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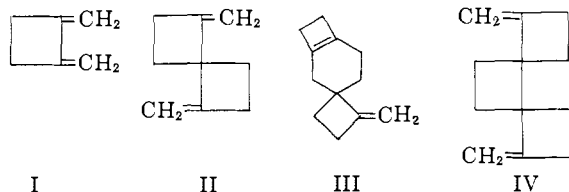
Chemistry of Allene. I. Cyclopolymerization. Synthesis and Chemistry of 1,2,4- and 1,3,5-Trimethylenecyclohexane and 1,3,5,7-Tetramethylenecyclooctane

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

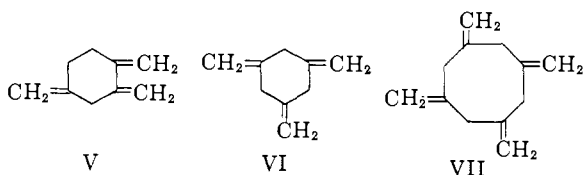
RECEIVED OCTOBER 29, 1958

The cyclopolymerization of allene with phosphorus-modified nickel carbonyl catalysts has given two trimers, identified as 1,2,4- and 1,3,5-trimethylenecyclohexane (V and VI), and a remarkably stable tetramer, identified as 1,3,5,7-tetramethylenecyclooctane (VII). The chemistry of these compounds is described.

The thermal polymerization of allene has been reported by Lebedev¹ to give a series of cyclic products to which structures I-IV were assigned.



We have found that in the presence of certain phosphorus-modified nickel carbonyl catalysts, cyclopolymerization proceeds in an entirely different fashion. The products that have been isolated comprise two highly reactive trimers and a surprisingly stable tetramer. These compounds have been identified as the monocyclic exomethylene compounds V, VI and VII. No dimers were detected in the reaction products.



The reaction was conducted by heating allene at 105–110° in tetrahydrofuran at autogenous pressure in the presence of bis-(triphenyl phosphite)-nickel dicarbonyl for 5–6 hours. Under these conditions, 35% of the allene was converted to a mixture of trimers, and 6% was converted to the tetramer. Other catalysts for this reaction were tris-(triphenyl phosphite)-nickel carbonyl and triphenyl phosphite-nickel tricarbonyl, which gave 20–25% conversions to trimers, and bis-(triphenylphosphine)-nickel dicarbonyl, which gave a 7% conversion to trimers and an 18% conversion to tetramer.

The structures of the trimers were established by chemical and spectral studies. Hydrogenation of the mixed trimers at room temperature gave a mixture of *cis*- and *trans*-1,2,4-trimethylcyclohexane, and rearrangement with *p*-toluenesulfonic acid gave a mixture of 1,2,4- and 1,3,5-trimethylbenzene in a ratio of about 75:25. The infrared spectrum of the mixed trimers showed the presence of terminal methylene groups, and the proton magnetic resonance spectrum showed that one-half of the hydrogen atoms were attached to carbon of

(1) S. V. Lebedev and B. K. Merezhkovskii, *J. Russ. Phys. Chem. Soc.*, **45**, 1249 (1913); (*Chem. Zentr.*, **85**, 1410 (1914)).

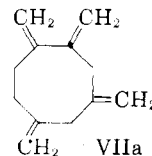
terminal methylene groups and the remainder to saturated carbon. On the basis of these data, the trimers were identified as 1,2,4-trimethylenecyclohexane (V) and 1,3,5-trimethylenecyclohexane (VI).

Separation of the trimers by vapor-phase chromatography showed that the mixture consisted of 80% of V and 20% of VI. The infrared absorption spectrum of pure V showed absorption at 3.2 (=CH), 3.5 (—CH), 6.1 (conjugated C=C) and 11.25 μ (terminal methylene). The ultraviolet spectrum showed λ_{\max} 213 m μ (ϵ 9100), thus confirming a conjugated diene structure.

The pure triene VI was obtained as a solid, m.p. 33.5–35°. The infrared spectrum showed absorption for the terminal methylene group (11.25 μ) and the absence of conjugated unsaturation.

The structure of the tetramer VII was deduced from elemental and spectral analyses. The elemental analysis, molecular weight and hydrogenation data indicated a C₁₂H₁₈ structure having four double bonds. The infrared spectrum showed absorption for a carbon-carbon double bond at 6.05 and 6.1 μ and for terminal methylene at 11.2 μ . There was no indication of conjugated unsaturation. Although there was considerable end-absorption (ϵ ca. 11,000), the ultraviolet absorption spectrum has no maximum above 210 m μ , probably indicating the absence of a conjugated double bond. The proton magnetic resonance spectrum indicated the presence of carbon-hydrogen saturation and unsaturation of equal intensities. Thus, eight hydrogen atoms are attached to saturated carbon atoms and an equal number are attached to the carbon atoms of the exomethylene groups. The structure that appears to be most consistent with these data is 1,3,5,7-tetramethylenecyclooctane (VII).² Additional confirmation for the structure was found in the proton magnetic resonance spectrum, in that the hydrogen atoms attached to

(2) An alternate structure VIIa has been called to our attention by Professor E. J. Corey of the University of Illinois. Our ultraviolet



and infrared absorption data do not eliminate this structure conclusively, since coplanarity of the diene unit is not possible in many of the configurations. The high end-absorption in the ultraviolet favors structure VIIa. However, it might be expected that the proton magnetic resonance spectrum would show two different types of hydrogen atoms attached to the exomethylene groups, as was observed with 1,2,4-trimethylenecyclohexane (V). Since this was not observed, the authors favor structure VII.

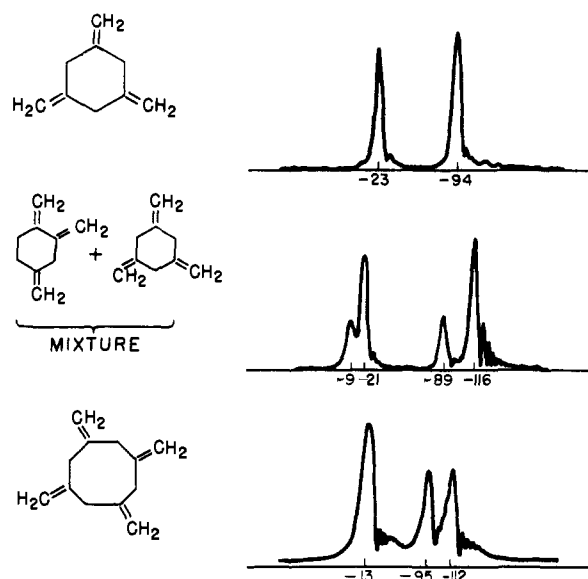


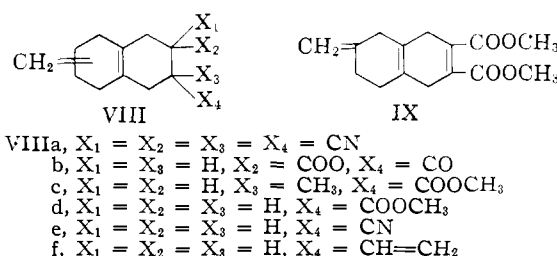
Fig. 1.—The hydrogen magnetic resonance spectra were obtained using a Varian high resolution n.m.r. spectrometer and electromagnet at a frequency of 40 Mc. and a field of 9500 gauss. The spectra were calibrated in terms of displacements in cycles per second from the hydrogen resonance of water.

saturated carbons were of two types present in equal amounts. Reference to a molecular model of VII showed that one-half of the hydrogen atoms attached to saturated carbon are in, or adjacent to, the plane of the terminal methylene groups, and the remaining hydrogens are to the back or to the front of the molecule.

The trimers and tetramer obtained by the catalyzed reaction are clearly different from those prepared by Lebedev as shown by a comparison of the hydrogenation and refraction data. Thus, II (n_D^{20} 1.4806) absorbed 2 moles of hydrogen to give a C_9H_{16} compound, while V (n_D^{25} 1.4919) absorbed 3 moles of hydrogen to give a mixture of trimethylenecyclohexanes (C_9H_{18}). Similarly, III (n_D^{20} 1.4681) and IV (n_D^{20} 1.5262) absorbed 2 moles of hydrogen to give compounds of empirical formula $C_{12}H_{16}$, while VII (n_D^{25} 1.5102) absorbed 3.3 moles of hydrogen at room temperature.

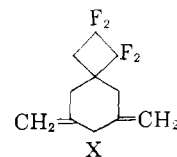
1,2,4-Trimethylenecyclohexane (V) readily underwent Diels-Alder reactions with typical dienophiles to give products that have been formulated as methylenecyclohexane derivatives (VIII) on the basis of elemental and spectral analyses. For example, reaction of the mixed trimers with tetracyanoethylene gave a high yield of 2,2,3,3-tetracyano-5-methylene-1,2,3,4,5,6,7,8-octahydronaphthalene (VIIIa). Similar products were obtained from maleic anhydride (VIIIb) and from dimethyl acetylenedicarboxylate (IX). In addition, methyl methacrylate reacted with the trimeric product to give 2-methoxycarbonyl-2-methyl-5(and/or -6)-methylene-1,2,3,4,5,6,7,8-octahydronaphthalene (VIIIc).

Compound VIIIc also was obtained by direct reaction of allene with methyl methacrylate in the presence of phosphorus-modified nickel carbonyls under cyclopolymerization conditions. Presum-



ably, 1,2,4-trimethylenecyclohexane was formed *in situ* and reacted with the dienophile to give the Diels-Alder adduct. In the same manner, reaction of allene with methyl acrylate, acrylonitrile and butadiene gave the corresponding methylenecyclohexane derivatives (VIIId, e, f).

Reaction of pure VI with tetrafluoroethylene gave a 34% yield of a monoadduct identified as 1,1,2,2-tetrafluoro-6,8-dimethylenespiro[3.5]nonane (X) on the basis of elemental and spectral analyses.



Whereas treatment of V with acid resulted in complete rearrangement of the double bond into the ring, reaction with potassium *t*-butoxide effected only partial isomerization. Although the product was not obtained in a pure state, spectral studies strongly indicated it to be 3,6-dimethylene-1-methylcyclohexene.

The chemistry of 1,3,5,7-tetramethylenecyclooctane (VII) was not studied extensively. No reaction occurred on attempted isomerization to tetramethylenecyclooctatetraene with *p*-toluenesulfonic acid or potassium *t*-butoxide.

Experimental

1,2,4- and 1,3,5-Trimethylenecyclohexane (V and VI).³—A 1.4-l. stainless steel pressure vessel was charged under nitrogen with 250 ml. of anhydrous tetrahydrofuran, 10 g. of finely ground calcium carbide, and 5 g. of bis-(triphenyl phosphite)-nickel dicarbonyl catalyst. The vessel was purged with nitrogen, cooled to -80° , and evacuated. Allene (80 g.) was added by distillation. The contents of the vessel were agitated and heated to 80° during 2 hours and the temperature was then increased at a rate of 15° /hour until the reaction began as indicated by a decrease in pressure. The mixture was heated at 108 – 109° for 5.5 hours during which time the pressure fell from 12.1 to 1.36 atm. The vessel was opened and the contents (326 g.) were combined with that of a similar run (326 g.).

The liquid was separated from the calcium carbide by decantation and distilled through a short Vigreux column. The distillate, b.p. 58° (200 mm.)– 62° (0.1 mm.), weighed 112 g., and 66.8 g. of viscous, brown material remained in the distillation flask. The liquid was redistilled through an efficient column containing Heli-pak to give 48.1 g. (30%) of colorless liquid, b.p. 68 – 69° (59–60 mm.), n_D^{25} 1.4919.

Anal. Calcd. for C_9H_{12} : C, 89.94; H, 10.07; hydrogenation (3 double bonds), 0.0503 g. H_2 /g. sample. Found: C, 90.15; H, 10.11; H_2 , 0.0471 g. H_2 /g. sample (94% of theoretical).

The infrared spectrum showed absorption in the double bond region at 6.05, 6.1, 11.25 and 11.27 μ in agreement with the proposed structures.

The mixture of trimers was separated by vapor-phase chromatography using a column containing Celite saturated

(3) R. E. Benson, U. S. Patent 2,839,570 (June 17, 1958).

at room temperature with dimethyltetramethylene sulfone. The column was operated at 93° with helium as the carrier gas (50 ml./min.). The product was shown to contain 80% 1,2,4- and 20% 1,3,5-trimethylenecyclohexane. The infrared spectrum of the 1,2,4-isomer showed absorption at 3.2 (=CH), 3.35 (-CH), 6.1 (C=C, conjugated) and 11.25 μ (terminal methylene). The ultraviolet spectrum showed λ_{\max} 213 $m\mu$ (ϵ 9100). The proton magnetic resonance spectrum indicated that V had been obtained in a pure state.

The 1,3,5-trimethylenecyclohexane (VI) was obtained as a white crystalline solid, m.p. 33.5–35°. The infrared spectrum of VI showed absorption at 3.25 (=CH), 3.35, 3.4, 3.5, 3.57 (-CH), 6.05 (C=C), 11.37 μ (terminal methylene).

Anal. Calcd. for C₆H₁₂: C, 89.94; H, 10.07. Found: C, 89.93; H, 10.27.

Various combinations of modified nickel carbonyl catalysts were examined for the cyclopolymerization reaction. When triphenyl phosphite and nickel carbonyl were used in a molar ratio of 0.0065:0.034, reaction occurred at 70–80° to give approximately 20% of the mixed trimers. With triphenyl phosphite and nickel carbonyl in molar ratio of 0.0645:0.0075, reaction began at a temperature of 115–120° and gave a 20% yield of trimers. Bis-(triphenylphosphite)-nickel dicarbonyl catalyzed the cyclopolymerization of allene at 85° to give a 7% conversion to trimers. Traces of trimeric products were formed with tris-*p*-methoxyphenylphosphinenickel tricarbonyl catalyst.

Isomerization of 1,2,4- and 1,3,5-Trimethylenecyclohexane. A. With *p*-Toluenesulfonic Acid.—To a solution of 2.8 g. of mixed trimers in 65 ml. of deaerated chloroform was added 0.1 g. of *p*-toluenesulfonic acid monohydrate. The solution was refluxed under nitrogen for 43 hours. The resulting yellow solution was washed with dilute sodium hydroxide solution and with water and was dried over magnesium sulfate. The chloroform was removed by distillation and the remaining oil was distilled through a small column to give 1.6 g. of colorless liquid, b.p. 72° (28 mm.), n_D^{20} 1.5013. Infrared analysis of the distillate indicated it to contain 1,2,4-trimethylbenzene (75%) and 1,3,5-trimethylbenzene (25%).

B. With Potassium *t*-Butoxide.—The mixed trimers (11.7 g.) were added to a solution of potassium *t*-butoxide prepared from 0.3 g. of potassium and 100 ml. of dry *t*-butyl alcohol. The resulting solution was refluxed under nitrogen on a steam-bath overnight. A small amount of insoluble material was present in the flask. The mixture was poured into water, 50 ml. of petroleum ether was added, and the organic layer was washed with water 3 times. The liquid was dried over magnesium sulfate and a small amount of phenothiazine was added. Distillation yielded 4.8 g. of colorless liquid, b.p. 78° (54 mm.), n_D^{20} 1.5252. The product reacted readily with bromine in carbon tetrachloride solution. It appeared to be mainly 3,6-dimethylene-1-methylcyclohexene containing some 1,3,5-trimethylbenzene and possibly a small amount of 1,2,4-trimethylbenzene, as indicated by infrared and ultraviolet spectral analyses. The ultraviolet spectrum showed λ_{\max} 276 $m\mu$ (ϵ 17,300), λ_{\max} 267 $m\mu$ (ϵ 18,400) and λ_{\max} 259 $m\mu$ (ϵ 15,850). The observed λ_{\max} value (267 $m\mu$) for the principal absorption band was in agreement with the calculated value (269 $m\mu$), and differed from that of 3,6-dimethylenecyclohexane (262.5 $m\mu$)⁵ by the expected 5 $m\mu$ attributable to the methyl group.

Some higher-boiling product (b.p. ca. 115° (0.5 mm.)) also was formed in this reaction.

Hydrogenation of 1,2,4- and 1,3,5-Trimethylenecyclohexane.—In an effort to prevent possible rearrangement of the unsaturated product, the hydrogenation was conducted initially in the presence of nickel catalyst before completing the reaction with platinum catalyst. Approximately 0.5 g. of freshly prepared Raney nickel catalyst⁶ which was evolving hydrogen was added to a solution of 2.06 g. of the mixed trimers in 100 ml. of deaerated ethyl alcohol. The reaction mixture was hydrogenated at room temperature and 2.7

atm. hydrogen pressure. Approximately 60% of the theoretical amount of hydrogen was absorbed in 2 hours. Platinum-on-carbon catalyst (0.2 g.) was added and the hydrogenation was continued overnight.

The reaction mixture was filtered through Celite to remove the catalyst. Petroleum ether was added to the filtrate and the reaction solution was washed 3 times with water to remove the alcohol. The organic layer was dried and the petroleum ether was removed by distillation. The product remaining was distilled to give 1.2 ml. of colorless liquid, b.p. 65–68° (57 mm.). Infrared analysis of this liquid indicated it to be chiefly a mixture of *cis*- and *trans*-1,2,4-trimethylcyclohexane possibly containing small amounts of 1,3,5- and 1,2,4-trimethylbenzene. A few weak, unassigned bands may be attributable to the presence of 1,3,5-trimethylcyclohexane.

Diels-Alder Adducts of 1,2,4-Trimethylenecyclohexane. A. 5-Methylene-1,2,3,4,5,6,7,8-octahydro-2,2,3,3-naphthalenetetracarboxitrile (VIIIa).—To a solution of 1.0 g. of tetracyanoethylene⁷ in 7 ml. of acetone was added 1.5 ml. of the mixed trimers. The resulting solution became warm and almost refluxed. The solution was allowed to stand for 0.5 hour and 20 ml. of petroleum ether was added. The white crystals which separated were removed by filtration and washed with petroleum ether, m.p. 98–98.5°. The compound sublimed readily at 80° (0.1 mm.).

Anal. Calcd. for C₁₈H₁₂N₄: C, 72.56; H, 4.87. Found: C, 72.95; H, 4.89.

B. 5-Methylene-1,2,3,4,5,6,7,8-octahydro-2,3-naphthalenedicarboxylic Anhydride (VIIIb).—To a solution of 3.0 g. of maleic anhydride in 100 ml. of benzene was added 3.0 ml. of the mixed trimers. The resulting solution became warm and 0.2 g. of phenothiazine was added. The solution was flushed with nitrogen and allowed to stand overnight. Most of the benzene was removed by distillation at 50° under reduced pressure. Petroleum ether was added to the resulting solution. On standing, white plates separated, m.p. 82–83°.

Anal. Calcd. for C₁₈H₁₄O₃: C, 71.54; H, 6.47. Found: C, 71.00; H, 6.48.

C. Methyl 2-Methyl-5-(and/or 6)-methylene-1,2,3,4,5,6,7,8-octahydro-2-naphthoate (VIIIc).—A glass tube was charged with 5 g. of trimers, 0.2 g. of phenothiazine and 15 ml. of methyl methacrylate. The tube was flushed with nitrogen and sealed. The vessel was heated on a steam-bath with occasional shaking for 3 hours and then heated overnight. Distillation gave 6.4 g. of the adduct VIIIc, b.p. 69–71° (0.3 mm.), n_D^{20} 1.5000. The infrared spectrum of the product was identical with that obtained from the reaction of allene with methyl methacrylate in the presence of bis-(triphenyl phosphite)-nickel dicarbonyl catalyst.

A 1-l. stainless-steel vessel was charged with 185 ml. of stabilized methyl methacrylate, 5 g. of bis-(triphenyl phosphite)-nickel dicarbonyl catalyst, 0.5 g. of phenothiazine and 40 g. (0.5 mole) of allene. The contents of the vessel were heated at 100–115° for 6 hours, during which time the pressure fell from 14.3 to 0.2 atm. Distillation of the product gave 121 g. of recovered methyl methacrylate, 43 g. of colorless oil (A), b.p. 100–130° (0.5 mm.), and 23 g. of viscous residue. Redistillation of (A) yielded 33.0 g. (45% yield) of VIIIc as a colorless oil, b.p. 90° (1.0 mm.), n_D^{20} 1.5012–1.5018. The infrared spectrum showed absorption at 3.25 (=CH), 3.45 (-CH), 5.75 (ester carbonyl), 6.05 (C=C), 7.25 (CH₃-) and 11.35 μ (terminal methylene).

Anal. Calcd. for C₁₄H₂₀O₂: C, 76.32; H, 9.15; mol. wt., 220; sapon. equiv., 254. Found: C, 76.53; H, 9.51; mol. wt., 224; sapon. equiv., 255.

D. Methyl 5-(and/or 6)-Methylene-1,2,3,4,5,6,7,8-octahydro-2-naphthoate (VIIId).—A 1-l. stainless-steel pressure vessel was charged with 125 ml. of stabilized methyl acrylate, 5 g. of bis-(triphenyl phosphite)-nickel dicarbonyl catalyst and 40 g. of allene. The mixture was heated at 145–155° for 4 hours. Distillation of the resulting product gave 55.8 g. of colorless oil, b.p. 100–148° (1.2 mm.) and 40.3 g. of viscous, higher-boiling residue. The distillate was added to that of a similar preparation (78.5 g.) obtained from the reaction of 70 g. of allene with 200 ml. of methyl acrylate at 140–150° for 7 hours. Distillation through an 8-inch Vigreux column yielded 22.3 g. of VIIIId as a colorless oil, b.p. 77.5° (0.07 mm.).

(7) T. L. Cairns, *et al.*, *THIS JOURNAL*, **79**, 2340 (1957).

(4) We are indebted to Dr. B. C. Anderson for this experiment.

(5) W. J. Bailey and R. Barclay, Jr., Abstracts, 130th Meeting of A.C.S., September, 1956, p. 6-O.

(6) "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., p. 176.

Anal. Calcd. for $C_{18}H_{18}O_2$: 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_2-) 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_D^{20} 1.5198.

Anal. Calcd. for $C_{12}H_{18}N$: 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 VIII f, b.p. 123–123.5° (23 mm.), n_D^{20} 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 $C_{15}H_{18}$: 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_D^{20} 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_D^{20} 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-Tetramethylenecyclooctane (VII).—1,3,5,7-Tetramethylenecyclooctane 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_D^{20} 1.5102.

Anal. Calcd. for $C_{12}H_{18}$: 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 $m\mu$, 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.

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Chemistry of Allene. II. Reaction of Allene with Acetylenes

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

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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-trimethylenecyclooctene (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 paper¹ 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-tetramethylenecyclooctane, respectively.

It has now been found that reaction of allene

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

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

(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.