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The Prins Reaction of Cyclooctene and Cyclododecene

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The reaction products of the sulfuric acid-catalyzed condensation of cyclooctene or cyclododecene with formaldehyde in acetic acid at 40 °C were investigated. The reaction of cyclooctene gave a mixture of 4,5-hexamethylene-1,3-dioxane, 2-cyclooctenylmethyl acetate, and 1-acetoxy-2-acetoxymethylcyclooctane, while the reaction of cyclododecene gave a mixture of cyclic ethers; one was identified as 3-oxabicyclo[10,3,0]-6-pentadecene, and the others were estimated to be 15-acetoxy-3-oxabicyclo[9,3,1]pentadecane and 12,17-dioxatricyclo[13,3,0,$0^{10,14}$]-2-octadecene.

The condensation of cyclopentene or cyclohexene with formaldehyde in the presence of acid-catalysts, Prins reaction, has been the subject of several investigations,$^{1-5)}$ and the mechanism of the acid-catalyzed reaction of cyclohexene in acetic acid has been studied quite extensively.$^{2-5)}$ However, the acid-catalyzed condensation of medium-sized cyclic olefins with formaldehyde is almost unknown.

In this report, the sulfuric acid-catalyzed condensation of cyclooctene or cyclododecene with formaldehyde in acetic acid was investigated.

Results and Discussion

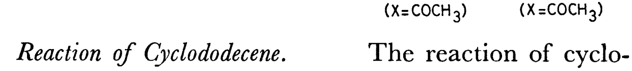
Reaction of Cyclooctene. Cyclooctene was treated with a 1.4-fold molar amount of paraformaldehyde in acetic acid in the presence of sulfuric acid. The reaction gave roughly two fractions. The glpc of the lower-boiling fraction indicated that it consisted of two components, I and IIa, and its IR spectrum demonstrated the presence of an ester group and an ether group in it. By the hydrolysis of the fraction with Claisen alkali, IIa was converted into 2-cyclooctenylmethanol (IIb), while I stayed unchanged. Compounds I and IIb were isolated by column chromatography on alumina. In the IR spectrum of I, the absorption of the ether group was observed at 1150—1030 cm^{-1} but no absorption of the ester group. On the NMR spectrum, there was a quartet at τ 5.1—5.6; this was attributed to the methylene protons adjacent to two oxygen atoms. On the basis of the elementary analysis and the spectroscopic properties of I, compound I was confirmed to be 4,5-hexamethylene-1,3-dioxane.

Compound IIa was isolated from the lower-boiling fraction by preparative glpc or by column chromatography on silica gel. The IR spectrum of IIa indicated the presence of an acetoxy group and a double bond in IIa. The position of the double bond was determined by a comparison of the NMR spectra of IIa and its hydrogenation product (III). The signals in the NMR spectrum of IIa at τ 7.5—7.9, which corresponded to 3H and to the allylic protons, disappeared in that of III. Thus, the double bond was assumed to be adjacent to the tertiary carbon atom. On the basis of the spectroscopic properties of IIa and IIb, they were identified as 2-cyclooctenylmethyl acetate and 2-cyclooctenylmethanol respectively.

The higher-boiling fraction was identified as 1-acetoxy-2-acetoxymethylcyclooctane (IVa). Compound IVa had the typical IR absorption of the acetoxy group at 1710 and 1220 cm^{-1}. In its NMR spectrum, two sharp signals of acetoxy protons at τ 8.80 and 8.10, and two multiplets of methyne and methylene protons at τ 5.3—5.0 and 6.4—6.1, were observed.

To determine the structure IVa was hydrolyzed with Claisen alkali to IVb (X=H); IVb was compared with authentic 2-hydroxymethylcyclooctan-1-ol prepared from cyclooctanone. The spectroscopic data and the glpc-retention times of the two compounds were identical. Thus, IVa was confirmed to be 1-acetoxy-2-acetoxymethylcyclooctane.

On the basis of the glpc of the crude reaction product, the product was found to contain 5 wt% of I, 20 wt% of IIa, 65 wt% of IVa, and 10 wt% of unknown substances.



I

IIa
($X=COCH_3$)

IVa
($X=COCH_3$)

Reaction of Cyclododecene. The reaction of cyclododecene with a 1.4-fold molar amount of paraformaldehyde in acetic acid in the presence of sulfuric acid was attempted. The fractional distillation of the reaction product gave, roughly, two fractions. The glpc indicated that the lower-boiling fraction consisted of V and that the higher-boiling fraction was a mixture of VIa and VII.

Compound V showed the typical IR absorption of ether group at 1050 and 1020 cm^{-1}, and the NMR signals at τ 6.0—6.4 and 6.5—7.0 were attributed to the oxygen-linked methylene protons. To determine the relative position of the double bond in V, compound V was hydrogenated to VIII and the NMR spectra of V and VIII were compared with each other. The proton counts of allylic protons at τ 7.5—8.2, which disappeared after the hydrogenation of V, were less than 4H; this suggested that the double bond was not flanked by two methylene group, but was, rather, situated adjacent to the tertiary carbon atom. To clarify

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1) R. P. Stapp and J. C. Randall, *J. Org. Chem.*, **35**, 2948 (1970).

2) J. Matti, *Bull. Soc. Chim. Fr.*, 4 **51**, 974 (1932); S. Olsen and H. Padberg, *Z. Naturforsch.*, **1**, 448 (1946); S. Olsen, *ibid.*, **1**, 671 (1946); S. Olsen, *Angew. Chem.*, **59**, 32 (1947).

3) A. T. Blomquist and J. Wolinsky, *J. Amer. Chem., Soc.*, **79**, 6025 (1957).

4) L. J. Dolby, *J. Org. Chem.*, **27**, 2971 (1962).

5) E. Smissman and R. A. Mode, *J. Amer. Chem. Soc.*, **79**, 3447 (1957).

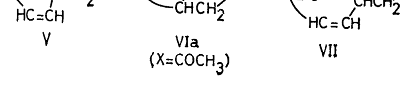
whether compound V had a 3,4-disubstituted tetrahydrofuran ring or a 3,4,5-trisubstituted tetrahydropyran ring, the ether ring in VIII was cleaved with hydrogen iodide and the resultant diiodomethyl compound was treated with lithium aluminum hydride to give IX. Compound IX demonstrated spectroscopic properties and glpc-retention times identical with those of authentic 1,2-dimethylcyclododecane prepared from 2-methyl-2-carbethoxycyclododecanone.

On the basis of the spectroscopic properties of V, VIII, and IX, and from these observations, they were identified as 3-oxabicyclo[10,3,0]-6-pentadecene (V), 3-oxabicyclo[10,3,0]pentadecane (VIII), and 1,2-dimethylcyclododecane (IX) respectively.

Compound VIa was isolated by a preparative glpc of the higher-boiling fraction. On the basis of the elementary analysis and the mass spectrum VIa was determined to be $C_{16}H_{28}O_3$. The IR and NMR spectra of VIa indicated the presence of an acetoxy group and an ether ring in it. To determine the size of the ether ring in VIa, VIa was converted to the tosylate, which was then treated with lithium aluminum hydride to give X.

If compound VIa had the 3,4-disubstituted tetrahydrofuran ring, X might be identical with VIII. Although the elementary analysis and mass spectra of VIII and X were identical, their IR and NMR spectra or their glpc-retention times were different. This obviates the presence of a 3,4-disubstituted tetrahydrofuran moiety in VIa.

Though there was no experimental evidence for the presence of a 3,4,5-trisubstituted tetrahydropyran ring in VI, it seemed reasonable to assume that VIa was 15-acetoxy-3-oxabicyclo[9,3,1]pentadecane, because no other ether ring could be formed from the mechanistic considerations and because such a 3,4,5-trisubstituted tetrahydropyran derivative had previously been obtained by the Prins reaction of cyclohexene.[3,4] Similarly, on the basis of the elementary analysis and mass spectrum compound VII was estimated to be $C_{16}H_{26}O_2$. The IR and NMR spectra justified the presence of two ether rings and a double bond in VII. The allylic protons in VII, which were estimated by a comparison of the NMR spectrum of VII with that of the product of the hydrogenation of VII, amounted to 3H; this suggested that the double bond was adjacent to the tertiary carbon atom. On the basis of the experimental results described here, the relative positions of the two ether rings and, thus, the structure of VII could not be elucidated. However, because no product derived from the carbonium ion formed by a hydride shift was found in any other product described in this paper, the migration of the carbonium-ion center seemed unlikely; it seemed, rather, reasonable to assume that the two ether rings were adjacent to each other. On the basis of these considerations, it was decided that compound VII was 12,17-dioxatricyclo[13,3,0,$0^{10,14}$]-2-octadecene.



The glpc of the reaction product indicated that the product contained 40 wt% of V, 20 wt% of VIa, 30 wt% of VII, and 10 wt% of unknown substances.

Experimental

All of the mps and bps are uncorrected. The IR spectra were recorded on a Hitachi EPI-G2 type grating infrared spectrometer, and the NMR spectra were taken on a JNM-3H-60 (60 MHz) NMR spectrometer (Japan Electron Optics Lab.) with tetramethylsilane as the internal standard. The chemical shifts (τ) were followed by the splitting patterns (s, singlet; d, doublet; t, triplet; m, multiplet) and the relative strengths. For the analyses by glpc, was used a GC-4B type Shimadzu Seisakusho gas chromatograph with a column 2.5 mm i.d. and 2 m in length; this column contained polyethylene glycol 20 M (20%) on Celite 545.

The paraformaldehyde, acetic acid, and sulfuric acid were used as received. The cyclooctene and the cyclododecene (a mixture of *ca.* 45% of the *cis*- and *ca.* 55% of the *trans*-isomer) received from Wako Chemicals were fractionally distilled. The cyclooctanone and cyclododecanone were prepared by the hydroboration of the corresponding olefins, followed by oxidation with hydrogen peroxide.

Prins Reaction of Cyclooctene. To stirred suspension of 24.0 g (0.64 mol) of paraformaldehyde in 92 ml of acetic acid and 15.5 ml of concentrated sulfuric acid, was added gradually a mixture of 50 g (0.46 mol) of cyclooctene and 41 ml of acetic acid at 40 °C; the solution was then stirred for additional 2 hr. After the addition of 100 ml of water and 50 ml of ether, the mixture was transferred to a separatory funnel. The water layer was removed and the organic layer was washed several times with a saturated aqueous sodium bicarbonate solution and twice with water, and then dried over anhydrous magnesium sulfate. The ether was removed *in vacuo*, and the residual oil was fractionally distilled; Fraction 1 (0.8 g, bp 31 °C/15 mmHg), Fraction 2 (14.9 g, bp 76—77 °C/0.4 mmHg), Fraction 3 (21.5 g, bp 110—120 °C/0.4 mmHg), and a residue.

Fraction 1 was identified as the starting olefin.

Hydrolysis of Fraction 2. A solution of 10 g of Fraction 2 in Claisen alkali (10 g of potassium hydroxide in 31.2 ml of methanol and 8 ml of water) was refluxed for an hour, after which the reaction mixture was worked up; 7.4 g of a hydrolyzed product (bp 90—93 °C/0.4 mmHg) was thus obtained. This substance was separated into benzene eluate and methanol eluate by column chromatography on alumina.

The removal of the solvent from the benzene eluate yielded 4,5-hexamethylene-1,3-dioxane; bp 70—71 °C/0.5 mm Hg; IR (neat) 1150, 1080, 1040, 1030 cm^{-1} (CH_2-O-CH_2-O-CH); NMR (CCl_4) τ 5.1—5.6 (q, 2H, O-C$\underline{H}_2$-O), 6.2—6.6 (m, 3H, CH-C$\underline{H}_2$-O+C$\underline{H}$-O), 7.5—9.0 (m, 13H, other $\underline{H}$); MS (*m/e*) 170 (3), 140 (24), 122 (100); Found: C, 70.36; H, 10.94%; Calcd for $C_{10}H_{18}O_2$: C, 70.54; H, 10.66%; mol. wt., 170.24.

The removal of the solvent from the methanol eluate left 2-cyclooctenylmethanol (IIb); NMR (CCl_4) τ 4.3—4.6 (m, 2H, C$\underline{H}$=C$\underline{H}$), 6.5—6.9 (m, 3H, -C$\underline{H}_2$-O$\underline{H}$), 7.8—8.6 (m, 11H, other $\underline{H}$); Found: C, 76.56; H, 11.84%. Calcd for

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[6] A. P. Krapcho, J. Diamanti, C. Cayen, and R. Bingham, "Organic Synthesis," Vol. 47 (1967), p. 22.

$C_9H_{16}O$: C, 77.09; H, 11.50%.

2-Cyclooctenylmethyl acetate (IIa) was isolated by preparative glpc or by column chromatography; IR (neat) 1720, 1220 cm^{-1} (CH_3COO), 1650 cm^{-1} (C=C); NMR (CCl_4) τ 4.2—4.7 (m, 2H, $C\underline{H}$=$C\underline{H}$), 6.1—6.4 (m, 2H, -$C\underline{H}_2$-O), 7.5—7.9 (m, 3H, $C\underline{H}_2$-CH=CH-$C\underline{H}$), 7.9—8.1 (s, 3H, $C\underline{H}_3COO$), 8.1—8.9 (m, 8H, other $\underline{H}$); MS (*m/e*) 182 (3), 140 (3), 122 (100), 107 (77); mol. wt. for $C_{11}H_{18}O_2$, 182.25.

Fraction 3 was confirmed to be 1-acetoxy-2-acetoxymethylcyclooctane (IVa); IR (neat) 1710, 1220 cm^{-1} (CH_3COO); NMR (CCl_4) τ 5.0—5.3 (broad m, 1H, $C\underline{H}$-$OCOCH_3$), 6.1—6.4 (m, 3H, $C\underline{H}_2$-$OCOCH_3$+$C\underline{H}$-CH_2-), 7.8—9.0 (m, 19H, $C\underline{H}_3CO$ (s×2)+other $\underline{H}$); MS (*m/e*) 212 (8), 199 (2), 182 (10), 164 (13), 154 (14), 140 (100); mol. wt. for $C_{13}H_{22}O_4$, 242.31.

Hydrogenation of IIa to III. In a 200 ml Erlenmeyer flask, were placed a Raney-Ni catalyst (prepared from 5.0 g of Ni-Al alloy (20%)), 50 ml of ethanol, and 5.0 g of IIa. The mixture was stirred with a magnetic stirrer, after which hydrogen was bubbled through it for 1 hr. The catalyst was then removed from the reaction product by filtration.

The removal of the ethanol from the filtrate yielded cyclooctylmethyl acetate (III); IR (neat) 1730, 1230 cm^{-1} (CH_3COO); NMR (CCl_4) τ 6.2—6.3 (d, 2H, $C\underline{H}_2$-O), 8.0 (s, 3H, $C\underline{H}_3CO$), 8.2—9.0 (m, 15H, other $\underline{H}$); MS (*m/e*) 184 (3), 124 (18), 96 (100), 82 (37); Found: C, 64.59; H, 9.32%. Calcd for $C_{11}H_{20}O_2$: C, 64.44; H, 9.16%; mol. wt., 184.27.

Hydrolysis of IVa. When compound IVa was hydrolyzed with Claisen alkali, 2-cyclooctenylmethanol was obtained; IR (neat) 3300, 1020 cm^{-1} (CH); NMR (CCl_4) τ 5.5—5.8 (m, 2H, O$\underline{H}$), 5.8—6.3 (m, 1H, $C\underline{H}$-OH), 6.3—6.9 (m, 2H, -$C\underline{H}_2$-OH), 7.8—9.0 (m, 13H, other $\underline{H}$); MS (*m/e*) 156 (8), 140 (64), 122 (100); glpc-retention time (220 °C, 67 ml-H_2/min), 11.4 min; Found: C, 68.02; H, 11.60%. Calcd for $C_9H_{18}O_2$: C, 68.31; H, 11.47%; mol. wt., 158.32.

Synthesis of IVb. 2-Carbethoxycyclooctanone[6] was treated with lithium aluminum hydride in tetrahydrofuran. The subsequent work-up of the reaction product yielded authentic IVb. The glpc-retention time and the spectroscopic properties of the authentic sample were identical with those of IVb.

Prins Reaction of Cyclododecene. To a stirred suspension of 9.2 g of paraformaldehyde (0.25 mol) in 35.0 ml of acetic acid and 6.1 ml of concentrated sulfuric acid, was added gradually a mixture of 30.0 g of cyclododecene (0.18 mol), 10.0 ml of acetic acid, and 8.0 ml of ether at 40 °C, after which the mixture was stirred for additional 2 hr. The subsequent work-up of the reaction product yielded 14.2 g of Fraction 1 (bp 53—56 °C/0.5 mmHg), 6.7 g of Fraction 2 (bp 103—105 °C/0.5 mmHg), 11.3 g of Fraction 3 (bp 140—150 °C/0.5 mmHg), and a residue.

Fraction 1 was identified as cyclododecene by glpc and its IR spectrum.

Fraction 2 was identified as 3-oxabicyclo[10,3,0]-6-pentadecene (V); IR (neat) 1050, 1020 cm^{-1} (CH_2-O-CH_2); NMR (CCl_4) τ 4.5—4.9 (m, 2H, $C\underline{H}$=$C\underline{H}$), 6.0—6.4 (m, 2H, $OC\underline{H}_2$), 6.5—7.0 (m, 2H, $OC\underline{H}_2$), 7.5—8.2 (m, 4H, allyl $\underline{H}$+tertiary $\underline{H}$), 8.2—9.5 (m, 14H, other $\underline{H}$); MS (*m/e*) 208 (100), 177 (8), 165 (6); mol. wt. for $C_{14}H_{24}O$, 208.33.

Fraction 3 was treated with Claisen alkali, and the resultant oil was separated into the ether eluate and the methanol eluate by column chromatography on alumina. The removal of the solvent from the ether eluate left 12,17-dioxatricyclo-[13,3,0,0^{10,14}]-2-octadecene (VII); mp 92—95 °C (methanol); IR (KBr) 1060, 1050 cm^{-1} (CH_2-O-CH_2), 980 cm^{-1} (C=C); NMR (CCl_4) τ 4.4—4.8 (m, 2H, $C\underline{H}$=$C\underline{H}$), 6.0—7.0 (m, 8H, $C\underline{H}_2$-O-$C\underline{H}_2$), 7.2—7.9 (m, 3H, allyl $\underline{H}$), 7.9—9.4 (m, 13H, other $\underline{H}$); MS (*m/e*) 250 (100), 219 (22), 209 (27); Found: C, 76.57; H, 10.69%. Calcd for $C_{16}H_{26}O_2$: C, 76.75; H, 10.47%; mol. wt., 250.23. From the ethanol eluate, a mixture of 3-oxabicyclo[9,3,1]pentadecan-15-ol (VIb, X=H) (*ca.* 67%) and VII (*ca.* 33%) was obtained; NMR (CCl_4) τ 4.4—4.8 (m, $C\underline{H}$=$C\underline{H}$), 5.8 (m, $C\underline{H}_2$-O-$C\underline{H}_2$+$C\underline{H}$-$OCOCH_3$), 7.3—9.3 (m, O$\underline{H}$, which disappeared upon deuterium exchange+other $\underline{H}$).

15-Acetoxy-3-oxabicyclo[9,3,1]pentadecane (VIa) was isolated by the preparative glpc of Fraction 3; IR (neat) 1720, 1230 cm^{-1} (CH_3COO), 1060, 1020 cm^{-1} (CH_2-O-CH_2); NMR (CCl_4) τ 5.0—5.3 (m, 1H, $C\underline{H}$-$OCOCH_3$), 6.4—6.6 (m, 4H, $C\underline{H}_2$-O-$C\underline{H}_2$), 8.0—9.0 (m, 23H, $C\underline{H}_3COO$ (s)+other $\underline{H}$); MS (*m/e*) 268 (3), 250 (3), 226 (4), 208 (100); Found: C, 71.61; H, 10.53%. Calcd for $C_{16}H_{28}O_3$: C, 71.60; H, 10.52%; mol. wt., 268.38.

Hydrogenation of V to VIII. The Raney-Ni catalyst prepared from 3.0 g of Ni-Al alloy was used for the hydrogenation of V in 50 ml of ethanol. The subsequent work-up of the product yielded 5.0 g of 3-oxabicyclo[10,3,0]pentadecane (VIII); bp 110—115 °C/2 mmHg; IR (neat) 1110, 1060 cm^{-1} (CH_2-O-CH_2); NMR (CCl_4) τ 6.1—6.9 (q×2, 4H, $C\underline{H}_2$-O-$C\underline{H}_2$), 7.7—8.2 (m, 2H, $C\underline{H}$), 8.2—9.0 (m, 20H, other $\underline{H}$); MS (*m/e*) 210 (9), 209 (6), 208 (14), 179 (10), 149 (10), 135 (17), 121 (17), 109 (16), 95 (56), 82 (100); glpc-retention time (230 °C, 47 ml-H_2/min), 44.0 min; Found: C, 79.44; H, 12.65%. Calcd for $C_{14}H_{26}O$: C, 79.93; H, 12.46%.

Conversion of VIII to 1,2-Dimethylcyclododecane (IX). A mixture of 3.0 g of VIII and 25 ml of an aqueous solution of hydrogen iodide (47%) was refluxed for 3 hr. After the subsequent addition of water to the reaction mixture, the product was extracted with three 50-ml portions of ether. The ethereal extract was dried over anhydrous magnesium sulfate. To the stirred suspension of 1.7 g of lithium aluminum hydride in 70 ml of tetrahydrofuran, was added the ethereal extract, and then the mixture was refluxed for 3 hr. The lithium aluminum hydride remaining in the reaction mixture, was decomposed by addition of water, and the resultant solution was filtered. The filtrate was washed with sulfuric acid and water, and dried over anhydrous magnesium sulfate. The ether was removed from the filtrate, and the residual oil was separated into an *n*-hexane eluate and an ether eluate by column chromatography on alumina. From the *n*-hexane eluate, 0.8 g of 1,2-dimethylcyclododecane (IX) was obtained, while from the ether eluate, 1.0 g of VIII was recovered. IX; IR (neat) 2900, 2850, 1440, 720 cm^{-1} (alkane); NMR (CCl_4) τ 8.2—9.0 (m, 22H, $\underline{H}$ on ring), 9.0—9.4 (m, 6H, $C\underline{H}_3$); MS (*m/e*) 196 (100), 182 (10), 168 (32), 139 (36); glpc-retention time (180 °C, 44 ml-H_2/min), 37.0 min; Found: C, 85.34; H, 14.37%. Calcd for $C_{14}H_{28}$: C, 85.63; H, 14.37%; mol. wt., 196.36.

Conversion of VIb to 3-oxabicyclo[9,3,1]pentadecane (X). To a stirred solution of 14.3 g of *p*-toluenesulfonyl chloride in 20 ml of pyridine, which had been cooled in an ice-water bath, was added a solution of 4.0 g of a mixture of VIb (*ca.* 67%) and VII (*ca.* 33%) in 20 ml of pyridine. The reaction mixture was warmed to room temperature and stirred for an additional 15 hr. After the addition of 150 ml of water to the reaction mixture, the product was extracted with ether. The ethereal extract was washed with a 6 M hydrogen chloride solution, a saturated aqueous sodium carbonate solution, and water, and dried over anhydrous sodium sulfate. The resultant ether solution was added slowly to a suspension of 1.3 g of lithium aluminum hydride in 70 ml of tetrahydrofuran. When the resultant mixture was worked up and the less volatile VII was removed by distillation to yield X; IR (neat) 1080 cm^{-1} (CH_2-O-CH_2); NMR (CCl_4) τ 6.0—7.0 (m, 4H, $C\underline{H}_2$-O-$C\underline{H}_2$), 7.6—9.3 (m, 22H, other $\underline{H}$); MS (*m/e*) 210 (9), 209 (9), 208 (17), 179 (9), 135 (17), 121 (22), 109 (39), 95 (69), 82 (100); glpc-retention time (230 °C, 47 ml-H_2/min), 46.5 min; Found: C, 80.15; H, 12.58%. Calcd for $C_{14}H_{26}O$: C, 79.93; H, 12.46%; mol. wt., 210.35.

Hydrogenation of VII. A solution of 5.0 g of VII in 30 ml of ethanol was treated with a Raney-Ni catalyst (from 5.0 g of Ni-Al alloy) in a hydrogen stream at atmospheric pressure; the subsequent work-up of the reaction product yielded 5.0 g of 12,17-dioxatricyclo[13,3,0,$0^{10,14}$]pentadecane; IR (neat) 1060, 1050 cm^{-1} (CH_2-O-CH_2); NMR (CCl_4) τ 6.0—7.2 (m, 8H, $C\underline{H}_2$-CH_2), 7.7—7.9 (m, 1H, $\underline{H}$ on ring), 7.9—9.2 (m, 19H, other $\underline{H}$).

Synthesis of IX. To a solution of 9.3 g of 2-methyl-2-carbethoxycyclododecanone[6] in 20 ml of ethanol, was added 70 ml of 6 M hydrogen chloride solution, after which the mixture was refluxed for 90 hr. The reaction product was then worked up, and 3.1 g of 2-methylcyclododecanone (XII) (bp 85—90 °C/3 mmHg) was thus obtained.

In a 300-ml, four-necked flask fitted with a mechanical stirrer, dropping funnel, a reflux condenser, and a gas-inlet tube, and flushed with nitrogen, were placed 9.8 ml of *n*-butyllithium (15%) in *n*-hexane (0.10 mol) and 40 ml of ether. The solution was stirred vigorously, and then was added 5.5 g of methyltriphenylphosphonium bromide (0.02 mol) and then 3.0 g of XII (0.015 mol). The mixture was subsequently refluxed for 12 hr. When the reaction mixture was worked up, 0.5 g of 2-methyl-1-methylenecyclododecane (XIII) (bp 75—78 °C/2 mmHg) was obtained. A solution of 1.0 g of XIII in 20 ml of ethanol was treated with a Raney-Ni catalyst (from 2.0 g of Ni-Al alloy) in a hydrogen stream at atmospheric pressure; the subsequent work-up of the product yielded 1.0 g of 1,2-dimethylcyclododecane (bp 48—49 °C/25 mmHg). The spectroscopic properties and the glpc-retention time were identical with those described for IX.