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Layered Compounds. XVIII1). Synthesis of a Paracyclophane Containing the 1,2,3,4,5-Hexapentaene Group and the Stereochemistry of Its Formation

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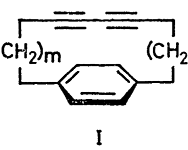
Novel cyclic 1,2,3,4,5-hexapentaene compounds were synthesized from cyclic diyne-diol IX *via* diallene-dibromide X in order to study transannular electronic interaction. A diallene-dibromide Xc-I obtained from a diyne-diol isomer IXc-I was debrominated with active zinc to give cyclic hexapentaene IIc, whereas the other diallene-dibromide Xc-II derived from the second diyne-diol isomer IXc-II was not. The X-ray crystallographic analysis of the dibromide Xc-I was then carried out, and the *s-trans* structure was assigned to the dibromide. On the basis of this result, the stereochemistry of the transformation from diyne-diol to the hexapentaene group was discussed. The electronic spectrum of a cyclophane IIa containing the hexapentaene group showed a transannular π-electronic interaction between the benzene ring and the hexapentaene group, unlike those of the other hexapentaene derivatives, IIc and XV.

In the previous paper we reported that the electronic spectra of [*m.n*]paracyclophadiynes (I) show remarkable transannular interaction between the benzene nucleus and the diacetylenic unit as the numbers of the bridge methylene chains, *m* and *n*, decrease.2) However, the absorption band of the diacetylene unit is partially submerged into the strong short-wavelength band of the benzene chromophore. Accordingly, the spectra have been mainly interpreted in terms of the long-wavelength band of the latter chromophore. For the clearer elucidation of the transannular electronic interaction between two different chromophores, a distinct observation of the absorption bands due to both chromophores is desirable. For that purpose, we have undertaken to study a paracyclophane IIa containing a benzene nucleus and a 1,2,3,4,5-hexapentaene group which shows a characteristic, strong absorption band in a longer wavelength region than that of the former chromophore.3)



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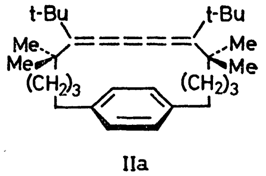


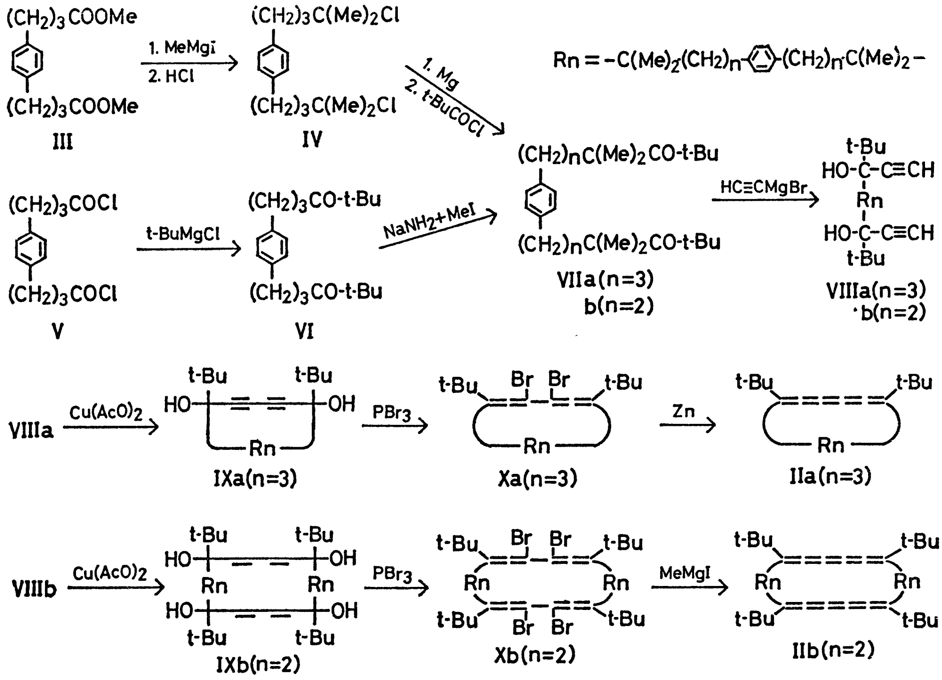
IIa

The present paper deals with the syntheses and properties of IIa and related compounds and discusses stereochemical process concerning the formation of the 1,2,3,4,5-hexapentaene group from 2,4-butadiyne-1,6-diol derivatives *via* an intermediate diallene-dibromide like X. Three cumulenic compounds, IIa, IIb, and IIc, are the first cyclic 1,2,3,4,5-hexapentaene derivatives except for some annulenes having a formal hexapentaene group.4)

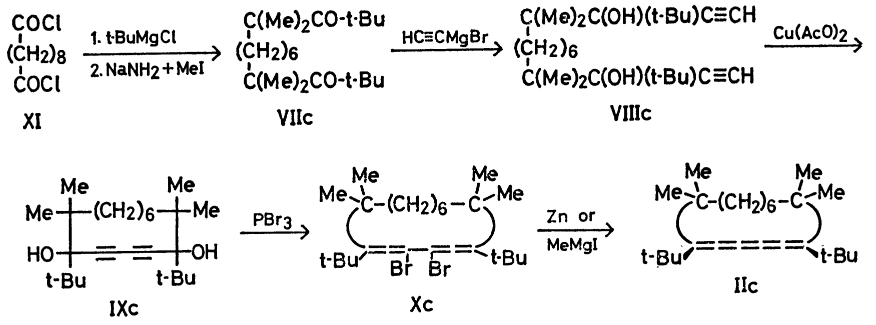
Results and Discussion

Synthesis. The syntheses of the cyclic hexapentaenes IIa, IIb, and IIc, are outlined in Schemes 1 and 2. By the reaction of the bis-Grignard compound of the dichloride IV with pivaloyl chloride in the presence of copper powder and cuprous chloride,5) a diketone VIIa was obtained in a low yield (14%), along with a large amount of olefinic compounds. The syntheses of the diketones VIIb and VIIc were achieved *via* two steps from acid chlorides V and XI respectively. Thus, two diketones, VI and 2,2,13,13-tetramethyl-3,12-tetradecanedione, which were obtained from V and XI in 87 and 65% yields respectively, were subjected to methylation with sodium amide and methyl iodide to give VIIb and VIIc in 53 and 37% yields respectively. This methylation process needs to be repeated to give good yields of VII. The reaction of the highly-branched diketone VII with ethynylmagnesium bromide6) was barely completed after 7—10 days at 35 °C to afford a 68—80% yield of a diyne-diol VIII. Such a slow reaction is obviously caused by the bulkiness around the α-carbon atoms adjacent to the carbonyl group, because an unbranched ketone XVI gives a 61% yield of a diyne-diol XVII even under the mild conditions of room temperature for 4 hr. The intramolecular oxidative coupling reaction of the diyne-diol VIII was carried out by the use of a high-dilution technique to give cyclic monomers, IXa and IXc, in 13 and 32% yields respectively.7) On the other hand, the oxidative coupling of VIIIb afforded a cyclic dimer IXb (34% yield) in place of the cyclic monomer, probably because of internal steric hindrance in the monomer. By column chromatography with silica gel, each of the cyclic monomers IXa and IXc were separated into two isomers, a meso and a racemic, distinguishable by means of the IR spectra.

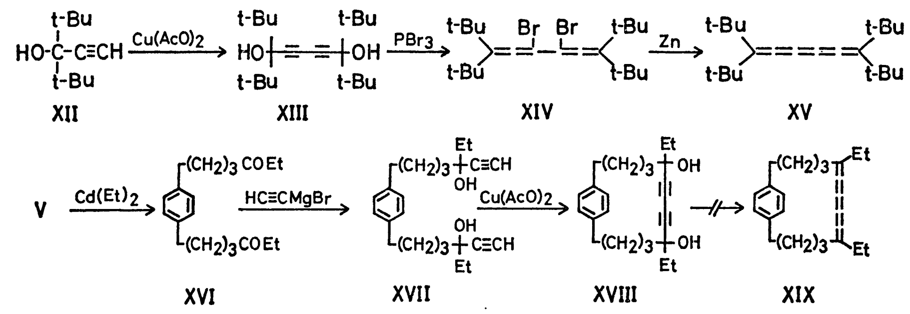
Both isomers of IXc, the first-eluted one IXc-I and the second-eluted one IXc-II, were individually treated with phosphorus tribromide8a) to derive diallene-dibromides Xc-I and Xc-II respectively. By the debromination of Xc-I with active zinc powder,8a) followed by chromatography with neutral alumina, a cyclic hexapentaene IIc was obtained as pale greenish yellow crystals in a 71% yield, whereas the same treatment of Xc-II gave no product with a spectrum characteristic of the hexapentaene group. On the other hand, upon debromination reaction with methylmagnesium iodide,8b) both Xc-I and Xc-II afforded the desired compound IIc. This reaction sequence from the diyne-diol IXc to IIc is of particular interest with regard to the stereochemistry in the reaction mechanism, which will be discussed below.



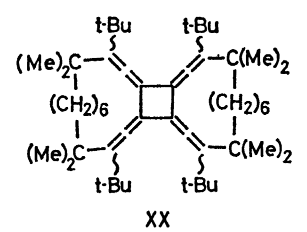
Scheme 1.



Scheme 2.



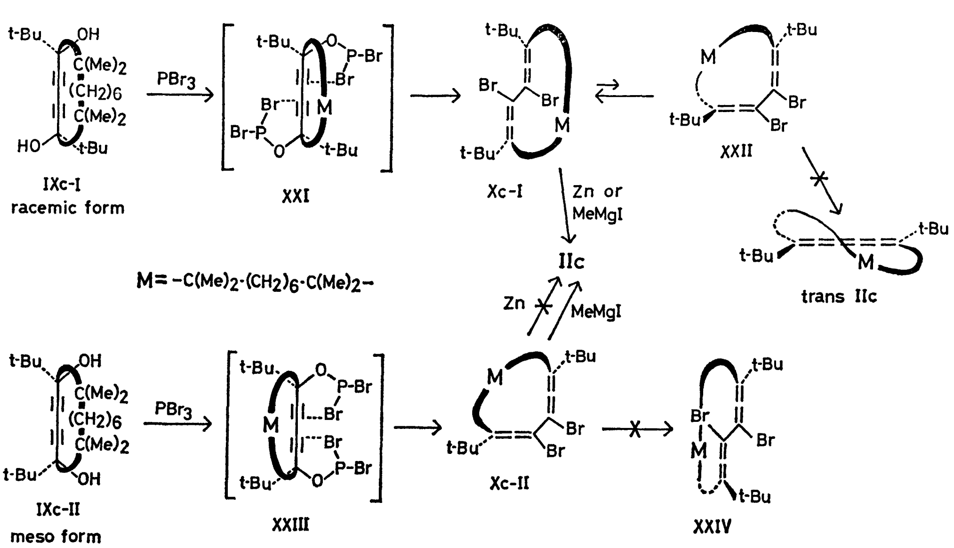
Scheme 3.



XX

Upon melting (146—147 °C), IIc immediately solidified to give white crystals with a mp of 280—282 °C. On the basis of the elemental analysis, the mass spectrum, and the UV spectrum of tetrakis(di-*tert*-butylvinylidene)cyclobutane,[8c] this product is assumed to be a dimer XX, the configuration of which has not yet been determined.

The debromination of diallene-dibromide Xa obtained in a 62% yield through the same treatment of IXa as in the case of IXc, was carried out by the active zinc method above-stated to give the desired cyclic hexapentaene IIa as a greenish yellow oil. Also, by debromination with methylmagnesium iodide, the



Scheme 4.

tetraallene-tetrabromide Xb derived from IXb gave a cyclic bishexapentaene IIb as greenish yellow crystals, which showed an electronic spectrum characteristic of the hexapentaene group. Tetra-*tert*-butyl-1,2,3,4,5-hexapentaene XV[8c] was prepared *via* the synthetic route shown in Scheme 3 for spectral reference.

In preliminary experiments, the preparation of a simpler cyclic hexapentaene XIX from XVIII was attempted by the following methods: 1) phosphorus diiodide,[9] 2) phosphorus tribromide in pyridine,[10] 3) phosphorus tribromide followed by active zinc, 4) stannous chloride-hydrogen chloride,[11] and 5) methylmagnesium bromide, but all the methods failed to give XIX.

Crystal Structure of Diallene-dibromide Xc-I. The diallene-dibromide Xc-I obtained from the first-eluted diyne-diol IXc-I is considered as an important key substance for clarifying the reaction mechanism for the well-known formation of the hexapentaene group from the diyne-diol derivative, as will be described below. In order to determine the geometrical structure of Xc-I and then to elucidate the stereochemical course of the formation of the hexapentaene IIc, X-ray crystallographic analysis was carried out.

The diallene-dibromide Xc-I was crystallized from ethyl acetate as colorless columns.

Crystal data: $C_{26}H_{42}Br_2$, Mol wt$=514.4$, triclinic,
$a=9.662$, $b=16.761$, $c=8.306$ Å; $\alpha=88.12°$, $\beta=92.30°$, $\gamma=92.73°$;
$V=1341.9$ Å^3; $D_m=1.267$, $D_x=1.273$ gcm^{-3}; $Z=2$,
Space group P$\bar{1}$.

The crystal selected for data collection was of the approximate dimensions of $0.13\times0.10\times0.23$ mm and was mounted with the c-axis coincident to the ϕ-axis of the goniostat. The intensity data were collected with $2\theta<55°$ on a fully-automatic Hilger four-circle diffractometer using Zr-filtered Mo-Kα radiation and the ω-2θ scan technique. The intensities of 1863 independent reflections were recorded as observed. However, when the intensity of a standard reflection, $\bar{5}\bar{1}1$, was measured every 10 reflections, an obvious decay was discernible. Accordingly, the intensities of the observed reflections were corrected with the Lorentz and polarization factors after a decay correction corresponding to the decay curve of the $\bar{5}\bar{1}1$ reflection. No absorption corrections were made.

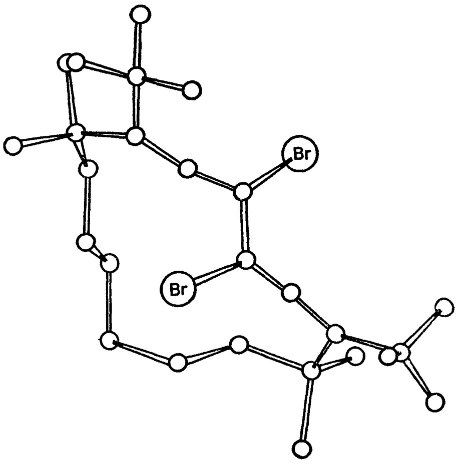


Fig. 1. Crystal structure of diallene-dibromide Xc-I.

A three-dimensional Patterson synthesis was first computed, and the positions of the bromine atoms were deduced. All the carbon atoms were revealed after successive Fourier synthesis. Although the structure of this dibromide was partially disordered, the essential features of the molecule are shown in Fig. 1 with a final R index of 0.113. The figure clearly shows that the two bromine atoms are positioned in the manner of the *s-trans* form around the sp^2-sp^2 single bond and that the two *tert*-butyl groups are in the *cis* configuration with respect to the plane containing the two bromine atoms.

All the calculations were performed on a NEAC-700 computer at the Computation Center of Osaka University by the use of the following programs: PSSFR-5* and HBLS-IV.**

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* T. Sakurai, The Universal Crystallographic Computing System (I), p. 18, The Crystallographic Society of Japan, 1967.

** T. Ashida, The Universal Crystallographic Computing System-Osaka, p. 55, The Computation Center, Osaka University, 1973.

Stereochemical Aspect of the Formation of Hexapentaene. The stereochemistry of the reaction sequence from cyclic diyne-diol IXc to cyclic hexapentaene IIc is given in Scheme 4. The bromination of IXc with phosphorus tribromide is presumed to proceed in a stereospecific manner *via* a bis-dibromophosphite ester, XXI or XXIII, as a cyclic transition state,[13] since the halogenation of acetylenic alcohol with thionyl chloride[12] or phosphorus tribromide[13] has been well established or illustrated to follow the S_{Ni}' mechanism.

Thus, *s-trans*-diallene-dibromide Xc-I should be derived from the racemic form of the diyne-diol IXc-I *via* the bis-dibromophosphite ester XXI, whereas its *s-cis* conformer XXII seems to be hardly producible at all, for it is considerably strained, according to an examination with the Stuart-Briegleb molecular model. Similarly, the *s-cis*-dibromide Xc-II should be formed from the meso form of the diyne-diol IXc-II through the bis-dibromophosphite ester XXIII, and the corresponding *s-trans* conformer XXIV can not be yielded because of its highly strained system.***

As is shown in Fig. 1, X-ray crystallographic analysis assigned the *s-trans* structure of Xc-I to the diallene-dibromide which was obtained from the first-eluted diyne-diol IXc-I. Accordingly, this result demonstrates that the diyne-diol IXc-I is of the racemic form, whereas the second-eluted diyne-diol IXc-II must be of the meso form. Since *trans*-IIc, in which two *t*-butyl groups are bonded in the *trans* form to the hexapentaene group, can not at all expect to exist because of the short bridged chain, the debromination product IIc should have the *cis* configuration. Consequently, the fact that IIc is obtained from Xc-I by debromination with zinc powder, but not from Xc-II, clearly indicates that the debromination proceeds through the *trans* elimination mechanism. On the other hand, the debromination with methylmagnesium iodide might proceed by a mechanism other than E2 elimination, because both Xc-I and Xc-II afforded IIc by the reaction.

Electronic Spectra. Figure 2 records the electronic spectra of cyclic hexapentaenes as well as that of an open-chain analogue, tetra-*t*-butylhexapentaene XV. The spectrum of IIc is very similar to that of the reference compound XV. On the other hand, the hexapentaene cyclophane IIa shows a red shift of the longest wavelength band by 8 nm than the corresponding band of IIc, besides a slight change of the bands in the 220—270 nm region. A Stuart-Briegleb molecular model demonstrates that both cyclic hexapentaenes, IIc and IIa, are strainless and in similar steric environments around the hexapentaene group. Accordingly, it may be concluded that the red shift of the longest wavelength band of IIa is caused by transannular π-electronic interaction between the benzene ring and the 1,2,3,4,5-hexapentaene group. The longest wavelength bands of cyclic bis-hexapentaene IIb appear near the band positions of IIc, hence, such an interaction is hardly discernible.

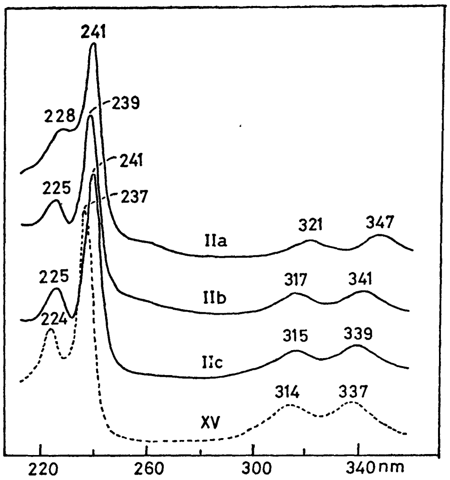

Fig. 2. Electronic spectra of cyclic cumulenes and tetra-*t*-butyl hexapentaene in ether.

Experimental

The melting points are uncorrected. The UV, IR, NMR, and mass spectra were measured on a Hitachi EPS-3T autorecording spectrophotometer, a Hitachi EPI-G2 spectrometer a Hitachi R-20 spectrometer, and a Hitachi RMU-7 spectrometer respectively.

p-*Bis(4-hydroxy-4-methylpentyl)benzene.* Into a solution of methylmagnesium iodide, prepared from magnesium (14 g, 0.58 mol) and methyl iodide (81 g, 0.57 mol) in 300 ml of ether, a solution of the diester III[14] (20 g, 0.072 mol) in 100 ml of ether was added over a period of 1.5 hr with stirring at reflux. The mixture was refluxed for 2 hr with stirring and then poured into a dilute sulfuric acid. The diol thus precipitated was collected, washed well with water, and dried. The filtrate was extracted with ether, followed by the usual work-up. After removing the solvent, the residue was chromatographed on 50 g of silica gel, using ether-petroleum ether (2 : 3) as an eluent, to yield white crystals. The total yield of the desired diol was 18 g (90%).

For analysis, a small amount of the sample was recrystallized from toluene to yield white crystals, mp 121—122 °C. Found: C, 77.73; H, 10.92%; Mol wt, 278 (mass spectrometry). Calcd for $C_{18}H_{30}O_2$: C, 77.65; H, 10.86%; Mol wt, 278. IR (KBr disk): 3280, 1510, 1190, and 826 cm^{-1}. NMR ($CDCl_3$), δ: 7.07 (s, 4H), 2.59 (t, 4H), 1.65∼1.5 (m, 8H), 1.32 (s, 2H), and 1.20 ppm (s, 12H).

p-*Bis(4-Chloro-4-methylpentyl)benzene (IV).* Into an ice-cooled mixture of the above diol (52 g), 100 ml of methanol, and 2 l of petroleum ether, a current of hydrogen chloride was passed for 6 hr with stirring. The upper organic layer of the mixture was then separated, washed with concd sulfuric acid, and allowed to stand overnight over sodium carbonate. The subsequent concentration of the solution gave colorless plates (44 g, 75%).

For analysis, a small amount of the sample was recrystallized from petroleun ether to yield colorless plates, mp 49—51 °C. Found: C, 68.44; H, 9.18; Cl, 22.42%. Calcd for $C_{18}H_{28}Cl_2$: C, 68.56; H, 8.95; Cl, 22.49%.

p-*Bis (4,4,6,6-tetramethyl-5-oxoheptyl) benzene (VIIa).* To magnesium (0.60 g, 0.025 mol) in 50 ml of dry ether, a solution of the dichloride IV (4.0 g, 0.013 mol) in 50 ml of ether was added dropwise in a 1.5 hr period with stirring under a nitrogen atmosphere. A mixture of copper powder

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*** Although the diallene-dibromides are also considered to yield by a "two-step mechanism" through a mono-dibromophosphite ester as a cyclic transition state, one may reach stereochemically the same result.

(1.5 g), cuprous chloride (2.4 g), freshly-prepared pivaloyl chloride (2.7 g, 0.022 mol), and 100 ml of ether in an alternative flask was cooled in an ice-salt bath, and into the mixture the above Grignard solution, filtered through glass-wool, was added dropwise over a period of 1 hr with vigorous stirring under a nitrogen atmosphere. Stirring was then continued for 4 hr at room temperature, after which the reaction mixture was poured into a dilute hydrochloric acid and the organic layer was separated. The aqueous layer was extracted with ether. The combined etherial solution was washed successively with dilute hydrochloric acid, a sodium bicarbonate solution, and water, and then dried over magnesium sulfate. After the solvent had been removed, the residue was chromatographed on 50 g of alumina, using ether-petroleum ether (1 : 3) as an eluent, to yield a colorless solid (0.63 g, 14% based on pivaloyl chloride).

For analysis a small amount of the sample was recrystallized from petroleum ether to yield colorless plates, mp 66—67 °C. Found: C, 80.95; H, 11.27%; Mol wt, 414 (mass spectrometry). Calcd for $C_{28}H_{46}O_2$: C, 81.10; H, 11.18%; Mol wt, 414. IR (KBr disk): 1674 cm^{-1} (C=O).

p-*Bis (5-*t*-butyl)-5-hydroxy-4,4-dimethyl-6-heptynyl) benzene (VIIIa).* To a solution of ethynylmagnesium bromide,[6] prepared from magnesium (31 g, 1.3 mol), ethyl bromide (140 g, 1.3 mol), and 1 l of dry tetrahydrofuran, a solution of the diketone VIIa (5.0 g, 0.012 mol) in 100 ml of tetrahydrofuran was added dropwise over a period of 30 min. The mixture was stirred for a week at 30—35 °C with the passage through of a slow stream of acetylene. After the addition of dilute sulfuric acid and salting-out, the mixture was extracted with ether. The ether extract was washed successively with dilute sulfuric acid, a sodium bicarbonate solution, and water, and then dried over magnesium sulfate. After the solvent had been removed, the residue was chromatographed on 120 g of silica gel, using ether–petroleum ether (1 : 4), to give a colorless oil (3.8 g, 68%); IR (neat), 3560 (OH) and 3305 cm^{-1} (C≡CH); NMR (CCl$_4$), δ: 7.00 (s, 4H), 2.5 (m, 4H), 2.33 (s, 2H), 1.8—1.5 (m, 10H), and 1.15 and 1.09 ppm (d, 30 H).

*5,10-Di-*t*-butyl-4,4,11,11-tetramethyl-6,8-[14]paracyclophadiyne-5,10-diol (IXa).* The intramolecular oxidative coupling of the bisethynyl compound VIIIa was accomplished in a manner similar to that previously reported.[2b] Into a mixture of 30 g of anhydrous cupric acetate and 1.5 l of pyridine, a solution of VIIIa (3.0 g) in 2 l of oxygen-free ether was added dropwise over a period of three days at 50 °C with vigorous stirring under a nitrogen atmosphere. After the addition, the reaction was continued for another day. The reaction mixture was then poured into a cold dilute sulfuric acid, and the organic layer was separated. The aqueous layer was extracted with ether, and the combined ethereal solution was washed well with dilute sulfuric acid, a sodium bicarbonate solution, and water successively, and dried over anhydrous magnesium sulfate. The solvent were removed under reduced pressure, and the residue was chromatographed on 120 g of silica gel to yield two compounds.

The first compound (230 mg, 7.7%) was eluted with ether-petroleum ether (1 : 2). It was confirmed to be the cyclic monomer IXa-I. For analysis, a small amount of the sample was recrystallized from carbon tetrachloride–petroleum ether, colorless needles, mp 161 °C. Found: C, 82.52; H, 10.76%. Mol wt, 464 (mass spectrometry). Calcd for $C_{32}H_{48}O_2$: C, 82.70; H, 10.41%. Mol wt, 464. UV (cyclohexane): λ_{max} 214, 220, 225, 247, 260, 265, 268, and 274 nm. IR (KBr disk): 3580, 3470, 1511, 1393, 1384, 1367, 1290, 1220, 1205, 1069, 1051, 980, 927, and 800 cm^{-1}.

The second substance (170 mg, 5.7%) was eluted with ether-petroleum ether (1 : 1). It was confirmed to be the cyclic monomer IXa-II. For analysis, a small amount of the sample was recrystallized from carbon tetrachloride-petroleum ether, white crystals, mp 175.5—176 °C. Found: C, 82.85; H, 10.64%; Mol wt, 464 (mass spectrometry). UV (cyclohexane): λ_{max} 214, 221, 226, 247, 260, 265, 267, and 273 nm. IR (KBr disk): 3570, 3480, 1506, 1385, 1366, 1297, 1227, 1208, 1195, 1124, 1074, 1053, 1040, 1006, 998, 983, 932, 884, and 803 cm^{-1}.

7,8-Dibromo-5,10-di-t-butyl-4,4,11,11-tetramethyl-5,6,8,9-[14]-paracyclophatetraene (Xa). A mixture of the diyne-diol IXa (100 mg, 0.22 mmol), phosphorus tribromide (1 g, 3.7 mmol), and 50 ml of dry benzene was stirred at 50 °C for 3 hr under a nitrogen atmosphere. The reaction mixture was then poured into ice-water and extracted with ether. The ethereal solution was washed successively with dilute hydrochloric acid, a sodium carbonate solution, and water, and then dried over anhydrous magnesium sulfate in a dark and cold room. The solvent was removed under reduced pressure, and the residue was recrystallized from chloroform-methanol to yield a white solid (93 mg, 62%).

For analysis, a small amount of the sample was recrystallized from chloroform–methanol, white crystals, mp 145—146 °C. Found: C, 65.16; H, 7.61%; Mol wt, 590 (mass spectrometry). Calcd for $C_{32}H_{46}Br_2$: C, 65.08; H, 7.85%; Mol wt, 590. UV (cyclohexane): λ_{max} 232 nm (ε 45300).* IR (KBr disk): 1938, 1510, 840, 685, and 654 cm^{-1}.

*5,10-Di-*t*-butyl-4,4,11,11-tetramethyl-5,6,7,8,9-[14]paracyclophapentaene (IIa).* A mixture of diallene-dibromide Xa (50 mg, 0.085 mmol) and 5 g of active zinc powder[8a] in 50 ml of dry ether was stirred for three days at room temperature under a nitrogen atmosphere. The reaction mixture was filtered through a short column of silica gel to remove the zinc under a nitrogen atmosphere. The filtrate was then concentrated under reduced pressure, and the residue was chromatographed on 20 g of silica gel, using petroleum ether as an eluent and under a nitrogen atmosphere, to give a greenish yellow oil; MS (*m/e*), 430 (M$^+$), 373 (M−Bu-*t*) and 316 (M−2Bu-*t*); NMR (CCl$_4$), δ: 6.90 (s, 4H), 2.7—2.4 (m, 4H), 1.4 (m, 8H), and 1.27 and 1.25 ppm (d, 30H); UV: Fig. 2.

2,2,13,13-Tetramethyl-3,12-tetradecanedione. A mixture of freshly-prepared acid chloride XI (30 g, 0.13 mol), copper powder (25 g), cuprous chloride (50 g), and 300 ml of dry ether was cooled in an ice-salt bath. Into the mixture a solution of *tert*-butylmagnesium chloride, prepared from magnesium (12 g, 0.49 mol) and *tert*-butyl chloride (45 g, 0.49 mol) in 300 ml of dry ether, was added dropwise over a period of 6 hr with vigorous stirring. Stirring was continued overnight at room temperature. Water was added to decompose the excess of the Grignard reagent, and the mixture was poured into dilute hydrochloric acid and then extracted with ether, followed by the usual work-up. After the solvent had been removed, the residue was chromatographed on 120 g of silica gel, using 5% ether-petroleum ether as an eluent, to yield colorless crystals (23 g, 65%).

For analysis, a small amount of the sample was recrystallized from *n*-hexane, colorless needles, mp 24—25 °C (lit,[15] bp 178—182 °C/1 mmHg). Found: C, 76.27; H, 12.46%. Calcd for $C_{18}H_{34}O_2$: 76.54; H, 12.13%. IR(neat): 1705 cm^{-1} (C=O).

2,2,4,4,11,11,13,13-Octamethyl-3,12-tetradecanedione (VIIc). A mixture of the above diketone (28 g, 0.099 mol) and sodium

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* In the previous paper (Ref. 3) this value was erroneously reported as 45.3×10^4.

amide (40 g, 1.0 mol) in 300 ml of benzene was refluxed for 24 hr. To the cold mixture, methyl iodide (210 g, 1.5 mol) was added for 1 hr, after which the mixture was refluxed for 3 hr with stirring. Methanol was added to decompose the excess sodium amide, after which the reaction mixture was poured into dilute hydrochloric acid and extracted with ether, followed by the usual work-up. After the solvent had been removed, the residue was subjected to the above treatment for exhaustive methylation once again. The resulting product, obtained by removing the solvent, was chromatographed on 200 g of neutral alumina, using ether-petroleum ether (1 : 4) as an eluent, to yield white crystals (12 g, 37%).

For analysis, a small amount of the sample was recrystallized from *n*-hexane, colorless plates, mp 40—41 °C. Found: C, 77.91; H, 12.70%; Mol wt, 338 (mass spectrometry). Calcd for $C_{22}H_{42}O_2$: C, 78.04; H, 12.50%; Mol wt, 338. IR (KBr disk): 1670 cm^{-1} (C=O).

3,12-Di-t-butyl-4,4,11,11-tetramethyl-1,13-tetradecadiyne-3,12-diol (VIIIc). The ethynylation of the diketone VIIc was accomplished in a manner similar to that described for the preparation of VIIIa. From 11 g of the diketone VIIc we obtained 10 g (79%) of the diyne-diol VIIIc as a colorless oil after chromatography on 150 g of silica gel, using ether–petroleum ether (1 : 9); IR (neat), 3490 (OH) and 3310 cm^{-1} (C≡CH); NMR (CCl$_4$), δ: 2.34 (s, 2H) and 1.8—1.1 ppm (m, 44H: 1.75 (s), 1.3 (m), 1.18 (s), and 1.10 (s)).

5,14-Di-t-butyl-6,6,13,13-tetramethyl-1,3-cyclotetradecadiyne-5,14-diol (IXc). The intramolecular oxidative coupling of VIIIc was accomplished in a manner similar to that described for that of VIIIa except for the following conditions: anhydrous cupric acetate, 60 g; VIIIc, 5.0 g; reaction temperature, 60 °C; dropping period, five days. The residue obtained by removing the solvent was chromatographed on 200 g of silica gel to yield two compounds.

The first compound (980 mg, 20% yield) was eluted with ether-petroleum ether (1 : 20); it was the cyclic monomer IXc-I (racemic isomer). For analysis, a small amount of the sample was recrystallized from carbon tetrachloride, colorless needles, mp 202 °C (dec, in sealed tube). Found: C, 80.15; H, 11.67%; Mol wt, 388 (mass spectrometry). Calcd for $C_{26}H_{44}O_2$: C, 80.35; H, 11.41%; Mol wt, 388. UV (cyclohexane): λ_{max} 225, 236, 248, and 261 nm. IR (KBr disk): 3583, 1395, 1385, 1367, 1287, 1253, 1222, 1202, 1063, 1036, 1006, 980, and 925 cm^{-1}.

The second substance (620 mg, 12%) was eluted with ether-petroleum ether (1 : 9); it was the cyclic monomer IXc-II (*meso* isomer). For analysis, a small amount of the sample was recrystallized from carbon tetrachloride, white crystals, mp 142—143 °C. Found: C, 80.30; H, 11.58%; Mol wt, 388 (mass spectrometry). UV (cyclohexane): λ_{max} 224, 235, 248, and 261 nm. IR (KBr disk): 3580, 3450, 1392, 1382, 1370, 1288, 1220, 1205, 1082, 1043, 1005, 975, and 937 cm^{-1}.

3,4-Dibromo-1,6-di-t-butyl-7,7,14,14-tetramethyl-1,2,4,5-cyclotetradecatetraene (Xc). The bromination of diyne-diol IXc was accomplished in a manner similar to that described in the case of IXa.

From the first-eluted diyne-diol IXc-I (3.0 g, 7.7 mmol), phosphorus tribromide (10 g, 37 mmol), and 50 ml of dry benzene, we obtained 1.7 g (43%) of diallene-dibromide Xc-I as white crystals after chromatography on 30 g of silica gel using *n*-hexane. For analysis, a small amount of the sample was recrystallized from carbon tetrachloride-methanol, white crystals, mp 132—134 °C. Found: C, 60.73; H, 8.46; Br, 31.22%; Mol wt, 514 (mass spectrometry). Calcd for $C_{26}H_{42}Br_2$: C, 60.70; H, 8.23; Br, 31.07%; Mol wt, 514. UV (cyclohexane): λ_{max} 231 nm (ε 38700). NMR (CCl$_4$), δ: 1.28 and 1.37 ppm. IR (KBr): 1950, 1928, 1364, 1222, 1205, 1158, 974, 685, and 653 cm^{-1}.

From the second-eluted diyne-diol IXc-II (3.0 g), diallene-dibromide Xc-II was obtained by the method described above, white crystals, mp 134—135 °C (from carbon tetrachloride-methanol). Found: C, 60.89; H, 8.48; Br, 31.42%. UV(cyclohexane): λ_{max} 231 nm (ε 41700). NMR (CCl$_4$), δ: 1.28 and 1.38 ppm. IR (KBr): 1950, 1925, 1363, 1221, 1204, 1156, 972, 685, and 653 cm^{-1}.

1,6-Di-t-butyl-7,7,14,14-tetramethyl-1,2,3,4,5-cyclotetradecapentaene (IIc). *Debromination with Active Zinc*: The debromination of Xc was accomplished in a manner similar to that described for the preparation of IIa. From Xc-I (200 mg), active zinc powder (5 g), and 80 ml of dry ether, cyclic hexapentaene IIc was obtained by chromatography on 10 g of neutral alumina, using petroleum ether under a nitrogen atmosphere, as pale greenish yellow plates (98 mg, 71%), mp 146—147 °C. MS (*m*/*e*): 354 (M$^+$), 297 (M−Bu-*t*), and 240 (M−2Bu-*t*). NMR (CCl$_4$), δ: 1.45—1.2 ppm (m). UV: Fig. 2.

Diallene-dibromide Xc-II was treated with active zinc under conditions as like those described above as possible. However, no spectral evidence characteristic of IIc was observed.

Debromination with Methylmagnesium Iodide: To a solution of Xc-I (83 mg) in 25 ml of dry ether, we added a solution of methylmagnesium iodide, prepared from magnesium (6 g) and methyl iodide (35 g) in 100 ml of ether; the mixture was then stirred overnight at room temperature under nitrogen atmosphere. After the decomposition of the excess of the Grignard reagent with a saturated ammonium chloride solution, the mixture was extracted with ether and dried over anhydrous sodium sulfate. The etherial solution obtained by passing the mixture through a short column of silica gel under nitrogen showed the λ_{max}'s characteristic of IIc.

Similarly, Xc-II gave the same results upon the same treatment.

p-Bis(5,5-dimethyl-4-oxohexyl)benzene (VI). The alkylation of V was accomplished in a manner similar to that described for the preparation of 2,2,13,13-tetramethyl-3,12-tetradecanedione. From 20 g of fresh acid chloride V, which had been prepared from *p*-bis(3-carboxypropyl)benzene,[14] we obtained 20 g (87%) of the diketone VI as colorless crystals after chromatography on 150 g of silica gel using ether-petroleum ether (1 : 9).

For analysis, a small amount of the sample was recrystallized from petroleum ether, white crystals, mp 45—46 °C. Found: C, 79.85; H, 10.44%. Calcd for $C_{22}H_{34}O_2$: C, 79.95; H, 10.37%. IR (KBr disk): 1675 cm^{-1} (C=O).

p-Bis(3,3,5,5-tetramethyl-4-oxohexyl)benzene (VIIb). The methylation of the above diketone was accomplished in a manner similar to that described for the preparation of VIIc. From 15 g of the diketone VI we obtained 9.4 g (53%) of the diketone VIIb as colorless crystals after chromatography on 100 g of silica gel using ether-petroleum ether (1 : 4).

For analysis, a small amount of the sample was recrystallized from *n*-hexane, colorless needles, mp 79—80 °C. Found: C, 80.56; H, 11.25%; Mol wt, 386 (mass spectrometry). Calcd for $C_{26}H_{42}O_2$: C, 80.77; H, 10.95%; Mol wt, 386. IR (KBr disk): 1660 cm^{-1} (C=O).

p-Bis(4-t-butyl-4-hydroxy-3,3-dimethyl-5-hexynyl)benzene (VIIIb). The ethynylation of the diketone VIIb was accomplished in a manner similar to that described for the preparation of VIIIa. From 9 g of the diketone VIIb we obtained 8.2 g (80%) of the diyne-diol VIIIb as a colorless solid (mp 63—65 °C) after chromatography on 150 g of silica gel using ether-petroleum ether (1 : 9); IR (KBr disk):

3250 (OH) and 3300 cm^{-1} (C≡CH); NMR (CCl_4), δ: 6.97 (s, 4H), 2.8—2.4 (m, 4H), 2.37 (s, 2H), 2.1—1.6 (m, 6H), and 1.20 ppm (s, 30H).

Oxidative Coupling of VIIIb. The oxidative coupling of VIIIb was accomplished in a manner similar to that described for the case of VIIIa except for the following conditions: anhydrous cupric acetate, 40 g; VIIIb, 3.0 g; dropping period, seven days. The residue obtained by removing the solvent was chromatographed on 120 g of silica gel, using ether-*n*-hexane (1 : 1), to yield the cyclic dimer IXb as white crystals (1.0 g, 33%). For analysis, a small amount of the sample was recrystallized from carbon tetrachloride, colorless fine crystals, mp 240—241 °C. Found: C, 82.23; H, 10.40%; Mol wt, 865 (osmometry). Calcd for $C_{60}H_{88}O_4$: 82.51; H, 10.16%; Mol wt, 873. UV(cyclohexane): λ_{max} 214, 220, 224, 248, 260, 265, 268, and 274 nm.

Tetraallene-tetrabromide Xb. The bromination of XIb was accomplished in a manner similar to that described for the preparation of Xa except for the use of benzene-chloroform (10 : 1) as a solvent. From 200 mg of IXb, 97 mg (38%) of tetraallene-tetrabromide Xb was obtained as fine white crystals, mp 204—205 °C (from chloroform-methanol). Mol wt, Found: 1092 (osmometry). Calcd for $C_{60}H_{84}Br_4$: 1124. UV (cyclohexane): λ_{max} 222 and 231 nm. IR (KBr disk): 1924 cm^{-1} (C=C=C).

Cyclic Bis-hexapentaene IIb. The debromination of tetraallene-tetrabromide Xb with methylmagnesium iodide was accomplished in a manner similar to that described for the case of Xc. From 200 mg of Xb, 54 mg (58%) of cyclic bis-hexapentaene IIb was obtained as greenish yellow crystals, which showed a negative Beilstein's test and which were decomposed in the range of 180—200 °C, after chromatography on 10 g of neutral alumina using ether–petroleum ether (1 : 9). The UV spectrum of IIb is shown in Fig. 2.

*3,8-Di-*t*-butyl-2,2,9,9-tetramethyl-4,6-decadiyne-3,8-diol (XIII).* A mixture of di-*tert*-butyl ethynyl carbinol[16] (XII) (10 g) and anhydrous cupric acetate (30 g) in 400 ml of pyridine was stirred for 24 hr at 50 °C under a nitrogen atmosphere. The reaction mixture was poured into cooled dilute sulfuric acid and extracted with ether, followed by the usual work-up. The residue obtained by removing the solvent was chromatographed on silica gel using petroleum ether-ether (5 : 1) to yield 6.8 g (69%) of pale yellow crystals.

For analysis, a small amount of the sample was recrystallized from *n*-pentane-carbon tetrachloride, white crystals, mp 166 °C. Found: C, 78.83; H, 11.66%. Calcd for $C_{22}H_{38}O_2$: C, 78.98; H, 11.45%. IR (KBr disk): 3480 cm^{-1} (OH). NMR ($CDCl_3$), δ: 1.90 (s, 2H) and 1.17 ppm (s, 36H).

*5,6-Dibromo-3,8-di-*t*-butyl-2,2,9,9-tetramethyl-3,4,6,7-decatetraene (XIV).* The bromination of the diyne-diol XIII was accomplished in a manner similar to that described for the preparation of Xa. From 6 g of XIII, 85 g of phosphorus tribromide, and 100 ml of benzene we obtained 5.2 g (63%) of diallene-dibromide XIV as a white solid after recrystallization from chloroform-methanol. The further recrystallization of this solid gave white plates, mp 232—233 °C (sealed tube). Found: C, 57.53; H, 8.23; Br, 34.38%. Calcd for $C_{22}H_{36}Br_2$: C, 57.40; H, 7.88; Br, 34.72%. IR (KBr disk): 1937 cm^{-1} (C=C=C). UV (cyclohexane): λ_{max} 231 nm (ε 43500). NMR ($CDCl_3$), δ: 1.27 ppm (s).

*1,1,6,6-Tetra-*t*-butylhexapentaene (XV).* The debromination of XIV with active zinc was accomplished in a manner similar to that described for the case of Xa. From XIV (200 mg) and active zinc powder (3 g), 81 mg (62%) of the hexapentaene XV was obtained as yellow crystals, mp 182—184 °C (lit,[8c] mp 188—189 °C). NMR (CCl_4), δ: 1.29 ppm (s) (lit,[8c] 1.28 ppm (s) in $CDCl_3$). The UV spectrum of XV is shown in Fig. 2.

p-*Bis(4-oxohexyl)benzene (XVI).* A suspension of diethylcadmium,[17] prepared from magnesium (3.9 g, 0.16 mol), ethyl bromide (18 g, 0.17 mol), cadmium chloride (24 g, 0.13 mol), and 150 ml of ether, was cooled in an ice-salt bath. Into the mixture a solution of freshly-prepared acid chloride V (5.5 g, 0.019 mol) in 50 ml of benzene was added dropwise over a period of 20 min with vigorous stirring. The mixture was stirred for an hour and then for a further hour at room temperature. After the addition of dilute sulfuric acid and extraction with ether, followed by the usual work-up, the residue obtained by removing the solvent was chromatographed on 40 g of silica gel, using ether-petroleum ether (1 : 4), to give colorless needles (3.9 g, 74% from V).

For analysis, a small amount of the sample was recrystallized from carbon tetrachloride, colorless needles, mp 36—37 °C. Found: C, 78.82; H, 9.65%. Calcd for $C_{18}H_{26}O_2$: C, 78.79; H, 9.55%.

p-*Bis(4-ethyl-4-hydroxy-5-hexynyl)benzene (XVII).* The ethynylation of the diketone XVI was accomplished in a manner similar to that described for the preparation of VIIIa, but in this case the completion of the reaction required 4 hr. From 2.5 g of the diketone XVI, 1.8 g (61%) of the diyne-diol XVII was obtained as a pale yellow oil after chromatography on 50 g of silica gel using ether-petroleum ether (1 : 2), NMR (CCl_4), δ: 7.00 (s, 4H), 2.58 (t, J=7 Hz, 4H), 2.25 (s, 2H), 1.97 (s, 2H), 1.9—1.4 (m, 12H), and 0.98 (t, J=7 Hz, 6H).

4,9-Diethyl-5,7-[12]paracyclophadiyne-4,9-diol (XVIII). The intramolecular oxidative coupling of XVII was accomplished in a method similar to that described for the case of VIIIa except for the following conditions: XVII, 2.9 g; reaction temperature, 40 °C; dropping period, 4 days. The residue obtained by removing the solvent was chromatographed on 80 g of silica gel to yield two compounds.

The first compound (500 mg, 17%) was eluted with ether-petroleum ether (1 : 4), it was the cyclic monomer XVIII-I; colorless crystals (from carbon tetrachloride-petroleum ether), mp 155—156.5 °C. Mol wt, Found: 324 (mass spectrometry). Calcd for $C_{22}H_{28}O_2$: 324. UV (cyclohexane): λ_{max} 214, 221, 225, 250, 259, 266, and 273 nm. NMR ($CDCl_3$), δ: 7.12 (s, 4H), 2.7—2.5 (m, 4H), 2.1—1.4 (m, 14H), 1.60 (q, J=7 Hz), and 0.98 ppm (t, J=7 Hz, 6H). IR (KBr disk): 3340 cm^{-1} (OH).

The second substance (520 mg, 18%) was eluted with ether-petroleum ether (2 : 3); it was the cyclic monomer XVIII-II, white fine crystals (from carbon tetrachloride-petroleum ether), mp 156—158 °C. Mol wt, 324 (mass spectrometry). UV (cyclohexane): λ_{max} 214, 220, 225, 245, 259, 264, and 273 nm. NMR ($CDCl_3$), δ: 7.11 (s, 4H), 2.7—2.5 (m, 4H), 2.1—1.4 (m, 14H), 1.61 (q, J=7 H_2), and 0.97 ppm (t, J=7 Hz, 6H). IR (KBr disk): 3540, 3400, and 3340 cm^{-1} (OH).

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References

1) Part XVII: N. Kannen, T. Umemoto, T. Otsubo, and S. Misumi, *Tetrahedron Lett.*, **1973**, 4537.

2) a) T. Matsuoka, Y. Sakata, and S. Misumi, *ibid.*, **1970**, 2549; b) T. Matsuoka, T. Negi, T. Otsubo, Y. Sakata, and S. Misumi, This Bulletin, **45**, 1825 (1972); c) T. Matsuoka, T. Negi, and S. Misumi, *Synth. Commun.*, **2**, 87 (1972).

3) T. Negi, T. Kaneda, Y. Sakata, and S. Misumi, *Chem. Lett.*, **1972**, 703.

4) J. Ojima, T. Katakami, G. Nakaminami, and M. Nakagawa, *Tetrahedron Lett.*, **1968**, 1115; K. Fukui, T. Okamoto, and M. Nakagawa, *ibid.*, **1971**, 3121; T. Katakami, S. Tomita, K. Fukui, and M. Nakagawa, *Chem. Lett.*, **1972**, 225.

5) C. J. Stehman, N. C. Cook, and F. C. Whitmore, *J. Amer. Chem. Soc.*, **71**, 1509 (1949); N. C. Cook and W. C. Percival, *ibid.*, **71**, 4141 (1949).

6) L. Skattebøl, E. R. H. Jones, and M. C. Whiting, "Organic Syntheses," Coll. Vol. 4, p. 792 (1963).

7) G. Eglinton and A. R. Galbraith, *J. Chem. Soc.*, **1959**, 889.

8) a) F. Bohlmann and K. Kieslich, *Chem. Ber.*, **87**, 1363 (1954); b) L. Skattebøl, *Tetrahedron Lett.*, **1965**, 2175; *Tetrahedron*, **21**, 1357 (1965): c) H. D. Hartzler, *J. Amer. Chem. Soc.*, **88**, 3155 (1966); *ibid.*, **93** 4527 (1971).

9) R. Kuhn and K. Wallenfels, *Ber.*, **71**, 783 (1938).

10) R. Kuhn and J. Jahn, *Chem. Ber.*, **86**, 759 (1953).

11) R. Kuhn and H. Krauch, *ibid.*, **88**, 309 (1955).

12) Y. R. Bhatia, P. D. Landor, and S. R. Landor, *J. Chem. Soc.*, **1959**, 24; S. R. Landor and R. Taylor-Smith, *Proc. Chem. Soc.*, **1959**, 154.

13) H. Fischer, "The Chemistry of Alkenes," ed. by S. Patai, Interscience Publishers, New York, N. Y. (1964), p. 1042, 1110.

14) D. J. Cram, N. L. Allinger, and H. Steinberg, *J. Amer. Chem. Soc.*, **76**, 6132 (1954).

15) A. D. Petrov, E. B. Sokolova, and C. L. Kao, *Zh. Obshch. Khim.*, **30**, 1107 (1960); *Chem. Abstr.*, **55**, 374 (1961).

16) W. J. Hickinbottom, A. A. Hyatt, and M. B. Sparke, *J. Chem. Soc.*, **1954**, 2529.

17) H. Gilman and J. F. Nelson, *Rec. Trav. Chim.*, **55**, 518 (1936).