 40° (0.3 mm.), 46 – 51° (2 mm.), n_D^{25} 1.5790.

Hydrogenation of the $C_{10}H_{10}$ Fraction.—A solution of 240 g. of the $C_{10}H_{10}$ fraction in 250 ml. of methanol was shaken at room temperature in the presence of 1.0 g. of Adams

catalyst under hydrogen introduced at a constant pressure of 50 p.s.i. from a reservoir until no more hydrogen was absorbed. After removing the catalyst by filtration, the filtrate was poured into 500 ml. of water and the resulting mixture extracted exhaustively with low boiling petroleum ether. The combined extracts were dried over anhydrous sodium sulfate, the solvent removed, and the residue fractionated through a 6 ft. by 13 mm. Podbielniak column operated at a reflux ratio of about 75 to 1. The fractionation resulted in the isolation of three pure components (see Fig. 1).

Component I (76 g.): b.p. 182.4° (cor.), n_D^{25} 1.4870, d_4^{25} 0.8569. *Anal.* Calcd. for $C_{10}H_{14}$: C, 89.48; H, 10.52. Found: C, 89.36; H, 10.68.

Component II (58 g.): b.p. 186.9° (cor.), n_D^{25} 1.4720, d_4^{25} 0.8511. *Anal.* Calcd. for $C_{10}H_{18}$: C, 86.90; H, 13.11. Found: C, 86.65; H, 13.35.

Component III (90 g.): b.p. 191.3° (cor.), n_D^{25} 1.4593, d_4^{25} 0.8348. *Anal.* Calcd. for $C_{10}H_{20}$: C, 85.62; H, 14.38. Found: C, 85.72; H, 14.30.

2,4-Diacetyl-amino-1-butylbenzene.—Component I and an authentic sample of *n*-butylbenzene were converted to 2,4-diacetyl-amino-1-butylbenzene by the procedure of Ipatieff and Schmerling,⁷ m.p. and mixed m.p. 216 – 218° .

1-Ethylcyclooctene (IV).—1-Ethylcyclooctene was prepared by the method used by Godchot and Cauquil⁸ for the preparation of 1-methylcyclooctene. A solution of 16.0 g. (0.127 mole) of cyclooctanone in 100 ml. of absolute ether was added to the Grignard reagent prepared from 7.5 g. of magnesium and 45 g. (0.29 mole) of ethyl iodide. After stirring for 2 hours at gentle reflux, the mixture was poured onto a mixture of 20 g. of ammonium chloride and 300 g. of cracked ice. The ether layer was separated, washed once with water, and dried over anhydrous sodium sulfate. Removal of the ether by distillation left a residue of 17.5 g. of nearly colorless oil, 1-ethylcyclooctanol. The 1-ethylcyclooctanol was dehydrated by heating until distillation occurred at atmospheric pressure. Low-boiling petroleum ether was added to the wet distillate and the solution dried over anhydrous sodium sulfate. After removing the solvent the residue was distilled to give 10 g. (57%) of 1-ethylcyclooctene, b.p. 186 – 187° , n_D^{25} 1.4714, d_4^{25} 0.8482.

Anal. Calcd. for $C_{10}H_{18}$: C, 86.90; H, 13.10. Found: C, 86.92; H, 12.89.

Ethylcyclooctane (V).—Hydrogenation of 10 g. (0.0725 mole) of 1-ethylcyclooctene in 50 ml. of glacial acetic acid in the presence of pre-reduced Adams catalyst was complete in 1 hour and required one molar equivalent of hydrogen. The catalyst was removed by filtration, the filtrate added to 100 ml. of water, and the resulting mixture extracted exhaustively with low-boiling petroleum ether. The combined extracts were dried over anhydrous sodium sulfate, concentrated, and the residue distilled to give 10 g. (99%) of ethylcyclooctane, b.p. 191.4° (cor.), n_D^{25} 1.4567, d_4^{25} 0.8328.

Anal. Calcd. for $C_{10}H_{20}$: C, 85.62; H, 14.38. Found: C, 85.62; H, 14.56.

Separation of $C_{10}H_{10}$ into Two Components. A. Orange $C_{10}H_{10}$ Component (VI).—A solution of 145 g. of freshly distilled $C_{10}H_{10}$ fraction in 200 ml. of petroleum ether was extracted by vigorous shaking in a separatory funnel with eight 100-ml. portions of 30% aqueous silver nitrate. All of the yellow color was present in the water layer. To the combined aqueous extracts was added 200 g. of sodium chloride and the resulting mixture subjected to steam distillation until no more yellow oil distilled over. The distillate was extracted exhaustively with low boiling petroleum ether, the extracts dried over anhydrous sodium sulfate, concentrated, and the residue distilled to give 67 g. of orange liquid, b.p. 79° (18 mm.), n_D^{25} 1.5685. Careful fractionation through a Piros-Glover micro spinning band column gave orange $C_{10}H_{10}$ component with b.p. 83.3° (20 mm.) (cor.), n_D^{25} 1.5682, d_4^{25} 0.9315.

Anal. Calcd. for $C_{10}H_{10}$: C, 92.26; H, 7.74. Found: C, 92.10; H, 7.74.

B. Colorless $C_{10}H_{10}$ Component.—The petroleum ether layer left from the aqueous silver nitrate extraction described above was dried over anhydrous sodium sulfate, concentrated, and the residue distilled to give 50.3 g. of color-

(5) Boiling and melting points are uncorrected unless otherwise indicated.

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

(7) Ipatieff and Schmerling, *This Journal*, **54**, 1056 (1937).

(8) Godchot and Cauquil, *Compt. rend.*, **185**, 1202 (1927).

less liquid, b.p. 84–86° (18 mm.), n_D^{25} 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_D^{25} 1.5808; reported for *cis*-1-phenyl-1,3-butadiene, b.p. 71° (11 mm.), n_D^{25} 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, ethylcyclooctane, was isolated as described above (6.0 g., 86%), b.p. 188.5–189°, n_D^{25} 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_D^{25} 1.4887. Reported for *n*-butylbenzene,^{9a,b} b.p. 183.1°, n_D^{25} 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

(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).

Anal. Calcd. for $C_{10}H_{10}Br_2$: 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_D^{25} 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.

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

EASTON, PENNA.

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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 Meister¹ 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

work² and statements in the monographs written by Reppe³ and a text based on Reppe's reports⁴ indicate that these hydrocarbons were originally considered to be cyclodecapentaene (two stereoisomeric forms) and cyclododecahexaene.

The catalytic polymerization of acetylene to

(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.

(1) Reppe, Schlichting and Meister, *Ann.*, **590**, 93 (1948).