Anal. Calcd. for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79. Found: C, 74.14; H, 8.75.[8]

The infrared spectrum showed absorption at 3.25 (=CH), 3.45 (—CH), 5.75 (ester carbonyl), 6.05 (C=C), 7.25 (CH_3—) and 11.25 μ (terminal methylene group). The Raman spectrum showed absorption at 6.05, 6.00 and 5.82 μ. The 6.00 μ band is indicative of the internal double bond in the proposed structure.

E. 5(and/or 6)-Methylene-1,2,3,4,5,6,7,8-octahydro-2-naphthonitrile (VIIIe).—A mixture of 125 g. of stabilized acrylonitrile, 5 g. of bis-(triphenyl phosphite)-nickel dicarbonyl catalyst, 1 g. of phenothiazine, 50 g. of allene and 150 ml. of tetrahydrofuran was heated at 80–85° in a pressure vessel for 6 hours. The solvent was removed from the resulting mixture by distillation and the product was distilled at reduced pressure through a still heated by vapors of liquids boiling at successive temperatures of 100°, 138° and approximately 200°. The distillate, which weighed 37.7 g., was redistilled through a spinning band column to obtain 8.4 g. of VIIIe, b.p. 90° (0.3 mm.), $n^{25}D$ 1.5198.

Anal. Calcd. for $C_{12}H_{15}N$: C, 83.18; H, 8.73; N, 8.09. Found: C, 82.85; H, 9.12; N, 8.59.

F. 5-Methylene-2(and/or 3)-vinyl-1,2,3,4,5,6,7,8-octahydronaphthalene (VIIIf).—A mixture of 100 g. of allene, 80 g. of butadiene, 5 g. of bis-(triphenyl phosphite)-nickel dicarbonyl, 10 g. of calcium carbide and 200 ml. of tetrahydrofuran was heated at 115–140° and autogenous pressure for 7 hours. The resulting product was distilled through an 8-inch Vigreux column to separate it from the non-volatile material, and the distillate was redistilled through an efficient column to obtain the adduct VIIIf, b.p. 123–123.5° (23 mm.), $n^{25}D$ 1.5162. The infrared spectrum showed the presence of a terminal methylene group (11.3 μ) and a vinyl group (10.05 and 11.00 μ).

Anal. Calcd. for $C_{13}H_{18}$: C, 89.59; H, 10.41; hydrogenation, 0.0345 g. H_2/g. sample (three double bonds). Found: C, 89.89; H, 10.48; H_2, 0.0274 g. H_2/g. sample (79% of theoretical).

G. Dimethyl 5(and/or 6)-Methylene-1,4,5,6,7,8-hexahydro-2,3-naphthalenedicarboxylate (IX).—To 7.1 g. (0.05 mole) of dimethyl acetylenedicarboxylate containing 0.2 g. of phenothiazine was added in 5 portions 8.9 g. (0.074 mole) of the trimeric product. Heat was evolved and the flask was cooled in an ice-bath. The reaction was completed by heating at 100° for one hour. Distillation yielded 8.3 g. of IX, b.p. 149–150° (0.4 mm.), $n^{25}D$ 1.5240. The infrared spectrum showed absorption at 3.25 (=CH), 3.4, 3.45 and 3.5 (—CH), 5.8 (C=O), 6.0 (C=C), 7.9 (ester carbonyl) and 11.25 μ (terminal methylene).

Anal. Calcd. for $C_{15}H_{18}O_4$: C, 68.68; H, 6.91. Found: C, 68.84; H, 6.93.

1,1,2,2-Tetrafluoro-6,8-dimethylenespiro[3.5]nonane (X).[4]—Reaction of 6 g. of VI with 20 g. of tetrafluoroethylene containing 0.5 g. of phenothiazine at 150° for 15 hours in a sealed vessel yielded 3.68 g. (34% yield) of X, b.p. 76° (20 mm.), $n^{25}D$ 1.4315.

Anal. Calcd. for $C_{11}H_{12}F_4$: C, 59.99; H, 5.49; F, 34.51. Found: C, 60.48; H, 5.93; F, 34.34.

The infrared spectrum showed absorption at 3.25 (=CH), 3.4 and 3.5 (—CH), 6.03 (C=C), 7–9 (—CF) and 11.13 μ (terminal methylene). The proton and nuclear magnetic resonance spectra were in accord with the proposed structure.

1,3,5,7-Tetramethylenecyclooöctane (VII).—1,3,5,7-Tetramethylenecyclooöctane was isolated from the higher-boiling product formed in the cyclopolymerization reaction. The conversion to tetramer was about 7% with bis-(triphenylphosphine)-nickel dicarbonyl. The product was isolated by distillation, b.p. 60° (3.5 mm.), $n^{25}D$ 1.5102.

Anal. Calcd. for $C_{12}H_{16}$: C, 89.94; H, 10.07; mol. wt., 160; hydrogenation (4 double bonds), 0.0503 g. H_2/g. sample. Found: C, 90.16; H, 10.24; mol. wt., 145; hydrogenation, 0.043 g. H_2/g. sample (85% of theoretical).

The infrared spectrum showed absorption at 3.25 and 3.3 (=CH), 3.4 (—CH), 6.05 and 6.1 (C=C) and 11.2 μ (terminal methylene). There was no indication of the presence of a conjugated double bond. The ultraviolet spectrum showed no maximum above 210 mμ, further indicating the absence of a conjugated double bond. The proton magnetic resonance spectrum indicated the presence of CH saturation and unsaturation of equal intensity. The spectrum of the hydrogen attached to saturated carbon was split into two equal parts.

Acknowledgments.—The authors gratefully acknowledge the determination and interpretation of infrared and ultraviolet absorption spectra by Miss N. E. Schlichter and Mr. C. B. Matthews, and of the n.m.r. spectra by Dr. H. Foster and Dr. W. D. Phillips. In addition, we wish to acknowledge the many helpful discussions of the infrared spectra with Professor R. C. Lord of Massachusetts Institute of Technology.

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[8] The Diels–Alder adducts are air-sensitive, and difficulty was experienced in obtaining satisfactory analytical data in some cases.

[CONTRIBUTION NO. 490 FROM THE CENTRAL RESEARCH DEPARTMENT EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

Chemistry of Allene. II. Reaction of Allene with Acetylenes

BY R. E. BENSON AND R. V. LINDSEY, JR.

RECEIVED OCTOBER 29, 1958

The reaction of allene with acetylene in the presence of nickel acetylacetonate has given 3,5-dimethylenecyclohexene (I) in 45% yield and 3,5,7-trimethylenecyclooöctene (II) in 5% yield. This reaction was extended to several substituted acetylenes to give mixtures of 1- and 2-substituted 3,5-dimethylenecyclohexenes. With bis-(triphenyl phosphite)-nickel dicarbonyl catalyst, allene and acetylene gave a mixture of 3,5- and 3,6-dimethylenecyclohexene.

The previous paper[1] reported the one-step synthesis of novel exomethylene ring compounds by cyclopolymerization of allene with phosphorus-modified nickel carbonyl catalysts. This cyclization reaction gave trimers and a tetramer that were identified as 1,2,4- and 1,3,5-trimethylenecyclohexane and 1,3,5,7-tetramethylenecyclooöctane, respectively.

It has now been found that reaction of allene with acetylene in the presence of certain nickel catalysts provides a direct synthesis of exomethylene cyclic compounds containing ring unsaturation. Compounds of this type previously have been obtained only by more complex syntheses.[2,3]

Reaction of two moles of allene with one mole of acetylene at 80° and autogenous pressure in the presence of nickel acetylacetonate catalyst gave a

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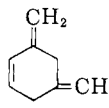
[1] R. E. Benson and R. V. Lindsey, Jr., THIS JOURNAL, **81**, 4247 (1959).

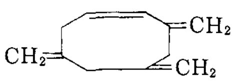
[2] W. J. Bailey and J. Rosenberg, *ibid.*, **77**, 73 (1955).

[3] W. J. Bailey and J. Barclay, Jr., Abstracts, 130th Meeting of A.C.S., September, 1956, p. 6-O.

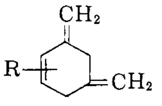
45% yield of the triene, 3,5-dimethylenecyclohexene (I), and about 5% of the tetraene, 3,5,7-trimethylenecycloöctene (II). Nickel cyanide and nickel ethyl acetoacetate also catalyzed the formation of I under similar conditions in yields of 45 and 37%, respectively.



I



II



III, R = CH_3
IV, R = C_6H_5
V, R = $CH_2=CH$

With bis-(triphenyl phosphite)-nickel dicarbonyl catalyst at 80–85° and atmospheric pressure, a mixture of trienes was obtained in 43% yield. This mixture was separated by vapor-phase chromatography and shown to consist of about 40% of I and 60% of the known[3] isomeric 3,6-dimethylenecyclohexene prepared by pyrolysis of 1,4-bis-(acetoxymethyl)-cyclohexene.

Reaction of allene with substituted acetylenes including methylacetylene, phenylacetylene and vinylacetylene gave the corresponding dimethylenecyclohexenes (III, IV and V). The product from methylacetylene was a mixture of 1- and 2-methyl-3,5-dimethylenecyclohexene containing primarily the 1-methyl isomer.

Although nickel acetylacetonate is known to convert acetylene to cycloöctatetraene under conditions similar to those employed in these reactions, no detectable amount of cycloöctatetraene was formed when two moles of allene per mole of acetylene were used. Cycloöctatetraene was formed, however, when an excess of acetylene was present.

The product (I) obtained with nickel acetylacetonate catalyst was shown to be a cyclic triene of formula C_8H_{10} by elemental and spectral analyses and by quantitative hydrogenation studies. The infrared spectrum showed absorption at 3.25 and 3.3 (=CH), 3.4 (—CH), 6.05, 6.1 and 6.25 (C=C) and 11.45 μ (=CH_2). The ultraviolet spectrum showed λ_{max} 233 mμ (ϵ 16000) with weaker bands at λ_{max} 263 mμ (ϵ 2440) and λ_{max} 273 mμ (ϵ 1700). The proton magnetic resonance spectra showed that an equal number of hydrogen atoms were attached to saturated carbon and to the carbon of the terminal methylene groups. The intensity for the hydrogen atoms attached to the ring double bond appeared to be low. However, because of the rather flat and extended absorption in this region, an error in establishing the base line may account for this observation.

Hydrogenation of I with platinum oxide catalyst in glacial acetic acid gave a mixture of *cis*- and *trans*-1,3-dimethylcyclohexane. Isomerization of I with *p*-toluenesulfonic acid, palladium-on-carbon, or potassium *t*-butoxide gave *m*-xylene. These data establish the structure of I as 3,5-dimethylenecyclohexene. The compound is surprisingly stable thermally, 65% being recovered on refluxing for 6.5 hours.

The reaction of methylacetylene with allene yielded a triene of empirical formula C_9H_{12}. The infrared and proton magnetic resonance spectra indicated the product to be 1- and/or 2-methyl-3,5-dimethylenecyclohexene. The product was shown to be a mixture containing primarily the 1-isomer by isomerization with *p*-toluenesulfonic acid to a mixture of 1,2,4- and 1,3,5-trimethylbenzene consisting primarily of the 1,2,4-isomer.

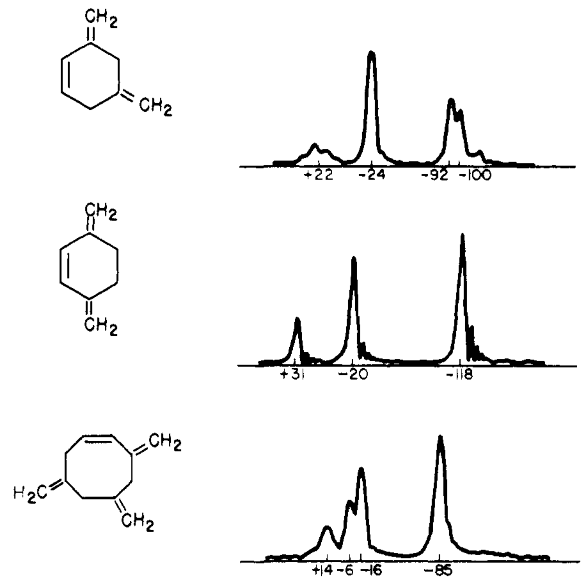


Fig. 1.—The hydrogen magnetic resonance spectra were obtained using a Varian high resolution n.m.r. spectrometer and electromagnet at a frequency of 40 Mc. and a field of 9500 gauss. The spectra were calibrated in terms of displacements in cycles per second from the hydrogen resonance of water.

The structures of the trienes IV and V obtained from allene with phenylacetylene and monovinylacetylene, respectively, have been assigned by analogy and on the basis of elemental and spectral data.

The higher-boiling product (II) from the synthesis of I analyzed for $C_{11}H_{14}$ and, on hydrogenation at room temperature, absorbed approximately four moles of hydrogen. The proton magnetic resonance spectrum of the unsaturated product indicated the presence of six hydrogen atoms attached to carbon of terminal methylene groups and two hydrogen atoms attached to carbon of a ring double bond. The latter two hydrogen atoms were not equivalent and only two of the terminal methylene groups were indicated to be equivalent. The presence of six hydrogen atoms attached to saturated carbon of the methylene type was also indicated. These data require a cycloöctene ring having one terminal methylene group conjugated with the ring double bond, and bearing two additional terminal methylene groups. Of the various possible structures, only 3,5,7-trimethylenecycloöctene is consistent with these data.

The ultraviolet absorption spectrum of II failed to show absorption above 210 mμ, indicating the absence of a normal conjugated double bond. However, the infrared spectrum showed absorption at 6.15 μ, which is typical of cycloöctratetraene. Reference to a molecular model of 3,5,7-trimethylenecycloöctene indicated that it is not possible for the ring double bond and the adjacent terminal methylene group to become planar without considerable strain. This presumably accounts for the absence of typical double bond absorption for this compound. A somewhat similar situation exists in cyclooctatetraene, which cannot assume a planar configuration. Thus, cyclooctatetraene has no maximum absorption above 220 mμ, in contrast to the linear 1,3,5,7-octatetraene which absorbs at 290 and 304 mμ.[4,5]

Experimental

3,5-Dimethylenecyclohexene (I).—A 1-liter stainless steel pressure vessel was flushed with nitrogen and charged with 10 g. of nickel acetylacetonate, 15 g. of finely ground calcium carbide and 200 ml. of anhydrous tetrahydrofuran. The vessel was cooled to −80° and evacuated. Allene (100 g., 2.5 moles) was added by distillation and the vessel was then allowed to warm to room temperature. Acetylene (approximately one-half mole) was pressured into the vessel which was agitated and heated during 2 hours to 80–85°. A pressure of 10–14 atm. was usually attained before initiation of reaction, as evidenced by a rapid pressure decrease. The temperature of the vessel was held at 80–85° and acetylene was injected intermittently until the total pressure drop of the acetylene reservoir corresponded to the charging of approximately 1.3–1.5 moles of acetylene. Heating at 80–85° was continued until the pressure in the vessel had fallen to 2.4 atm. This usually required 4–5 hours.

The product was decanted from the calcium carbide, and the dark liquid was steam distilled. The organic layer was washed four times with water. Infrared analysis of the crude product failed to detect the presence of cyclooctatetraene in experiments in which allene and acetylene were used in approximately 2:1 molar ratios. However, to assure complete removal of cyclooctatetraene, the organic layer was washed twice with 25% aqueous silver nitrate and then dried over magnesium sulfate. In a typical experiment, products from 3 runs involving a total of 278 g. (6.95 moles) of allene and approximately 4.4 moles of acetylene were combined. Distillation yielded 160.7 g. (44% yield) of 3,5-dimethylenecyclohexene, b.p. 73° (98 mm.), $n^{25}\text{D}$ 1.5133–1.5141, and 89 g. of higher-boiling product. Analytical data were obtained on a sample of b.p. 65.5° (77 mm.), $n^{25}\text{D}$ 1.5130.

Anal. Calcd. for C_8H_{10}: C, 90.50; H, 9.50; mol. wt., 106; hydrogenation, 0.057 g. H_2/g. sample (three double bonds). Found: C, 90.37; H, 9.85; mol. wt., 101; hydrogenation, 0.0602 g. H_2/g. sample.

Nickel cyanide and nickel ethyl acetoacetate were effective catalysts for the formation of I in yields of 45 and 37%, respectively, under the same conditions described for nickel acetylacetonate.

Isolation of 3,5,7-Trimethylenecyclooctene (II).—The combined higher-boiling products from several preparations of I with nickel acetylacetonate catalyst were distilled through an efficient column. After removal of a small amount of I there was obtained a small, intermediate cut, b.p. 40–68° (11 mm.). Continued distillation yielded II, b.p. 69.5–70° (11 mm.), $n^{25}\text{D}$ 1.5217–1.5221. The infrared spectrum showed absorption at 11.2 (=CH$_2$) and 6.1 with shoulder at 6.15 (C=C), 3.4 (saturated CH), 3.25 and 3.3 μ (=CH). The ultraviolet spectrum showed essentially no absorption above 210 mμ.

Anal. Calcd. for $C_{11}H_{14}$: C, 90.35; H, 9.65; hydrogenation. 0.0552 g. H_2/g. sample (four double bonds). Found: C, 90.97; H, 9.72; hydrogenation, 0.0500 g. H_2/g. sample (91% of theoretical for four double bonds).

3,5-Dimethylene-1(and 2)-methylcyclohexene (III).—In the same manner described for the preparation of I, allene (60 g.) and methylacetylene (30 g.) were charged into a pressure vessel containing tetrahydrofuran, calcium carbide and nickel acetylacetonate catalyst. The pressure fell from 6.7 to 4 atm. in 1.5 hours at 80°. The run was terminated at this point because of a mechanical failure. Distillation yielded 3,5-dimethylene-1(and 2)-methylcyclohexene, b.p. 80° (60 mm.), $n^{25}\text{D}$ 1.5129.

Anal. Calcd. for C_9H_{12}: C, 89.94; H, 10.07. Found: C, 89.87; H, 10.09.

The infrared spectrum showed absorption at 3.25 (=CH), 3.4, 3.45 and 3.5 (—CH), 6.05 and 6.2 (C=C), 7.25 (CH$_3$) and 11.35 and 11.55 μ (=CH$_2$). The proton magnetic resonance spectrum was consistent with the proposed structure except that the intensity of the proton resonance of the hydrogen atom attached to the ring double bond was slightly low.

3,5-Dimethylene-1(and/or 2)-phenylcyclohexene (IV).—The reaction of 62 g. (1.55 moles) of allene with 62 g. (0.607 mole) of phenylacetylene at 80–85° for 8 hours in the presence of 10 g. of nickel acetylacetonate, 15 g. of calcium carbide and 180 ml. of tetrahydrofuran yielded a brown mixture. The liquid was decanted from the calcium carbide, and the tetrahydrofuran was removed by distillation. The resulting product was distilled at 1 mm. in a vapor-bath still heated first by refluxing xylene and then by refluxing cresol. The distillate was collected in a trap cooled to −80°, and was redistilled through a 4-inch Vigreux column. The liquid (25.5 g.) of b.p. 61–72° (0.07 mm.) was redistilled. Infrared and proton magnetic resonance analyses of the product, b.p. 77° (0.2 mm.), were consistent with the proposed structures. The infrared spectrum showed absorption at 3.25 and 3.3 (=CH), 3.4, 3.45 and 3.5 (—CH), 6.1 (unconjugated C=C), 6.2, 6.35 and 6.65 (conjugated C=C) 11.25 (=CH$_2$), 13.2 and 14.4 μ (monosubstituted benzene). Satisfactory elemental analyses were not obtained because of the extreme sensitivity of the product to air.

Anal. Calcd. for $C_{14}H_{14}$: C, 92.26; H, 7.74. Found: C, 90.70; H, 7.89.

3,5-Dimethylene-1(and/or 2)-vinylcyclohexene (V).—A 1-liter stainless steel pressure vessel was charged with 10 g. of nickel acetylacetonate, 10 g. of finely ground calcium carbide and 150 ml. of tetrahydrofuran. The vessel was flushed with nitrogen, cooled, and evacuated. Monovinylacetylene (20 g.) and allene (32 g.) were added. The vessel was heated at 70° for 8 hours, during which time the pressure fell from 5.4 to 2 atm. Distillation yielded several fractions including 7.5 g. of the vinyl compound, b.p. 48–50° (3.5 mm.), $n^{25}\text{D}$ 1.5662–1.5672.

Anal. Calcd. for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 91.12; H, 9.34.

The infrared spectrum of a similar sample (b.p. 44° (2.9 mm.), $n^{25}\text{D}$ 1.5653) was consistent with the proposed structures. The spectrum showed absorption at 3.25 (=CH), 6.05 and 6.15 (C=C), 11.25, with shoulder at 11.45 (=CH$_2$), and 10.15 and 11.1 μ (CH=CH$_2$).

Isomerization of 3,5-Dimethylenecyclohexene (I). **A. With Palladium-on-carbon Catalyst.**—A mixture of 3.0 ml. of I and 0.3 g. of 10% palladium-on-carbon catalyst was heated carefully. At a bath temperature of approximately 60°, compound I began to reflux vigorously and the heating bath was removed. After approximately 5 minutes, the vigorous reaction subsided and the mixture was heated at 140–155° for 18 hours. The catalyst was removed by filtration to give a colorless oil, $n^{25}\text{D}$ 1.4968 (lit. $n^{25}\text{D}$ 1.4951 for *m*-xylene)[6]. Infrared analysis confirmed the liquid to be *m*-xylene, possibly containing traces of *o*- and *p*-xylene.

B. **With *p*-Toluenesulfonic Acid Catalyst.**—A solution of 0.3 g. of *p*-toluenesulfonic acid monohydrate in 25 ml. of chloroform was deaerated and 3.4 g. of I was added. The solution was refluxed under nitrogen for 4 hours, washed with 1% sodium hydroxide and water, and dried over magnesium sulfate. Distillation yielded 1.9 g. (56% yield) of *m*-xylene, b.p. 76–77° (109 mm.), $n^{25}\text{D}$ 1.4942. Infrared analysis confirmed the oil to be *m*-xylene, possibly containing traces of *o*- and *p*-xylene.

C. **With Potassium *t*-Butoxide Catalyst.**—A solution of potassium *t*-butoxide was prepared under nitrogen from 0.2 g. of potassium and 25 ml. of dry *t*-butyl alcohol. Compound I (5.0 g.) was added and the solution was refluxed for 3.5 hours under nitrogen, poured into water, and extracted with petroleum ether. Distillation yielded 1.36 g. of colorless oil, b.p. 72–74° (96 mm.), $n^{25}\text{D}$ 1.4929. Redistillation gave *m*-xylene, b.p. 71° (90 mm.), $n^{25}\text{D}$ 1.4962. The identity of the product was confirmed by infrared analysis.

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(4) A. C. Cope and M. Burg, This Journal, **74**, 168 (1952).

(5) G. F. Woods and L. H. Schwartzman, *ibid.*, **71**, 1396 (1949).

(6) E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1941.

Hydrogenation of I to *cis*- and *trans*-1,3-Dimethylcyclohexane.—A solution of 2.6 g. of I in 60 ml. of glacial acetic acid containing 0.3 g. of platinum oxide catalyst was shaken in a hydrogenation apparatus at room temperature and 40 lb./sq. in. hydrogen pressure. The reaction appeared to be complete after 1.25 hours. The resulting mixture was filtered and the filtrate was cooled to −80°. Excess 20% sodium hydroxide solution was added to the partially solid mixture. Petroleum ether was added and the organic layer was separated, washed with water and dried over magnesium sulfate. The petroleum ether was removed by distillation and the remaining liquid was distilled to obtain 1.6 g. of colorless liquid, b.p. 58° (97 mm.), $n^{25}\text{D}$ 1.4173–1.4208, that was identified as a mixture of *cis*- and *trans*-1,3-dimethylcyclohexane by comparison of the infrared spectrum with those of authentic *cis*- and *trans*-1,3-dimethylcyclohexane.

Thermal Stability of I.—Compound I (4.8 g.) containing 0.1 g. of phenothiazine was refluxed under nitrogen at an oil-bath temperature of 145–150° for 6.5 hours. Distillation gave 3.2 g. (66%) of I. The product remaining in the distillation flask set to a glass-like material.

Silver Nitrate Complex of I.—The reaction of I with finely ground silver nitrate in ethanol yielded white crystals, m.p. 77–79° (sealed capillary, bath preheated to 70°). The complex was light sensitive. 3,5-Dimethylenecyclohexene was recovered by dissolving the complex in deaerated water and adding ammonium hydroxide until the silver oxide that initially separated had redissolved.

Isomerization of 3,5-Dimethylene-1(and 2)-methylcyclohexene (III).—Compound III was isomerized in chloroform solution with *p*-toluenesulfonic acid monohydrate catalyst. The product obtained, b.p. 83° (53 mm.), $n^{25}\text{D}$ 1.4951–1.4975, was shown by infrared analysis to be principally 1,3,5-trimethylbenzene containing a small amount of 1,2,4-trimethylbenzene. The literature values are: 1,3,5-trimethylbenzene, b.p. 164°, $n^{25}\text{D}$ 1.4967; 1,2,4-trimethylbenzene, b.p. 169°, $n^{25}\text{D}$ 1.5025.[6]

Isomerization of 3,5-Dimethylene-1(and/or 2)phenylcyclohexene (IV).—Compound IV was heated in a solution of chloroform containing a small amount of *p*-toluenesulfonic acid monohydrate. Distillation yielded an aromatic product, b.p. 75° (0.11 mm.), $n^{25}\text{D}$ 1.5930. The infrared and proton magnetic resonance spectra indicated the liquid to be a mixture of dimethylbiphenyls.

Preparation of 3,5- and 3,6-Dimethylenecyclohexene.—In two separate experiments a total of 160 g. (4 moles) of allene was treated with approximately 6.35 moles of acetylene at 80–85° and autogenous pressure in the presence of 10 g. of bis-(triphenyl phosphite)-nickel dicarbonyl catalyst and 400 ml. of benzene. The combined product (634 g.) was distilled through a short column to separate it from the catalyst, and the distillate was redistilled through a packed column. There was obtained 91.5 g. of colorless liquid, b.p. 91° (200 mm.) to 69.5–70° (87 mm.), $n^{25}\text{D}$ 1.5289–1.5300. A fraction, b.p. 75° (104 mm.), $n^{25}\text{D}$ 1.5281, was analyzed.

Anal. Calcd. for C_8H_{10}: C, 90.50; H, 9.50. Found: C, 90.89; H, 9.61.

The infrared spectrum of this product was quite similar to that of I, but the proton magnetic resonance spectrum was considerably different. The components of the mixture were separated by vapor-phase chromatography using a column packed with Celite saturated with silver nitrate at room temperature. The column was heated to 75° and helium was used as the carrier gas. The first fraction, which comprised 42% of the mixture, was identified as 3,6-dimethylenecyclohexene on the basis of spectral analyses. The proton magnetic resonance spectrum was in agreement with the proposed structure and the ultraviolet spectrum showed λ_{max} 273 mμ (ϵ 20,150), 262.5 mμ (ϵ 28,000) and 254 mμ (ϵ 23,800). These data are in agreement with recently reported values[3] for this compound. The infrared spectrum showed absorption at 3.25 and 3.3 (=CH), 3.45 and 3.5 (CH), 6.15, 6.45 and 6.65 (conjugated C=C) and 11.2 μ ($=CH_2$).

The retention time and infrared spectrum for the second component (57%) were the same as those of authentic I. A third component, which was present in approximately 1% concentration, was not identified.

An analysis of the entire reaction product from a similar preparation indicated the presence of 57.5% of the 3,6-isomer and 41.5% of the 3,5-isomer. Similarly, the product obtained from the reaction of allene with acetylene at atmospheric pressure in the presence of bis-(triphenyl phosphite)-nickel dicarbonyl catalyst contained 40.5% of the 3,6-isomer and 57.4% of the 3,5-isomer.

Isomerization of these products with 10% palladium-on-charcoal catalyst gave a mixture of *m*- and *p*-xylene.

The triene mixture was separated by use of vapor-phase chromatography.[7] A 1.6 cm. × 183 cm. copper tube was packed with 4-methyl-4-nitroheptanedinitrile on fire brick and heated to 100°. Helium was used as the carrier gas at about 500 ml./min. for 2.5-ml. samples of the triene mixture. The 3,6-isomer was obtained in a pure state as shown by spectral and gas chromatographic analyses, b.p. 75° (100 mm.), $n^{25}\text{D}$ 1.5419.[3]

Acknowledgments.—The authors gratefully acknowledge the determination and interpretation of infrared and ultraviolet absorption spectra by Miss N. E. Schlichter and Mr. C. B. Matthews, and of the n.m.r. spectra by Dr. H. Foster and Dr. W. D. Phillips.

[7] We are indebted to Dr. B. C. Anderson for this study.

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[CONTRIBUTION NO. 503 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

Chemistry of Allene. III. Chemistry of 3,5-Dimethylenecyclohexene

BY R. E. BENSON, R. V. LINDSEY, JR., AND B. C. ANDERSON

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The chemistry of 3,5-dimethylenecyclohexene, which is readily accessible from allene and acetylene, has been studied. Reactions with electrophilic and nucleophilic reagents have led to the formation of aromatic derivatives, whereas reactions proceeding *via* free-radical processes have yielded non-aromatic structures.

The synthesis of 3,5-dimethylenecyclohexene (I) in 45% yield from allene and acetylene was reported previously.[1] This unusual triene was found to isomerize readily to *m*-xylene with *p*-toluenesulfonic acid, potassium *t*-butoxide or palladium-on-carbon catalysts. It was, however, quite stable thermally in the absence of oxygen. Further studies of I are now reported.

Reactions of the triene with electrophilic, nucleophilic and free-radical reagents have been examined. Most of the reactions appear to proceed by attack of the reagent at the exocyclic conjugated methylene group. With the exception of free radical-type reactions, the ultimate products were aromatic derivatives.

The triene I was extremely sensitive to air and reacted with oxygen at 0–5° in the absence of added catalyst to yield a viscous, polymeric peroxide. The

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[1] R. E. Benson and R. V. Lindsey, Jr., THIS JOURNAL, **81**, 4250 (1959).