Some difficulty was experienced in finding hydrolysis conditions vigorous enough to break the glucosidic linkage without too extensive demethylation of the hexose phenylosotriazole moiety. The first satisfactory results were obtained as follows. Permethylated leucrose phenylosotriazole (422 mg.) was heated for seven hours at 95° with 5 ml. of 90% formic acid. The hydrolysate was concentrated *in vacuo* to a gum which was dissolved in 0.2 ml. of methanol. Dropwise addition of 1 ml. of water threw out an oil. The aqueous methanol solution was pipetted off and the oil was washed five times with water. The combined solutions were saved for the isolation of tetramethylglucose.

A portion of the oil (155 mg. of a total 205 mg.) was converted to the 3,5-dinitrobenzoate (28 mg., 9.4% based on permethylated leucrose phenylosotriazole). Crystallization from methanol yielded 19.4 mg. of product melting at 125.5–126.5°. The melting point upon admixture with the 3,5-dinitrobenzoate from inulin (m.p. 127–128°) was 125.5–126.5°. The X-ray diffraction patterns of the derivatives were the same.

The tetramethylglucose was identified as follows. The aqueous solution was evaporated to gummy crystals which were purified by sublimation and crystallization from petroleum ether; yield 77 mg. (42%); m.p. 88–92°. The X-ray diffraction pattern was the same as that of an authentic sample of 2,3,4,6-tetra-*O*-methyl-D-glucose (m.p. 89–93°).

Hydrolysis of permethylated leucrose phenylosotriazole under milder conditions (1 hr. at 95° in 90% formic acid) led to a 22% yield of the 3,5-dinitrobenzoate.

5-*O*-β-D-Glucopyranosyl-D-*arabino*-hexose Phenylosotriazole Heptaacetate.—5-β-(Tetraacetylglucopyranosyl)-1,2-acetone-3,6-diacetyl-D-glucose (317 mg.), prepared by Freudenberg and v. Oertzen,[7] was saponified with sodium methoxide. Deionization and lyophilization gave 165 mg. of 5-β-D-glucopyranosyl-1,2-diacetone-D-glucose in the form of a white powder (86%). The acetone group was removed by heating with 1.9 ml. of 0.1 *N* HCl for 2 hr. at 70°. Deionization and lyophilization yielded 121 mg. (82%) of 5-glucosylglucose. Heating at 100° for 1 hr. with phenylhydrazine and sodium acetate gave 107 mg. (58%) of an amorphous osazone (m.p. 135–140°). This was converted to the phenylosotriazole (70.3 mg., 80%) which on acetylation with acetic anhydride and pyridine gave 107 mg. (90%) of the crude heptaacetate. Crystallization from alcohol gave bars melting at 168–169°.

Anal. Calcd. for $C_{32}H_{39}N_3O_{6}$: C, 53.26; H, 5.45; N, 5.82. Found: C, 53.2; H, 5.52; N, 6.06.

The infrared spectrum and the X-ray diffraction patterns of this β-form of the heptaacetate were distinctly different from those of leucrose phenylosotriazole heptaacetate (m.p. 150–151°).

Acknowledgment.—We are indebted to Drs. R. J. Dimler, M. L. Wolfrom, J. W. Van Cleve and H. M. Tsuchiya for valuable advice and assistance, to C. H. Van Etten and Mrs. Clara McGrew for microanalyses, to Henry Zobel for X-ray diffraction patterns and Dr. L. J. Wickerham for the yeast studies.

PEORIA, ILLINOIS

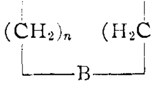
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Macro Rings. XIII. Synthesis and Properties of 1,7-Cyclododecadiyne and Related Compounds[1]

BY DONALD J. CRAM AND NORMAN L. ALLINGER

RECEIVED OCTOBER 14, 1955

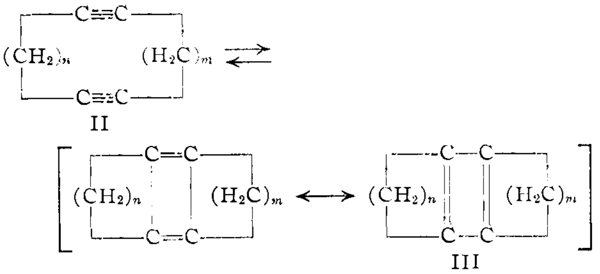
Compounds I have been prepared with $n = m = 4$ and $A = B = —C{\equiv}C—$, $A = —C{\equiv}C—$ and $B = —CHOHCO—$, $A = —C{\equiv}C—$ and $B = —COCO—$, and $A = B = —CH{=}CH—$ (*cis*); and with $n = m = 3$, and $A = B = —CH{=}CH—$ (*cis*), $A = —CH{=}CH—$ (*cis*), $B = —C{\equiv}C—$, A —CH=CH— (*cis*) and $B = —CHOHCO—$, $A = —CH{=}CH—$ (*cis*), and $B = —COCO—$, and $A = —CH{=}CH—$ (*cis*) and $B = —CHOHCHOH—$ (*meso*). An anomalous transannular reaction was encountered when compound I ($n = m = 4$, $A = —C{\equiv}C—$ and $B = \underset{\underset{H_2N—N}{\|}}{C}—\underset{\underset{N—NH_2}{\|}}{C}—$) was treated with mercuric oxide, a bicyclic diene being the product.



I

Cyclobutadiene has to date evaded numerous attempts at its synthesis, although the dibenzo substance (biphenylene) and related compounds have been prepared repeatedly.[2] Recent calculations indicate that cyclobutadiene will not be stabilized by any appreciable resonance energy.[3] Synthetic experiments directed at preparation of the compound by conventional methods have produced other products, usually those derived by ring rupture and including acetylene.[4] This last observation plus the fact that the conversion of two molecules of acetylene into one of cyclobutadiene would involve very little molecular reorganization suggests that *in principle* such a dimerization is possible, although such a reaction is of course unknown.

In the present work a molecule has been so designed (II) as to encourage any tendency for acetylene dimerization that might exist.[5] Since the acetylenic linkages in II with $n = m = 3$ or 4 are properly situated to provide valency tautomer-



II

III

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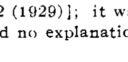
[1] This research was supported in part by a generous grant from the Upjohn Company, and in part was conducted under Contract AF 33(616)-146 with the United States Air Force, the sponsoring agency being the Aeronautical Research Laboratory of the Wright Air Development Center, Air Research and Development Command.

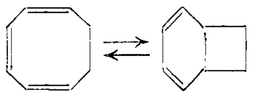
[2] (a) M. P. Cava and J. F. Stucker, *Chemistry & Industry*, 446 (1955); (b) W. Baker, M. P. V. Boarland and J. F. W. McOmie, *J. Chem. Soc.*, 1476 (1954); (c) W. Baker, *ibid.*, 258 (1945); (d) W. C. Lothrop, THIS JOURNAL, **63**, 1187 (1941).

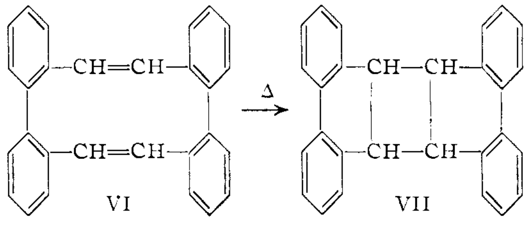
[3] D. P. Craig, *J. Chem. Soc.*, 3175 (1951).

[4] (a) R. Willstätter and W. von Schmaedel, *Ber.*, **38**, 1992 (1905); (b) E. R. Buchman, A.C.S. Meeting Abstracts, New York, N. Y., Sept., 1954, p. 9-O.

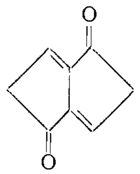
[5] The structurally similar compound  has been reported [Lespieau, *Compt. rend.*, **188**, 502 (1929)]; it was obtained in small yield, was poorly characterized, and no explanation was offered for its unexpected properties.

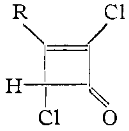
ism to give III with a minimum decrease in entropy, a better demonstration of the stability, or instability, of a cyclobutadiene system might be obtained than was afforded by the inability of various workers to prepare cyclobutadiene itself.[4] Two cases of valency tautomerism in not dissimilar systems have been found, that between IV and V[6] and that in which VI gives VII on heating.[7] The lack of tautomerism from VIII to its enol[8] has been taken as evidence for the absence of appreciable aromaticity in the pentalene system, and the inability of IX to undergo isotope exchange in D_3O^+ at C_α provides evidence for the relative lack of aromatic character in the cyclobutadiene system.[9]


IV V



VI VII

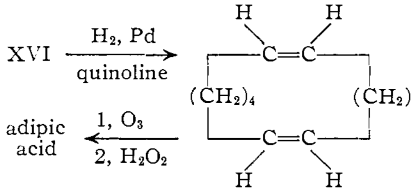

VIII



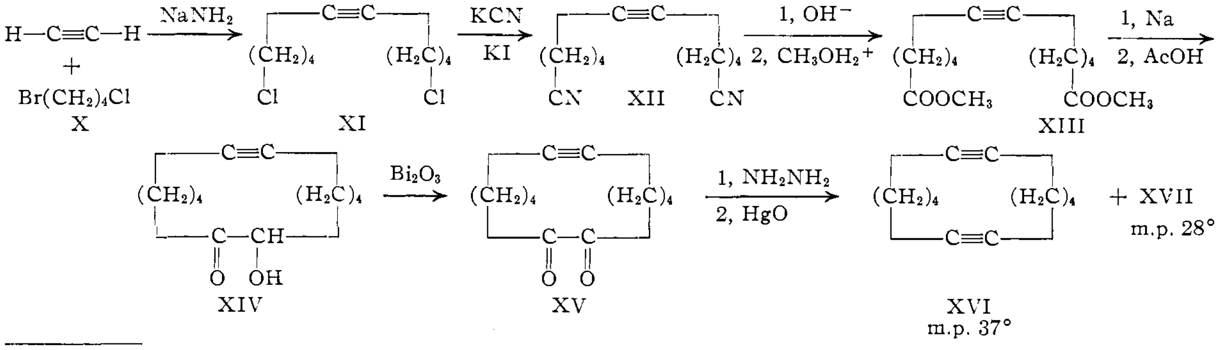
IX

Although single acetylenic linkages have been previously incorporated in carbocyclic rings,[10] the first carbocyclic diyne is reported in this paper. The formulations summarize the synthetic approach. Ester XIII was obtained in 76% over-all yield from X and when submitted to the action of sodium in xylene gave a 73% yield of acyloin XIV. This reaction represents the first example of a successful acyloin cyclization of an ester containing an acetylenic linkage. The structure of XIV was demonstrated by quantitative hydrogenation of the acetylenic linkage to give the known 2-hydroxycyclododecanone (XVIII), which was identified by its melting point and by that of its oxime. The acyloin XIV was converted through the diketone XV and dihydrazone XXIII to the diacetylene as formulated. The crude final product was found to be a three-to-one mixture of XVI and a second hydrocarbon XVII, the two substances being separated by chromatography on alumina. Diyne XVI was the more strongly adsorbed. Both substances solidified upon distillation, and after recrystallization gave XVI and XVII in 14 and 8% yields, respectively.

Quantitative hydrogenation of diyne XVI demonstrated that the substance contained two acetylenic linkages. Complete reduction of XVI gave cyclododecane, and partial reduction with a partially poisoned (quinoline) palladium-on-barium sulfate catalyst gave diene XIX. The relative position of the double bonds in XIX was shown to be 1,7 as expected by ozonolysis of the substance. The only non-polymeric material detected from decomposition of the ozonide with hydrogen peroxide was adipic acid (10% yield). The infrared spectrum of XVI shows $C \equiv C$ stretching[11] absorption at $4.50\ \mu$, and a very strong band at $13.11\ \mu$ which is empirically useful for identification purposes. The ultraviolet spectrum of the diyne shows only end absorption. Thus both spectroscopic and chemical evidence indicate that the diyne does not possess any tendency for tautomerization to the tricyclic cyclobutadiene structure III.



XIX



The structure of the second product XVII obtained along with diyne XVI was established as follows. Elementary analysis clearly showed that XVII had two more hydrogens than did XVI, and the ultraviolet spectrum of this material indicated

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

(7) G. Wittig, G. Koenig and K. Clauss, *Ann.*, **593**, 127 (1955).

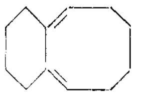
(8) H. J. Dauben, Jr., V. R. Ben and H. K. Chiang, Abstracts of the Meeting of the American Chemical Society, Los Angeles, Calif., March, 1953, p. 9-M.

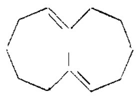
(9) J. D. Roberts, Abstracts of the Fourteenth Organic Symposium, June, 1955, p. 24.

(10) (a) A. T. Blomquist, R. E. Burge, Jr., and A. C. Sucsy, THIS JOURNAL, **74**, 3636 (1952); (b) V. Prelog, K. Schenker and H. H. Gunthard, *Helv. Chim. Acta*, **35**, 1598 (1952); (c) M. Stoll, J. Hulstkamp and A. Rouvé, *ibid.*, **31**, 543 (1948).

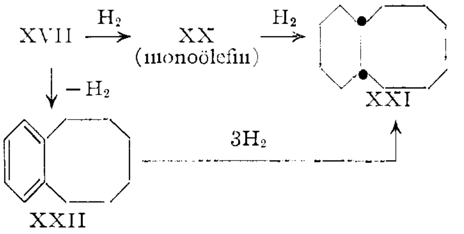
(11) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," J. Wiley and Sons, Inc., New York, New York, 1954.

that it was a conjugated diene λ_{max} 221 mμ, ϵ 6,440. The very strong band in the infrared spectrum at 12.20 μ indicated that at least one double bond was trisubstituted. The diene readily absorbed one mole of hydrogen to give a monoölefin XX, and much more slowly a second mole to give a saturated hydrocarbon XXI. The latter substance was completely transparent in the ultraviolet and was therefore bicyclic. Ozonolysis of diene XVII gave an ozonide, which when decomposed with hydrogen peroxide provided adipic acid (17% yield) as the only solid isolable product. This evidence limited the structure of XVII to one of two possibilities, XVIIa or XVIIb.[12]

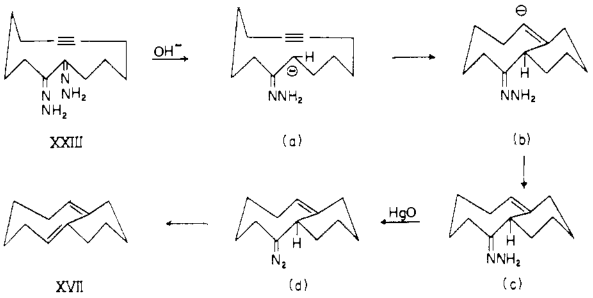

XVIIa


XVIIb

Dehydrogenation of XVII with palladium-on-charcoal at 250–320° gave approximately one mole of hydrogen and yielded as the product hydrocarbon XXII, the structure of which was demonstrated by a comparison of the physical properties, including spectra, with those of an authentic sample.[13] However, since in certain cases dehydrogenations of cycloheptane derivatives are known to lead to aromatic compounds by ring contraction,[14] the isolation of XXII could not be taken as definitive evidence for the ring structure of XVII. Hydrogenation of XXII with platinum in acetic acid gave an authentic sample of *cis*-[6.4.0]-bicyclododecane,[15] and this compound proved to be identical in physical properties, including infrared spectra, with compound XXI previously obtained. Thus XVII must have the structure XVIIa rather than the alternative XVIIb.



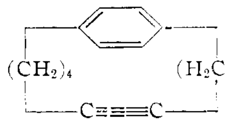
A reasonable path by which XVII could have arisen in the mercuric oxide oxidation of dihydrazone XXIII is outlined. Since XVII contains two more hydrogens than diyne XVI, and since the reaction involves treatment of a hydrazone with base, a Wolff–Kishner type of reduction is indicated. This kind of reduction involves the equivalent of a carbanion[16] (a), which as a strong base might add transannularly to the spatially adjacent acetylenic linkage to give (b) which then adds a proton to give (c). This hydrazone would be expected to oxidize to a diazo compound (d) which in turn would lose nitrogen to give a carbene, ultimately going to XVII by hydrogen migration.



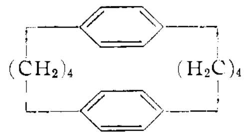
The conversion of a diazo function to an olefin has been detected previously,[17] and the conversion of camphor hydrazone to tricyclene upon treatment with mercuric oxide is a well known analogy[18] to the transformation from (c) to XVII.

In another run, when the oxidation of hydrazone XXIII was carried out as before except that a small amount of potassium hydroxide was added to the mixture as is commonly done,[10a,b] the yield of XVII was increased to 12%, while the yield of XVI fell to zero. This observation is in accord with a competing Wolff–Kishner reaction leading to XVII at the expense of XVI.

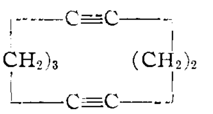
The absence of transannular electronic interactions between the two acetylenic functions of diyne XVI correlates with the absence of these effects in two somewhat similarly constituted cycles, XXIV[17] and XXV.[19] Since the lower homologs of XXV all show transannular effects,[19] the synthesis of diyne XXVI was undertaken in the hope that in this compound the two acetylenic functions would be forced into one another's electronic environment and would perhaps possess some cyclobutadiene-like character. Diester XXX was prepared by a method analogous to that used for the preparation of its homolog XIII, but unlike the higher homolog, XXX did not undergo acyloin ring closure. The bulk of the starting material was recovered unchanged after prolonged refluxing in toluene with excess sodium. This lack of reaction and recovery of starting diester has been observed in several



XXIV



XXV



XXVI

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(12) There is ample evidence [see E. A. Braude, *Chemistry & Industry*, 1557 (1954)] that the position of the maxima in the ultraviolet spectra of conjugated dienes cannot be predicted from Woodward's rules when the double bonds are contained in rings which are larger than 6-membered.

(13) The authors express their gratitude to Dr. R. Huisgen for a sample of this substance [see R. Huisgen and W. Rapp, *Ber.*, **85**, 826 (1952)].

(14) L. Ruzicka and C. F. Seidel, *Helv. Chim. Acta*, **19**, 424 (1936).

(15) Probably containing a small amount of the *trans* isomer [see R. P. Linstead, W. E. Doering, S. B. Davis, P. Leviue and R. R. Whetstone, THIS JOURNAL, **64**, 1985 (1942)].

(16) H. H. Szmant, H. F. Harnsberger, T. J. Butler and W. P. Barie, *ibid.*, **74**, 2724 (1952).

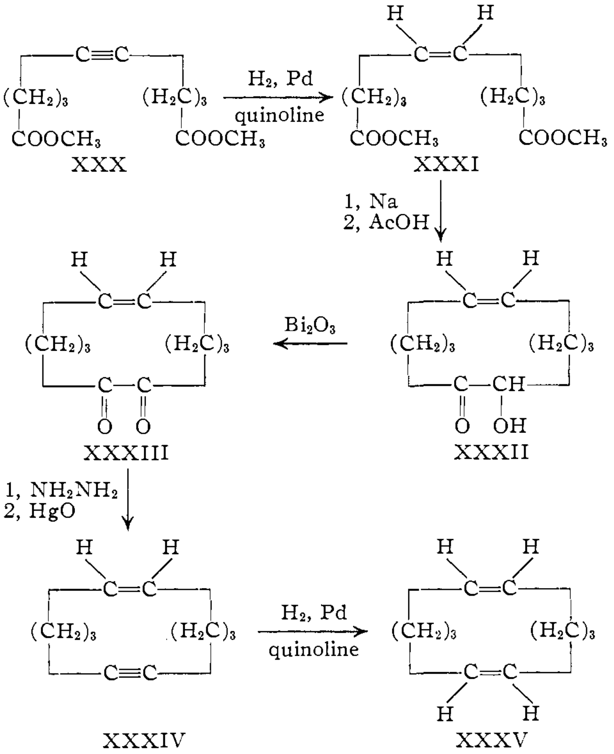
(17) D. J. Cram and M. Cordon, *ibid.*, **77**, 4090 (1955).

(18) M. Meerwein and K. van Emster, *Ber.*, **53**, 1815 (1920).

(19) D. J. Cram, N. L. Allinger and H. Steinberg, THIS JOURNAL, **76**, 6132 (1954).

previous instances[19,20] where the cyclic acyloin, had it been formed, would have been somewhat strained. A little polymer was also obtained in each case. These systems are to be contrasted with those in which polymer is the principal or sole reaction product.[19–21] A plausible interpretation of these results follows. If the cyclic acyloin is formed in the usual manner but is unstable for steric reasons, it might undergo aldol-type polymerization, as was observed in the acyloin reactions of dimethyl glutarate and pimelate.[22] In another case the polymer formed in an acyloin reaction was demonstrated not to contain α-ketol linkages.[23] In rings in which the cyclic product is too unstable to form at all it seems plausible that the minute amount of polymer formed is a true linear acyloin polymer which is formed at a very low rate because of high dilution on the surface of the sodium.

Reduction of XXX to the corresponding *cis*-olefin XXXI was accomplished cleanly and easily with hydrogen and palladium-on-barium sulfate with a trace of added quinoline.[24] Ester XXXI underwent acyloin cyclization to give XXXII in 78–81% yields. The greater yields of XXXII compared to the yields of sebacoin obtained under identical conditions (56–62%) are attributed to the relatively greater steric stability of the *cis*-acyloin XXXII as compared to that of the corresponding saturated compound. The hydrogen–hydrogen repulsions in XXXII do not appear to be nearly as great as those in sebacoin. The structure of XXXII was confirmed by reducing a sample to the known *meso*-1,2-cyclodecanediol. Oxidation[25] of XXXII furnished the unsaturated diketone XXXIII which was converted to the olefinic acetylene XXXIV (see formulation). The structure of this last substance was confirmed by quantitative hydrogenations which showed the presence of one acetylenic and one ethylenic linkage. The fully hydrogenated product was shown to be cyclodecane by comparison of its physical properties, including infrared spectrum, with those of an authentic sample from which they were indistinguishable. The 1,6-relationship of the unsaturated linkages follows from the method of synthesis. The infrared spectrum of XXXIV shows a weak band at 4.49 μ which is assigned to the triple bond (stretching), and a strong band at 14.10 μ which is assigned to the *cis*-olefin (out-of-the-plane hydrogen bending).[11] When XXXIV was reduced to the *cis*-diene XXXV, the former band disappeared and the latter was intensified and shifted to 14.20 μ. The ultraviolet spectra of XXXIV and XXXV are quite normal showing only end absorption of the expected intensity.



Experimental[26]

1,8-Dichloro-4-octyne (XXVII).[27]—Two moles (46 g.) of sodium was converted to sodamide in one liter of liquid ammonia, and a stream of acetylene was passed into the resulting mixture until two moles had been added and the solution cleared. The solution of sodium acetylide was then added to another flask containing two moles of sodamide in one liter of liquid ammonia, moisture being excluded throughout these operations. To the mixture thus formed was then added during 45 minutes 630 g. (4.0 moles) of 1-bromo-3-chloropropane, external cooling being applied as needed. The resulting mixture was stirred under reflux for 8 hours, and two liters of water was cautiously added. The organic phase was separated, and the aqueous phase was extracted with ether. The organic phases were washed in turn with water, dilute hydrochloric acid, water and dilute sodium carbonate. The organic phases were then combined and dried, and after removal of the solvent the residue was distilled through a 2-ft. Vigreux column. The following fractions were collected: (1) 2 g., b.p. to 46° (50 mm.); (2) 91 g., b.p. 46–70° (50 mm.), $n^{25}D$ 1.4615; (3) 10 g., b.p. 42–92° (4 mm.); (4) 128 g., b.p. 92-95° (4 mm.).

Fraction 4 was the desired dichloride, yield 36%, $n^{25}D$ 1.4838. Analysis indicated that the compound was not completely pure, but refractionation did not improve the sample. The material was used directly in the next step.

Anal. Calcd. for $C_8H_{12}Cl_2$: C, 53.65; H, 6.76. Found: C, 55.11; H, 7.26.

1,8-Dicyano-4-octyne (XXVIII).—Dichloride XXVII, 32.9 g., was dissolved in 250 ml. of ethanol and to this solution was added 56 g. of potassium cyanide and 4 g. of potassium iodide in 110 ml. of water.[28] The resulting solution was heated under reflux with stirring for 24 hours, and after the addition of another 56 g. of potassium cyanide, heating was continued for an additional 24 hours. About 200 ml. of solvent was then distilled, the residue was diluted with

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[20] (a) N. L. Allinger and D. J. Cram, THIS JOURNAL, **76**, 2362 (1954); (b) J. Abell and D. J. Cram, *ibid.*, **76**, 4406 (1954).

[21] A. C. Cope and E. C. Herrick, *ibid.*, **72**, 983 (1950).

[22] M. Cordon, J. D. Knight and D. J. Cram, *ibid.*, **76**, 1643 (1954).

[23] D. J. Cram and N. L. Allinger, *ibid.*, **76**, 726 (1954).

[24] This catalyst has received extensive use in this Laboratory and has been found superior to the Lindlar catalyst [H. Lindlar, *Helv. Chim. Acta*, **35**, 446 (1952)] in reproducibility and ease of preparation. Hydrogenation over this catalyst is highly specific for acetylenes giving cleanly *cis*-olefins. This method has been successfully employed as a quantitative analytical method for acetylenic linkages.

[25] W. Rigby, *J. Chem. Soc.*, 793 (1951).

[26] All m.p.'s are corrected, b.p.'s are uncorrected. Ultraviolet spectra were determined on a Cary recording spectrophotometer, model 11 PMS, in 95% ethanol, and infrared spectra were recorded on a Perkin–Elmer recording spectrophotometer, model 21, with liquid films.

[27] This procedure is adapted from that of E. A. Bried and G. F. Hennion, THIS JOURNAL, **59**, 1310 (1937).

[28] J. R. Ruhoff, *Organic Syntheses*, Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 292.

water, and the product was extracted from the mixture with ether. The ether extracts were washed with 5% potassium hydroxide and water and were dried. The solvent was evaporated, and distillation gave after a small forerun the desired nitrile, b.p. 157–159° (4 mm.), wt. 20.0 g. (68%), n^{25}D 1.4719.

Anal. Calcd. for $C_{10}H_{12}N_2$: C, 74.96; H, 7.55. Found: C, 74.70; H, 7.45.

5-Decynedioic Acid (XXIX).—Nitrile XXVIII, 38.8 g., was heated under reflux in 350 ml. of 80% ethanol with 55.2 g. of potassium hydroxide for 6 hours, and after addition of 150 ml. of water about 250 ml. of solvent was distilled. The residue was cooled and diluted with 300 ml. of water. The resulting solution was acidified, and after thorough cooling at 0° the crystals were collected, wt. 47.0 g. (97%), white plates, m.p. 108–109.5°. An analytical sample was crystallized from benzene as needles, m.p. 109.2–110.1°.

Anal. Calcd. for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.85; H, 7.38.

5,6-Diketodecanedioic Acid.—The acetylenic acid XXIX, 2 g., was mixed with 5 ml. of concd. nitric acid, and the paste was carefully heated with a small flame.[29] As soon as the violent reaction began the flask was cooled in an ice-bath. The solution was then diluted with water, and 0.2 g. of unreacted starting material was removed by filtration. The desired product was extracted from the filtrate with several portions of ether, and the combined ether extracts were reduced to a volume of 10 ml. The product was precipitated by the slow addition of hexane and the crystals were collected, a yellow solid, wt. 0.8 g. This material was crystallized from acetone–benzene and gave 0.54 g. (23%) of a yellow crystalline powder, m.p. 132–135°. For analysis this material was recrystallized, m.p. 133.5–135.5°. The ultraviolet spectrum showed λ_{max} 417 mμ, ϵ 9.6; λ_{max} 260.5 mμ, ϵ 440.

Anal. Calcd. for $C_{10}H_{14}O_6$: C, 52.17; H, 6.13. Found: C, 52.15; H, 6.14.

Dimethyl 5-Decynedioate (XXX).—The acid XXIX was esterified by heating it for one hour in a solution composed of a 50 mole excess of methanol containing 10 wt. % of concd. sulfuric acid. The reaction mixture was cooled and poured into water, and the ester was extracted with ether. The ether extracts were washed with dilute sodium bicarbonate and water, were dried, and the ether was evaporated. Distillation of the residue furnished the ester as a colorless liquid, b.p. 133–134° (3 mm.), n^{25}D 1.4564, yield 92%.

Anal. Calcd. for $C_{12}H_{18}O_4$: C, 63.69; H, 8.02. Found: C, 63.95; H, 7.92.

Attempted Cyclization of Ester XXX.—An attempt was made to cyclize the acetylenic ester in the same manner used successfully to ring close the corresponding olefinic ester XXXI. To a suspension of 4.9 g. of sodium in 1.5 l. of refluxing toluene was added during 6 hours a solution of 10.0 g. of XXX in 150 ml. of toluene. No reaction was observed. The product was isolated as previously and was distilled through a 2-ft. Podbielniak-type column at 5.0 mm. to yield two fractions; (1) b.p. 115–133°, wt. 0.2 g., a yellow oil, n^{25}D 1.4693; (2) recovered XXX, b.p. 133–134°, n^{25}D 1.4574, wt. 8.7 g.

Dimethyl *cis*-5-Decenedioate (XXXI).—The acetylenic ester XXX, 19.2 g., was hydrogenated using 0.4 g. of 5% palladium-on-barium sulfate and 0.4 g. of pure (synthetic) quinoline[30] in 100 ml. of methanol. The mildly exothermic reaction ceased abruptly after 20 minutes, exactly one equivalent of hydrogen having been taken up. The catalyst was removed by filtration, and after distilling the solvent and quinoline the ester was distilled, b.p. 122–123° (3.5 mm.), n^{25}D 1.4494, wt. 18.9 g. (97%).

Anal. Calcd. for $C_{12}H_{20}O_4$: C, 63.13; H, 8.83. Found: C, 63.09; H, 8.80.

5-*cis*-Decenedioic Acid.—A sample of the acetylenic acid XXIX was hydrogenated to the olefinic acid in the same manner as described for hydrogenation of the corresponding ester XXX. The olefinic acid was crystallized from benzene–hexane and was obtained as small prisms, m.p. 77.4–78.6.

Anal. Calcd. for $C_{10}H_{16}O_4$: C, 59.98; H, 8.06. Found: C, 59.82; H, 8.07.

6-Hydroxy-7-keto-*cis*-cyclodecene (XXXII).—The olefinic ester XXXI, 62.7 g. in 450 ml. of toluene, was added during 18 hours to a suspension of 31.6 g. of highly dispersed sodium in 1.5 liters of refluxing toluene using the high-dilution apparatus previously described.[31] The resulting mixture was heated an additional hour, was cooled to 0°, and an excess of acetic acid was added followed by sufficient water to dissolve the salts. The toluene layer was separated and dried, and the toluene was distilled. The residue was then distilled through a 2-ft. Podbielniak-type column, and after a small forerun the acyloin was collected, a yellow oil, b.p. 106–108° (6 mm.), n^{25}D 1.5031, wt. 36.1 g. (78%). The compound solidified on standing, m.p. 44–45.5°. An analytical sample was crystallized from pentane at −10° to yield white prisms, m.p. 45.6–46.5°. The compound was stable when stored at 0° in the dark in a tightly stoppered bottle, but it decomposed upon standing in the laboratory.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.14; H, 9.47.

Bis-2,4-dinitrophenylhydrazone of XXXII.—This derivative of this acyloin was prepared in the usual way and was recrystallized from dioxane–ethanol to yield crimson needles, m.p. 277–279° dec.

Anal. Calcd. for $C_{22}H_{22}N_8O_8$: C, 50.19; H, 4.21. Found: C, 50.31; H, 4.21.

***meso*-1,2-Dihydroxy-6-*cis*-cyclodecene (XXXVI).**—One and one-tenth grams of acyloin XXXII was reduced with lithium aluminum hydride in ether in the usual way.[32] The reaction mixture was decomposed with water, and the ether layer was washed with dilute hydrochloric acid and water, was dried, and the solvent was evaporated. The resulting oily solid was dissolved in chloroform and was chromatographed on 30 g. of neutral alumina of activity III[33] with chloroform, 25-ml. fractions being collected. Fractions 1–5 contained 0.2 g. of an oil which was discarded. Fractions 6–10 were empty, and fraction 11 yielded 0.36 g. of a white solid, m.p. 120–125°. Fractions 12–16 gave white solids which were combined and crystallized from ethyl acetate–hexane to yield the desired diol as stout needles, m.p. 164.1–164.7°, wt. 0.35 g. Recrystallization did not affect the melting point.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.77; H, 10.52.

The *meso*-1,2-Dihydroxycyclodecane (XXXVII).—Diol XXXVI, 50.4 mg., was reduced to the saturated compound with platinum and hydrogen in methanol. The solution was freed of catalyst by filtration and the solvent was evaporated. Crystallization of the residue from hexane furnished 43.5 mg. of the diol as white plates, m.p. 133.3–135°. The mixed melting point with an authentic sample of the diol (obtained by lithium aluminum hydride reduction of sebacoin[10a,b] was undepressed.

6,7-Diketo-*cis*-cyclodecene (XXXIII).—The acyloin XXXII, 11.06 g., was heated at 90–100° under a nitrogen atmosphere in 60 ml. of acetic acid with 10.7 g. of bismuth trioxide for 45 minutes. The cooled solution was diluted with 40 ml. of ether followed by 40 ml. of pentane to precipitate the bismuth compounds. The solution was then filtered, and after evaporation of the solvent the product was distilled to give a deep yellow liquid, wt. 6.10 g. (56%), b.p. 91–93° (5.5 mm.), n^{25}D 1.4960, λ_{max} 402 mμ, ϵ 9.7; λ_{max} 255 mμ, ϵ 483. This material decomposed upon prolonged standing.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 71.94; H, 8.60.

The quinoxaline derivative was prepared by heating the diketone with a slight excess of *o*-phenylenediamine in acetic acid on the steam-bath for one hour.[34] The solution was diluted with water and the derivative crystallized. Recrystallization of this material from aqueous ethanol furnished almost white needles, m.p. 127.6–128.3°.

Anal. Calcd for $C_{16}H_{18}N_2$: C, 80.63; H, 7.61. Found: C, 80.60; H, 7.47.

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(29) A. Spieckermann, *Ber.*, **28**, 276 (1895).

(30) A sample of quinoline from coal tar was found to be unsuitable for this purpose.

(31) D. J. Cram and H. Steinberg, THIS JOURNAL, **73**, 5691 (1951).

(32) R. F. Nystrom and W. G. Brown, *ibid.*, **69**, 1197 (1947).

(33) H. Brockmann and H. Schodder, *Ber.*, **74B**, 73 (1941).

(34) N. J. Leonard and P. M. Mader, THIS JOURNAL, **72**, 5388 (1950).

6-*cis*-Cyclodecenyne (XXXIV).[35]—To a cooled solution of 6.1 g. of the diketone XXXIII in 5 ml. of absolute ethanol was added dropwise 3.5 g. of 95% hydrazine. The resulting solution was heated on the steam-bath for ten minutes, and the ethanol was removed in vacuum. Ten ml. of dry C.P. benzene was added to the residue, and the solvent was again removed in vacuum. This process was repeated once again, and the residual hydrazone was taken up in 50 ml. of warm benzene. This solution was added dropwise to a vigorously stirred suspension of 22 g. of yellow mercuric oxide and 10 g. of anhydrous magnesium sulfate in 65 ml. of refluxing benzene. Heating and stirring of the mixture was continued until the evolution of nitrogen had ceased (1 hour), and the cooled mixture was filtered through Celite. The solvent was evaporated from the filtrate, and the residue was distilled in a short-path still at a bath temperature of 130–170° (2 mm.). The distillate weighed 1.95 g. This material was dissolved in 10 ml. of pentane and the solution was placed on a column of 100 g. of alumina (activity I).[33] The elution was carried out with pentane. The first 10 ml. of eluent was discarded. The next 100 ml. of eluent was collected and was freed of solvent in vacuum. The residue was distilled under nitrogen with a bath temperature of 100° (20 mm.) to give the pure acetylene, a colorless liquid, wt. 0.91 g., $n^{25}\mathrm{D}$ 1.5078. The ultraviolet spectrum showed only end absorption; $\lambda_{220\ \mathrm{m}\mu}$, ϵ 345; $\lambda_{215\ \mathrm{m}\mu}$, ϵ 578; $\lambda_{210\ \mathrm{m}\mu}$, ϵ 1,140; $\lambda_{206\ \mathrm{m}\mu}$, ϵ 1,720. The infrared spectrum[11] showed the following bands of interest: 4.49 μ w, ($C\equiv C$ str.); 6.08 μ m, ($C=C$ str.); 7.11 μ w, (*cis*-olefin in-plane hydrogen bending); 14.02 μ s, (*cis*-olefin out-of-plane hydrogen bending).

Anal. Calcd. for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found: C, 89.60; H, 10.78.

A sample of the acetylene, 70.3 mg., was hydrogenated with 10 mg. of prereduced Adams catalyst in acetic acid. The hydrogen uptake was 38.0 ml. (22°) or 100% of three molar equivalents. The solution was filtered free of catalyst and was poured into water. The product was extracted with pentane, and the pentane extracts were washed and dried. After evaporation of the solvent, the residue was distilled with a bath temperature of 100° (20 mm.). The distillate was a colorless liquid, $n^{25}\mathrm{D}$ 1.4682, wt. 50 mg.; reported[10a] for cyclodecane, $n^{20}\mathrm{D}$ 1.4716. The infrared spectrum was found to be identical with that reported for cyclodecane.[10a]

Anal. Calcd. for $C_{10}H_{20}$: C, 85.62; H, 14.38. Found: C, 85.83; H, 14.20.

1-*cis*-6-*cis*-Cyclodecadiene (XXXV).[35]—Acetylene XXXIV, 414 mg., was hydrogenated with 50 mg. of palladium-on-barium sulfate in 10 ml. of methanol to which was added 2 drops of C.P. quinoline.[30] One equivalent of hydrogen was taken up in 40 minutes, whereupon the hydrogen uptake abruptly ceased. The solution was filtered and the filtrate was poured into water. The product was extracted with pentane, and the pentane extracts were washed with water, dilute hydrochloric acid and water, were dried, and the pentane was evaporated. Distillation of the residue under nitrogen furnished 345 mg. of the diene as a colorless oil, $n^{25}\mathrm{D}$ 1.4972. The compound solidified upon standing, m.p. 21.0–22.8°. The ultraviolet spectrum showed end absorption as follows: $\lambda_{220\ \mathrm{m}\mu}$, ϵ 268; $\lambda_{215\ \mathrm{m}\mu}$, ϵ 340; λ_{210} mμ, ϵ 468; λ_{206} mμ, ϵ 832. The infrared spectrum[11] showed the following bands of interest: 5.96, 6.05 μ m ($C=C$ str.); 7.14 μ w (*cis* in-plane hydrogen bending); 14.20 μ s (out-of-the-plane hydrogen bending).

Anal. Calcd. for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.06; H, 11.83.

1,10-Dichloro-5-decyne (XI).—The dichloride was prepared from 1-bromo-4-chlorobutane (X) (obtained from tetrahydrofuran)[36] and disodium acetylide in a manner similar to that described for the preparation of the lower homolog XXVII. From 686 g. of the chlorobromide there was obtained after distillation through a 2-ft. Vigreux column 290 g. (70%) of the dichloride, b.p. 122–125° (5 mm.); reported[37] b.p. 90–105° (0.8 mm.).

1,10-Dicyano-5-decyne (XII).—The nitrile was obtained in manner similar to that described for the preparation of the lower homolog XXVIII. From 290 g. of XI there was obtained 218 g. (83%), of the product, b.p. 177–179° (2.5 mm.), reported[37] b.p. 145° (0.8 mm.).

Dimethyl 6-Dodecynedioate (XIII).—The ester was obtained from the nitrile in 91% yield by the same procedure described for the conversion of XXVIII to XXX. The properties were b.p. 158–160° (4.5 mm.), $n^{25}\mathrm{D}$ 1.4583; reported[37] b.p. 120° (0.3 mm.), $n^{19}\mathrm{D}$ 1.4605.

7-Hydroxy-8-keto-cyclododecyne (XIV).—The acyloin reaction was carried out as described for the preparation of XXXII. Ester XIII, 13.0 g., in 100 ml. of toluene was added to 5.65 g. of sodium in 1.5 l. of refluxing toluene during 3.5 hours. The usual work-up procedure gave the dry toluene solution of the crude acyloin which was concentrated to a volume of 30 ml. Fifteen milliliters of hexane was added to the hot solution, and after cooling the solution to −10°, the acyloin was collected, white plates, wt. 7.25 g. (73%), m.p. 93–96°. For analysis a sample was twice recrystallized, m.p. 95.6–96.7°.

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 73.97; H, 9.33.

The compound was characterized by reducing (palladium-in-methanol) a 96-mg. sample to the corresponding saturated acyloin. The hydrogen uptake stopped after 102% of two equivalents had been absorbed. The product was crystallized from hexane in 86% yield, m.p. 76.5–77°. The reported[38] melting point of 2-hydroxycyclododecanone is 78–79°. The oxime was obtained as needles from ethanol, m.p. 128.8–129.9°, reported[38] m.p. 131–132°.

7,8-Diketocyclododecyne (XV).—Oxidation of 10.17 g. of acyloin XIV was carried out in a manner similar to that described for the preparation of XXXIII, except that the reaction period was extended to 1 hour, as an acyloin test on the reaction mixture after 45 minutes showed the presence of unreacted starting material. The crude diketone was isolated by distillation, b.p. 120–125° (5 mm.), wt. 9.5 g. Crystallization of this material from aqueous ethanol gave bright yellow needles, m.p. 84–86°, wt. 5.95 g. (59%). An analytical sample was twice recrystallized, m.p. 86.3–87.4°; $\lambda_{\max}$ 412 mμ, ϵ 20.2; $\lambda_{\text{shoulder}}$ 382 mμ, ϵ 19.6; $\lambda_{\max}$ 238 mμ, ϵ 907.

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 74.96; H, 8.39. Found: C, 75.11; H, 8.48.

The quinoxaline derivative was obtained in the previously described manner and was twice recrystallized from ethanol as white needles, m.p. 84.6–85.4°.

Anal. Calcd. for $C_{18}H_{20}N_2$: C, 81.77; H, 7.63. Found: C, 81.53; H, 7.53.

The dihydrazone XXIII, twice crystallized from benzene, was obtained as prisms, m.p. 155–159°.

Anal. Calcd. for $C_{12}H_{20}N_4$: C, 65.42; H, 9.15. Found: C, 65.45; H, 8.90.

1,7-Cyclododecadiyne (XVI).[35]—Seven and one-tenth grams (0.037 mole) of diketone XV was dissolved in 35 ml. of absolute ethanol and 4.7 g. of 95% hydrazine was added dropwise to the solution. The solution was allowed to stand at room temperature for ten minutes and was then heated on the steam-bath for a like period of time. The solvent was then removed from the solution in vacuum, and 25 ml. of dry benzene was added and likewise removed. The addition and removal of benzene was repeated twice more. The rather insoluble dihydrazone was then stirred with 10 g. of anhydrous magnesium sulfate in 100 ml. of refluxing benzene and 25.5 g. (0.118 mole) of yellow mercuric oxide was added portionwise during 15 minutes. Stirring and heating of the mixture was continued until the evolution of nitrogen ceased (2 hours). The mixture was cooled, and the solution was filtered free of solid (Celite). After removal of the solvent, the crude acetylene was distilled at a bath temperature of 120–190° (2 mm.), wt. 2.29 g. The crude material was dissolved in 10 ml. of pentane and chromatographed on 100 g. of alumina of activity I with pentane. The eluate was collected in three fractions: (1)

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[35] It was found that the liquid acetylenic hydrocarbons, and to a lesser extent the olefins, prepared in this work absorbed oxygen from the air rapidly, so the physical properties and analyses had to be carried out immediately upon preparation of a sample. A small sample of XXXIV upon standing in air gained 1% of its own weight in 10 minutes.

[36] M. S. Newman and J. H. Wotiz, THIS JOURNAL, **71**, 1292 (1949).

[37] B. W. Baker, R. W. Kierstead, R. P. Linstead and B. C. L. Weedon, *J. Chem. Soc.*, 1804 (1954).

[38] M. Stoll and A. Rouvé, *Helv. Chim. Acta*, **30**, 1822 (1947).

10 ml., (2) 100 ml., (3) 100 ml. Fraction 1 contained only compound XVII, fraction 2 was a mixture and fraction 3 contained only the expected acetylene XVI. Fraction 2 was therefore rechromatographed as before. The first two fractions collected (35 ml.) were shown by their ultraviolet spectra to contain considerable amounts of diene (XVII), while the latter fractions (125 ml.) were completely free of this material. The first two fractions of this chromatogram were combined with fraction 1 of the first chromatogram (diene fractions), and the latter fractions of the second chromatogram were combined with fraction 3 of the first chromatogram (acetylene fractions). The combined acetylene fractions were freed of solvent, and the residue was distilled under nitrogen to yield 0.84 g. (14%) of the pure acetylene XVI, $n^{25}\text{D}$ 1.5072. The compound readily solidified and when crystallized from methanol, was obtained as needles, m.p. 36.4–37.3°, $n^{25}\text{D}$ 1.5070 (supercooled liquid). The ultraviolet spectrum of this compound showed only end absorption; $\lambda_{220\ m\mu}$, ε 40; $\lambda_{215\ m\mu}$, ε 62; $\lambda_{210\ m\mu}$, ε 116; $\lambda_{205\ m\mu}$, ε 236. The infrared spectrum[11] showed the following: 4.40, 4.50 μ w (C≡C str.), no absorption 5–6.5 μ. Very strong bands useful for empirical identification occur at 7.32, 7.51 and 13.11 μ.

Anal. Calcd. for $C_{12}H_{16}$: C, 89.93; H, 10.07. Found: C, 90.08; H, 10.08.

1,7-*cis–cis*-Cyclododecadiene (XIX).[35]—Reduction of 340 mg. of the diacetylene XVI was carried out as described for the preparation of XXXV. The uptake of hydrogen ceased abruptly after 50 minutes, 98% of two molar equivalents having been absorbed. The catalyst was removed by filtration and the product was extracted with pentane. The pentane phase was washed with water, dilute hydrochloric acid and water, and was dried. After evaporation of the pentane the product was distilled under nitrogen at 25 mm. The diene was collected as a colorless liquid, $n^{25}\text{D}$ 1.4971, wt. 305 mg. (87%). The ultraviolet spectrum showed end absorption; λ_{max} 220 mμ, ε 145; λ_{max} 215 mμ, ε 184; λ_{max} 210 mμ, ε 315; λ_{max} 206 mμ, ε 725. The infrared spectrum[11] showed the complete absence of acetylene XVI. The following bands were found: 5.96 μ w, 6.05 μ m (C=C str.) 7.11 μ m (*cis*-olefin in-plane hydrogen bending), 13.96 μ s (*cis*-olefin out-of-the-plane hydrogen bending).

Anal. Calcd. for $C_{12}H_{20}$: C, 87.73; H, 12.27. Found: C, 87.54; H, 12.34.

Ozonolysis of 158 mg. of XIX was carried out in 5 ml. of methylene chloride at 0°. The resulting ozonide solution was added to 10 ml. of 15% hydrogen peroxide, and the mixture was stirred for three hours, during which time a voluminous white solid precipitated. The methylene chloride was evaporated from the mixture under vacuum at room temperature, then 0.5 ml. of 48% hydrobromic acid was added to destroy the excess peroxide. After 48 hours at room temperature the polymer was removed from the mixture by filtration, wt. 135 mg. The filtrate was frozen and the water was removed by lyophilization. The residue was crystallized from ethyl acetate and gave a brownish solid, wt. 42 mg. (10%), m.p. 146–149°. The reported[39] m.p. of adipic acid is 152°. The *p*-bromophenacyl ester of this material was prepared in the customary way, m.p. 152.6–153.9°; reported[39] m.p. 154°. An authentic sample of *p*-bromophenacyl adipate was prepared, m.p. 152.5–153.6°. The mixed m.p. was 153.2–154.2°.

One hundred and forty mg. of acetylene XVI was reduced with Adams catalyst in acetic acid. After 50 minutes the uptake of hydrogen ceased, 99% of four molar equivalents having been consumed. The reaction mixture was treated as described for hydrogenation of XXXIV to cyclodecane, and after distillation of the product there was obtained 130 mg. (88%) of a white solid, m.p. 58.5–60°; reported[40] m.p. for cyclododecane, 60–61°.

1,7-[6.4.0]-Bicyclododecadiene (XVII).[35]—The combined diene fractions from the chromatographic separation of XVI were freed of solvent, and the product was distilled yielding 0.44 g. (7.5%) of the pure diene as a colorless liquid, $n^{25}\text{D}$ 1.5200. The ultraviolet spectrum showed λ_{max} 222 mμ, ε 6,900. The infrared spectrum[11] showed the following bands of interest: 6.05 μ m (C=C str.) and 12.20 μ vs (trisubstituted olefin out-of-the-plane hydrogen bending). Empirically useful strong bands occur at 10.84, 11.00 and 11.71 μ. A sample of this material was crystallized from ethanol, m.p. 27.1–28.0°, $n^{25}\text{D}$ 1.5205 (supercooled liquid), λ_{max} 221 mμ, ε 6,640.

Anal. Calcd. for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.82; H, 11.24.

Ozonolysis of XVII was carried out at 0°, and the ozonide was decomposed with hydrogen peroxide as described for the ozonolysis of XIX. From 128 mg. of XVII there was obtained 59 mg. (17%) of a tan crystalline powder, m.p. 148–150.5°; reported[39] for adipic acid, m.p. 152°. The *p*-bromophenacyl ester melted at 153.9–154.6° and gave no mixed melting point depression with an authentic sample of *p*-bromophenacyl adipate (m.p. 152.6–153.6°).

Another oxidation experiment intended to lead from XXIII to XVI was carried out in a manner similar to that described, except that, following the common practice,[10a,b] 0.5 ml. of ethanol saturated with potassium hydroxide was added to the reaction mixture prior to the addition of the mercuric oxide. In this case the same kind of isolation procedure furnished after chromatography a crude diene fraction in 22% yield. No acetylene could be detected in the reaction mixture. The crude diene was contaminated in this case with other material which behaved in a similar manner upon chromatography. After distilling the diene, it was recrystallized to give a 12% yield of XVII, m.p. 23–26°, $n^{25}\text{D}$ 1.5205.

1-[6.4.0]-Bicyclododecene (XX).—Hydrogenation of XVII, 56 mg., was carried out in methanol with 10 mg. of palladium-on-carbon as catalyst. The hydrogen uptake ceased after 40 minutes, exactly one equivalent having been absorbed. The product was isolated as previously described and upon distillation at 25 mm. furnished 35 mg. of XX, $n^{25}\text{D}$ 1.5021. The infrared spectrum showed a strong band at 12.16 μ. The ultraviolet spectrum showed only end absorption as follows: $\lambda_{220\ m\mu}$, ε 1,600; $\lambda_{215\ m\mu}$, ε 2,900; $\lambda_{210\ m\mu}$, ε 4,650; $\lambda_{207\ m\mu}$, ε 5,500.

Anal. Calcd. for $C_{21}H_{20}$: C, 87.73; H, 12.27. Found: C, 87.95; H, 12.16.

[6.4.0]-Bicyclododecane (XXI).—A sample of diene XVII, 171 mg., was hydrogenated in acetic acid with Adams catalyst. In all, 99% of two molar equivalents of hydrogen were taken up; the first equivalent in 35 minutes and the second after an additional 6 hours. The product was isolated as usual and was distilled; a colorless liquid, $n^{25}\text{D}$ 1.4885, wt. 137 mg. (80%). The ultraviolet spectrum showed ε < 9 at 210 mμ.

Anal. Calcd. for $C_{12}H_{22}$: C, 86.66; H, 13.34. Found: C, 86.66; H, 13.53.

Benzocycloöctane (XXII).—Diene XVII, 151 mg., was heated with 10 mg. of palladium-on-charcoal for one hour at a temperature increasing from 240 to 320°. Approximately one mole of hydrogen was evolved. The product was taken up in pure pentane, and the solution was filtered. After evaporation of the solvent the product was distilled at 25 mm. The compound obtained was a colorless liquid, $n^{25}\text{D}$ 1.5370.

Anal. Calcd. for $C_{12}H_{16}$: C, 89.93; H, 10.07. Found: C, 89.94; H, 10.26.

An authentic sample of benzocycloöctane[13] was found to have $n^{25}\text{D}$ 1.5381. A comparison of the ultraviolet and infrared spectra of the two samples showed that they were identical.

A sample of benzocycloöctane, 203 mg., was reduced with platinum and hydrogen in acetic acid. The product was isolated as usual, as a colorless liquid, $n^{25}\text{D}$ 1.4888. The infrared spectrum of this compound was superimposable upon that of compound XXI obtained by hydrogenation of XVII.

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(39) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, New York, N. Y., 1948, p. 224.

(40) L. Ruzicka, M. Stoll, H. W. Huyser and H. A. Boekenoogen, *Helv. Chim. Acta*, **13**, 1152 (1930).