reactions between Fe(III) salts and organometallic compounds in the presence of unsaturated hydrocarbons contains zerovalent iron, which acts as the catalytically active component, to which the unsaturated hydrocarbons are coordinated. However, it cannot be excluded that the metal may undergo a formal oxidation in a transition state, especially in the case of the formation of those linear oligomers, in which hydrogen shift is involved.

In the case of $Fe(COT)_2$ one can reasonably assume that both cyclooctatetraene rings are displaced from their coordination sites by the unsaturated hydrocarbons to be oligomerized with formation of analogous π-type bonds with the metal. We actually observed in the nmr spectrum the progressive formation of free cyclooctatetraene when $Fe(COT)_2$ was dissolved in liquefied butadiene.

As previously indicated, $Fe(COT)_2$, simultaneously and in the same reaction conditions,[2] catalyzes oligomerizations involving hydrogen shift (linear trimerization of butadiene and linear codimerization butadiene–ethylene) as well as cycloadditions (dimerization of butadiene, trimerization of 1,2-disubstituted acetylenes, and codimerizations butadiene–1,2-disubstituted acetylenes), in which hydrogen shift is unnecessary. Hence, it is likely that the reaction of unsaturated hydrocarbons with $Fe(COT)_2$ yields several iron complexes, which are in equilibrium among themselves and which essentially differ in the number of the coordinated double bonds and in their geometric disposition around the metal atom.

Experimental Section

Cyclooligomerization of 2-Butyne Using $Fe(COT)_2$.—In a typical example, a 20-ml glass vial, in which the air had been removed by dry argon, was cooled to −10°, charged with 57 mg of recrystallized $Fe(COT)_2$ and 3 ml of 2-butyne, sealed, and maintained first for 15 hr at −10 to 0° and then 24 hr at room temperature. During this time a large amount of white crystals precipitates from the brown solution. The reaction mixture was dissolved in 20 ml of diethyl ether; the solution was washed with diluted hydrochloric acid and with water and dried ($MgSO_4$). Solvent and excess 2-butyne were distilled and the dry residue was recrystallized from ethanol. A 0.4-g (18%) sample of pure hexamethylbenzene was obtained.

Cycloaddition of 1,3-butadiene with 2-butyne using $Fe(COT)_2$ was by the same procedure as in the foregoing case. $Fe(COT)_2$ (40 mg), 2 ml of liquefied butadiene, and 1 ml of 2-butyne were charged, and the sealed vial was maintained 24 hr at room temperature. The vial was opened at −20° and the unreacted butadiene was vented off. The reaction mixture was dissolved in 20 ml of diethyl ether; the solution was washed with 0.1 N hydrochloric acid and with water and dried ($MgSO_4$). The ether was distilled, leaving 0.45 g (55%) of a high-boiling liquid (bp $\approx$ 140°), consisting essentially of 1,2-dimethyl-1,4-hexadiene. The identification was made by the vpc retention time and by the ir spectrum in comparison with the pure product.[13]

Cycloaddition of 1,3-Butadiene with Tolane Using the $FeCl_3$–(i-C_3H_7)MgCl–Etherate System. Synthesis of 1,2-diphenyl-1,4-cyclohexadiene was by the same procedure as in the foregoing cases, but charging was effected at −40° in the following order: 10 ml of diethyl ether (freshly distilled on $LiAlH_4$), 0.1 g of sublimed $FeCl_3$, 3 ml of liquefied butadiene, 1.7 g of tolane, and 1.5 ml of a 3.4 M solution of i-C_3H_7MgCl (Grignard) in diethyl ether. The sealed vial was maintained 48 hr at room temperature, and the brown reaction mixture was purified as described above. An aliquot (0.2 g) of the high-boiling residue ($\approx$2 g) was chromatographed in a silica gel column (30 × 1.5 cm) by eluting with n-heptane. The white crystals that collected after a first oily fraction were recrystallized from ethanol to yield 150 mg (68%) of pure product: mp 80–81°; uv max (Unicam SP 800, 230–450 nm range), 256 nm (log ϵ 3.83); ir (Perkin-Elmer 125), 695, 760, 1030, 1118 (aromatic C–H), 664, 1423, and 3030 cm^{-1} (*cis*-double bond); nmr (Varian HA, 100 Mc, room temperature, $CDCl_3$ solvent, TMS standard), δ 7.05 (s, 5, C_6H_5), 5.86 (t, 1, J = 2.7 Hz, —CH═), and 3.13 ppm (d, 2, J = 1.4 Hz, $-CH_2-$); mass spectrum (72 eV), m 232 (prevailing), 230 (aromatization product). Partial aromatization was observed also by vpc (C. Erba LAC 796, cyclohexamethanol succinate): o-diphenylbenzene as tail peak; main product retention time relative to diphenyl, 5.54 (200°).

Anal. Calcd for $C_{18}H_{16}$: C, 93.11; H, 6.89. Found: C, 93.3; H, 6.8; mol wt (Mechrolab), 234 ± 2.

Registry No.—2-Butyne, 503-17-3; tolane, 501-65-5; butadiene (1,3), 106-99-0; $FeCl_3$, 7705-08-0; FeA_3, 14024-18-1; i-PrMgCl, 1068-55-9; n-BuLi, 109-72-8; $Al(Et)_3$, 97-93-8; DPC, 17351-29-0.

Reaction of Methylmagnesium Iodide and Diethy 1,2-Cyclohexanedicarboxylates

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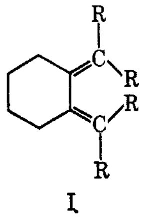
Received December 27, 1967

1,2-Diisopropylidenecyclohexane (I, R = CH_3)[1] has recently been obtained by photolysis of 1,1,3,3-tetramethyl-4,5,6,7-tetrahydro-2-indanone.[2] The preparation of this diene and its tetraphenyl analog (I, R = C_6H_5) were claimed earlier by Nazarov and Kuznetsov;[3] however, the physical properties reported for 1,2-diisopropylidenecyclohexane[3] are in almost perfect agreement with those of 1,2-diisopropylbenzene,[4] and we have not been able to reproduce their preparation of the tetraphenyl analog. In addition, our investigation of the products from the reaction of methylmagnesium iodide or methyllithium with the diethyl 1,2-cyclohexanedicarboxylates, which we report in this communication, has provided structural assignments which differ significantly from those reported by the Russian workers.[3]



I

Our work began with an examination of the reactions of diethyl 4-cyclohexene-*cis*-1,2-dicarboxylate. With a large excess (7.5 equiv) of methylmagnesium iodide, a good yield of *cis*-$\alpha,\alpha,\alpha',\alpha'$-tetramethyl-4-cyclohexene-1,2-dimethanol (II) was obtained, whereas the *cis*-

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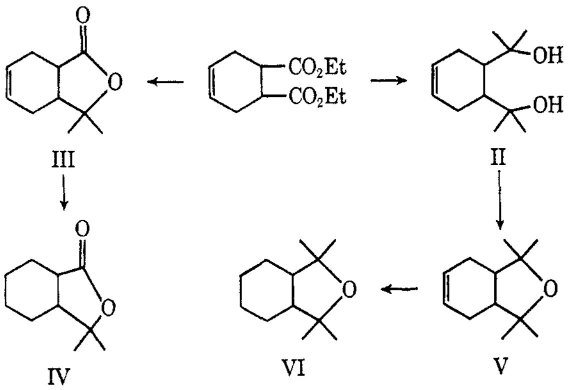
[1] Inspection of Stuart–Briegleb molecular models of exocyclic dienes of type I where R is alkyl or aryl suggest that rotation about the C_1–C_2 bond should be restricted by interaction of adjacent R groups and should prevent chair–chair interconversion. If this is true, these dienes should be disymmetric and capable of resolution into their optical antipodes.

[2] J. E. Starr and R. H. Eastman, *J. Org. Chem.*, **31**, 1393 (1966).

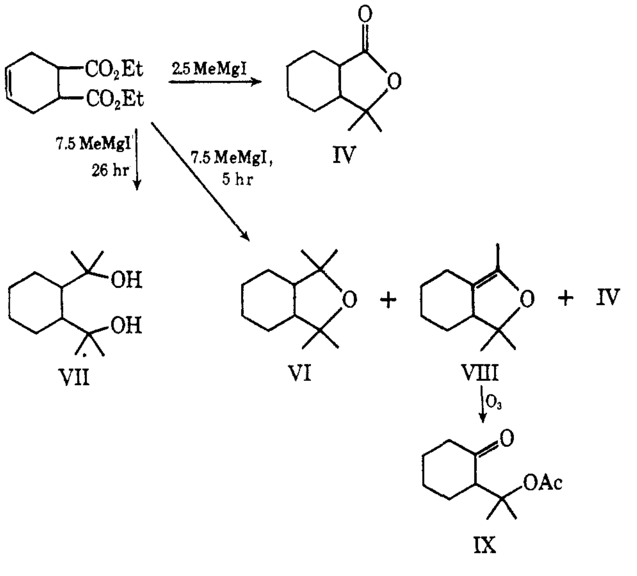
[3] I. N. Nazarov and N. V. Kuznetsov, *Bull. Acad. Sci. USSR*, 236 (1960).

[4] The Russian workers alleged to have obtained 1,2-cyclohexanedione and acetone by ozonolysis of this diene. Acetone was characterized as a 2,4-DNP derivative which was reported to melt at 195°. Authentic acetone 2,4-DNP melts at 125°.

lactone III[5] was produced with 2.5 equiv of Grignard reagent. Catalytic hydrogenation of lactone III gave the saturated lactone IV. The diol II readily lost water on distillation and afforded *cis*-unsaturated phthalan V which was reduced to the saturated phthalan VI.



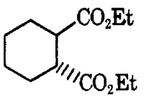
In a similar fashion, the reaction of 2.5 equiv of methylmagnesium iodide with diethyl *cis*-1,2-cyclohexanedicarboxylate gave the *cis*-lactone IV, whereas prolonged reaction with 7.5 equiv afforded the *cis*-diol VII. Interrupting the reaction with excess Grignard reagent after 5 hr gave, after distillation, a mixture of *cis*-lactone IV, *cis*-phthalan VI, and 2,4,4-trimethyl-3-oxabicyclo[4.3.0]-1-nonene (VIII). The *cis*-phthalan VI undoubtedly arises by dehydration of diol VII during the isolation by distillation and vpc. It was independently established that vacuum distillation of diol VII converts it, in large part, into phthalan VI. The probable intermediacy of lactone IV in the formation of the other products was shown by its conversion into a mixture of vinyl ether VIII and diol VII by reaction with methylmagnesium bromide. In this instance the diol was isolated from the distilland following low-temperature, vacuum distillation of vinyl ether VIII.



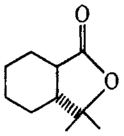
Identical results were noted when an excess of methyllithium was allowed to react with diethyl *cis*-1,2-cyclohexanedicarboxylate.

The structure of vinyl ether VIII was established by spectral analysis (see Experimental Section) and by ozonolysis to 2-(α-acetoxyisopropyl)cyclohexanone (IX) which was isolated as its 2,4-dinitrophenylhydrazone derivative.

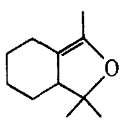
Turning next to diethyl *trans*-1,2-cyclohexanedicarboxylate (X), it was observed that 1.5–2.5 equiv of the Grignard reagent gave a complicated mixture of unreacted *trans*-diester X, vinyl ether VIII, *cis*-lactone IV, and *trans*-lactone XI. The small amount of *cis*-lactone most likely results from the *cis*-diester which is a contaminant of the *trans*-diester X. In one experiment a small amount of ethyl 2-acetyl-1-cyclohexanecarboxylate was also isolated, but this result could not be reproduced.



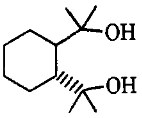
X



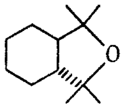
XI



VIII



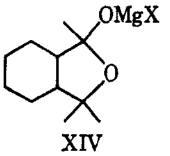
XIII



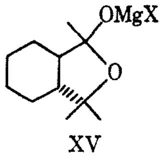
XII

When the reaction of the *trans*-diester X with 7.6 equiv of Grignard reagent was allowed to proceed for 17 hr, there was obtained the vinyl ether VIII contaminated with a small amount of *cis*-phthalan VI. When the same mixture was allowed to stir at reflux for 41 hr and the products were isolated by distillation, the major product was once again the vinyl ether VIII; however, in this instance it was contaminated by the *trans*-phthalan XII as well as the *cis*-phthalan VI, suggesting the formation of some *trans*-diol and its subsequent dehydration. When the Grignard reaction was allowed to proceed at reflux for 96 hr and was carefully worked up and subjected to column chromatography, a sample of the crystalline *trans*-diol XIII was obtained. Even under these vigorous circumstances the major product was vinyl ether VIII.

These observations provide another example of the difference in reactivity between axial and equatorial groups.[6] The equatorial carboethoxy group in the *cis*-diester reacts rapidly with 2 equiv of the Grignard reagent to give lactone IV. A somewhat slower reaction with the axial ester group leads to hemiketal salt XIV which is converted to vinyl ether VIII on hydrolytic work-up, or slowly to diol VII on prolonged standing with excess Grignard reagent. The Grignard reagent does not discriminate between the two equato-



XIV



XV

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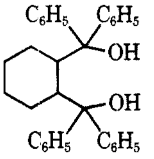
[5] N. P. Sopov [*J. Gen. Chem. USSR*, **26**, 1795 (1956)] originally formulated this product as 4,5-diacetylcyclohexene, but M. Mousseron, R. Jacquier, and J. Sovlier [*C. R. Acad. Sci., Paris*, **247**, 665 (1958)] later demonstrated its correct structure.

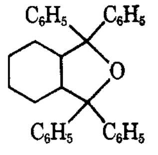
[6] E. L. Eliel, N. J. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, New York, N. Y., 1966, p 72.

rial ester groups in the *trans*-ester X, and reaction with 2 equiv affords unreacted ester X, lactone XI, and hemiketal salt XV. *trans*-Hemiketal XV, unlike *cis*-ketal XIV, appears to be quite stable and shows little tendency to react further with the Grignard reagent.

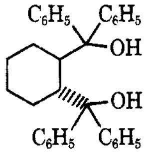
Unlike methylmagnesium bromide or methyllithium, phenyllithium does not distinguish between axial and equatorial carboethoxy groups since both *cis*- and *trans*-diesters were converted into diols XVI and XVII, in 45 and 44% yield, respectively. In a similar fashion, *p*-N,N-dimethylaminophenyllithium afforded a diol corresponding to XVI. The action of a variety of dehydrating agents on these diols afforded the corresponding phthalan derivatives, XVIII + XIX, in accord with the findings of Wittig and Waltnitzki.[7] No trace of the diene reported by Nazarov[3] has yet been found.



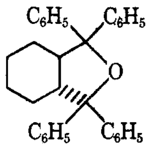
XVI



XVIII



XVII



XIX

Experimental Section[8]

Diethyl *cis*-4-Cyclohexene-1,2-dicarboxylate and Methylmagnesium Iodide. A. Methylmagnesium Iodide (7.5 Equiv).—To an ether solution of methylmagnesium iodide, which was prepared from 71.0 g (0.50 mol) of methyl iodide and 12.2 g (0.50 g-atom) of magnesium, was added dropwise an ether solution of 15 g (0.0663 mol) of diethyl *cis*-4-cyclohexene-1,2-dicarboxylate, and the mixture was stirred at room temperature for 19 hr. Saturated ammonium chloride solution (125 ml) was added dropwise, and the mixture was filtered. The aqueous layer was extracted with ether, and the combined ether layers were dried over anhydrous magnesium sulfate. The ether was removed under diminished pressure to leave a white solid. Recrystallization from pentane ether afforded 8.75 g (66.9%) of white crystals. A sublimed sample of diol II showed mp 122–123° (lit.[5] mp 119.5–120.5°); 3.05 and 6.05 μ; and nmr signals at 1.29 and 1.36 (4 CH_3), 2.20 (—CH_2—), 4.01 (—OH) and 5.67 ppm (CH═CH).

Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.94; H, 11.46.

Distillation of diol II at 10 mm using a bath temperature of 130–140° gave the unsaturated phthalan V: bp 74–75° (10 mm); $n^{22}\mathrm{D}$ 1.4739 (lit.[5] bp 97.5–98.5° (20 mm); $n^{20}\mathrm{D}$ 1.4778).

B. Methylmagnesium Iodide (2.5 Equiv).—This experiment was performed as is described above, except 24.2 g (0.170 mol) of methyl iodide and 4.13 g (0.170 g-atom) of magnesium were employed. Work-up of the reaction mixture afforded a liquid which slowly solidified. Recrystallization from pentane gave 4.40 g (33.6%) of lactone III, mp 61–63°. Sublimation *in vacuo* gave a pure sample of the lactone, mp 67–68° (lit.[5] mp 67–68°), ir, 5.70 and 6.10 μ, which exhibited nmr signals at 1.38 and 1.42 (2 CH_3), 1.90–2.57 and 5.75–5.80 ppm (CH═CH).

Catalytic hydrogenation of lactone III using ethanol as solvent and platinum oxide as catalyst gave a white solid (85.5% yield) which was recrystallized from pentane and displayed mp 74.5–76°. The ir spectrum was identical with that of an authentic sample of lactone IV.

Diethyl *cis*-1,2-Cyclohexanedicarboxylate. A. Reaction with Methylmagnesium Iodide (2.58 Equiv).—To a solution of methylmagnesium iodide, prepared from 24.2 g (0.170 mol) of methyl iodide and 4.13 g (0.170 g-atom) of magnesium, was added dropwise an ether solution of 15 g (0.0658 mol) of diethyl *cis*-1,2-cyclohexanedicarboxylate, bp 99–100° (0.85 mm), $n^{21}\mathrm{D}$ 1.4524. After the dropwise addition of 150 ml of saturated ammonium chloride solution, the mixture was filtered and the water layer was extracted with ether. The combined ether layers were dried, and the ether was removed under diminished pressure to give a white solid. Recrystallization from pentane gave 7.91 g (71.6%) of lactone IV: mp 76–77.5° (lit.[3] mp 75–77°); ir, 5.75 μ; and nmr singlets at 1.34 and 1.36 (2 CH_3), and broad signals between 0.82–2.42 and 2.70–3.24 ppm.

B. Reaction with Excess Methylmagnesium Iodide.—The mixture from methylmagnesium iodide, prepared from 71 g (0.50 mol) of methyl iodide, 12.2 g (0.50 g-atom) of Mg and 15 g (0.0658 mol) of diethyl *cis*-1,2-cyclohexanedicarboxylate, was allowed to stir at room temperature for 29 hr. Work-up in the usual manner gave a white solid. Sublimation *in vacuo* gave 3.51 g (27%) of diol VII: mp 105–106°; ir, 3.10 μ.

Anal. Calcd for $C_{12}H_{24}O_2$: C, 71.95; H, 12.08. Found: C, 72.30; H, 12.24.

C. Excess Methylmagnesium Iodide, Short Reaction Time.—The reaction was repeated exactly as described above, except the reaction was stopped after 5 hr at room temperature. The usual work-up gave a liquid residue which was distilled under diminished pressure to give 5.21 g of liquid, bp 62–68° (4.4 mm). Vpc analysis of this material indicated the presence of *cis*-phthalan VI and vinyl ether VIII in a 3:5 ratio. A vpc purified sample of *cis* VI exhibited $n^{25}\mathrm{D}$ 1.4636.

Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 79.23; H, 12.32. A vpc purified sample of vinyl ether VIII displayed $n^{25}\mathrm{D}$ 1.4742, a peak at 5.00 μ in the infrared, a parent ion of m/e 166 in its mass spectrum, and an nmr consistent with its structural assignment.

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.21; H, 11.10.

Recrystallization of the distilland obtained above gave 1.52 g of lactone IV, mp 75–76.5°.

Diethyl *trans*-1,2-Cyclohexanedicarboxylate. A. Reaction with Methylmagnesium Iodide (1.50 Equiv).—To an ether solution of methylmagnesium iodide, prepared from 14 g (0.0987 mol) of methyl iodide and 2.40 g (0.0987 g-atom) of magnesium, was added dropwise an ether solution of 15 g of diethyl *trans*-1,2-cyclohexanedicarboxylate, bp 103–104° (1.1 mm), $n^{21}\mathrm{D}$ 1.4486. The reaction mixture was stirred at room temperature for 3 hr and then worked up in the usual manner. Distillation gave two fractions: (a) 1.91 g of vinyl ether, bp 41–44° (2 mm), and (b) 8.13 g, bp 91–92° (2 mm). Vpc analysis of the latter fraction demonstrated it was composed of diethyl *trans*-1,2-cyclohexanedicarboxylate, *cis*-lactone IV, and *trans*-lactone XI in a ratio of *ca.* 5:3:1. *trans*-Lactone XI, mp 61–62.5°, showed absorption at 5.65 μ and nmr signals at 1.24 and 1.41 (2 CH_3) and a broad multiplet from 1.50 to 2.40 ppm.

When 7.90 g (0.047 mol) of lactone IV was added to an ether solution of methylmagnesium bromide (from 20.0 g, 0.141 mol, of methyl iodide) and the reaction was worked up in the usual manner, there was obtained by careful distillation 1.92 g of vinyl ether VIII, bp 51–52° (8 mm), and 5.0 g of a brownl liquid residue. Recrystallization of the residue from pentane gave 0.6 g of diol VII, mp 101–103°.

B. Excess Methylmagnesium Iodide, Short Reaction Time.—The reaction of methylmagnesium iodide, prepared from 71 g (0.5 mol) of methyl iodide and 12.2 g (0.5 g-atom) of magnesium, and 15 g (0.066 mol) of the *trans*-diester was allowed to proceed at room temperature for 17 hr. The usual work-up gave 5.04 g of a colorless oil, bp 54° (2 mm). Vpc analysis of this material indicates it was predominantly vinyl ether VIII containing a small amount of *cis*-phthalan VI. Identical results were obtained when methyllithium was used in place of methylmagnesium iodide.

C. Long Reaction Time.[9]—A reaction mixture identical with

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(7) G. Wittig and G. Waltnitzki, *Ber.*, **67**, 667 (1934).

(8) All boiling and melting points are uncorrected. Infrared spectra were measured with a Perkin-Elmer Infracord spectrometer, Model 137 B. Nmr spectra were determined with a Varian Associates A-60 spectrometer. Chemical shifts are given in parts per million downfield with tetramethylsilane as an internal reference. Microanalyses were performed by Dr. C. S. Yeh and associates.

(9) This experiment was performed by Mr. Stuart L. Cohen.

that described above was heated at reflux for 96 hr. A portion of the crude reaction product, 2.0 g, was placed on a column of neutral alumina. Elution with pentane afforded 1.4 g of vinyl ether VIII, and elution with chloroform and chloroform–methanol gave 246 mg of the *trans*-diol XIII which after repeated sublimation under reduced pressure showed mp 57–58°; ir 2.8 and 2.95 μ (-OH); and nmr 1.2 and 1.32 (s, 4-CH_3), 1.0–2.0 (broad m, 10), and 5.2 ppm (broad s, 2 **OH**).

Anal. Calcd for $C_{12}H_{24}O_2$: C, 71.94; H, 12.08. Found: C, 71.91; H, 12.15.

In one experiment the ether was inadvertently allowed to evaporate, and the dry reaction mixture was heated for 20 hr. Work-up gave, in addition to vinyl ether VIII, a small amount of a diol, mp 107–108°, identified with 2-(α-hydroxyethyl)-1-(α-hydroxyisopropyl)cyclohexane on the basis of its nmr spectrum: 1.08 (d, 3, -$CHCH_3$), 1.2 (s, 6, $C(CH_3)_2$), 3.2 (broad s, 2, **OH**), and 3.97 (m, 1, $CHCH_3$).

Anal. Calcd for $C_{11}H_{22}O_2$: C, 70.92; H, 11.91. Found: C, 70.59; H, 12.06.

trans-$\alpha,\alpha,\alpha',\alpha'$-**Tetraphenyl-1,2-cyclohexanedimethanol (XVII).**—The reaction of phenyllithium, prepared from 62.8 g (0.40 mol) of bromobenzene and 5.6 g (0.80 g-atom) of lithium, with 15 g (0.0658 mol) of diethyl *trans*-1,2-cyclohexanedicarboxylate afforded an oil which was recrystallized from ether–petroleum ether (bp 35–37°) to give 12.98 g (44%) of crude diol, mp 170–176°. Recrystallization from benzene–petroleum ether (bp 65–67°) afforded 10.25 g of crystalline diol: mp 183.5–184.5° (lit.[7] mp 185–185.5°); λ_{max} 255, 260, and 270 mμ (log ϵ 3.1, 3.16, and 3.02).

Dehydration with acetic acid–hydrochloric acid, acetic anhydride, iodine in benzene, or phosphorus oxychloride in pyridine gave the ether XIX, mp 225.5–226.5° (lit.[7] mp 221–221.5°); λ_{max} 258.5, 2645, 269 mμ (log ϵ 3.08, 3.176, 3.127).

Anal. Calcd for $C_{32}H_{30}O$: C, 89.26; H, 7.02. Found: C, 89.59; H, 7.22.

cis-$\alpha,\alpha,\alpha',\alpha'$-**Tetraphenyl-1,2-cyclohexanedimethanol (XVI).**—The reaction of phenyllithium with 15 g of diethyl *cis*-1,2-cyclohexanedicarboxylate gave 13.3 g (45%) of crude diol. Recrystallization from benzene–petroleum ether (bp 65–67°) afforded 7.25 g of white crystals, mp 213–214.5° (lit.[7] mp 203–206°); λ_{max} 254, 260.5, 270 mμ (log ϵ 3.02, 3.01, 2.79).

Dehydration of the *cis*-diol afforded the *cis* ether XVIII, mp 198.5–199° (lit.[7] mp 199°); λ_{max} 256, 261, 270 mμ (log ϵ 3.17, 3.22, 3.12).

trans-**Tetra(*p*-N,N-dimethylaminophenyl)-1,2-cyclohexanedimethanol.**—The reaction of *p*-N,N-dimethylaminophenyllithium, prepared from 40 g (0.20 mol) of *p*-bromo-N,N-dimethylaniline and 2.80 g (0.40 g-atom) of lithium, with 7.50 g (0.0329 mol) of diethyl *trans*-1,2-cyclohexanedicarboxylate afforded 6.92 g (33.9%) of pale yellow crystals which crystallized from ether–petroleum ether (bp 60–70°). Several recrystallizations from benzene–petroleum ether (bp 60–70°) afforded white crystals: mp 213–215°; λ_{max} 267 and 297 mμ (log ϵ 3.82 and 3.09); ir (Nujol) 3.0, 6.25, and 6.68 μ; and nmr signals at δ 1.2–1.8 (broad m), 2.62 (S, OH), 2.96 (S, $(CH_3)_2N$), 6.7–7.5 (ms). The mass spectrum[10] (direct probe, >200°) did not show a molecular ion, but displayed prominent ions at *m/e* 602 (100% P − 18), 333 (85%), 334 (95%), and 290 (40%).

Anal. Calcd for $C_{40}H_{52}N_4O_2$: C, 77.38; H, 8.44; N, 9.02. Found: C, 78.35, 77.68;[11] H, 8.56, 8.35; N, 9.18, 8.95.

Registry No.—II, 17351-08-5; III, 17351-09-6; IV, 17351-10-9; VI, 17351-11-0; VII, 17351-12-1; VIII, 17351-13-2; X, 17351-22-3; XI, 17351-14-3; XIII, 17351-15-4; XVI, 17351-16-5; XVII, 17351-17-6; XVIII, 17351-18-7; XIX, 17351-19-8; MeMgI, 917-64-6; diethyl *cis*-4-cyclohexene-1,2-dicarboxylate, 4841-85-4; 2-(α-hydroxyethyl)-1-(α-hydroxyisopropyl)cyclohexane, 17351-23-4; *trans*-tetra(*p*-N,N-dimethylaminophenyl)-1,2-cyclohexanedimethanol, 17366-26-6; diethyl *cis*-1,2-cyclohexanedicarboxylate, 17351-07-4.

An Attempted Ring Enlargement. III. The Synthesis and Decomposition of the Magnesium Salt of 1-Bromomethyl-1-cyclohexanol

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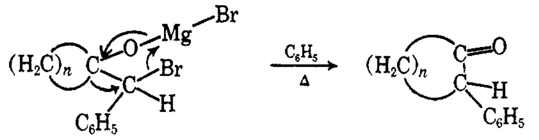
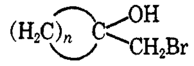
Two previous manuscripts reported a simple new method of ring enlargement, namely, the decomposition of the magnesium salts of 1-(α-bromobenzyl)-1-cycloalkanols[1] and 2-(α-bromobenzyl)-2-norbornanol[2] (eq 1). In order to investigate the synthetic generality of the method, the synthesis of compounds of the type depicted in structure **1** was undertaken. First, the



(1)

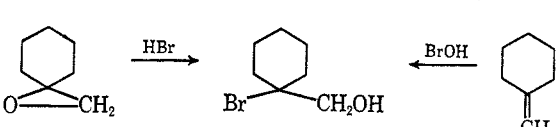
$n = 4–7$



1

$n = 4–7$

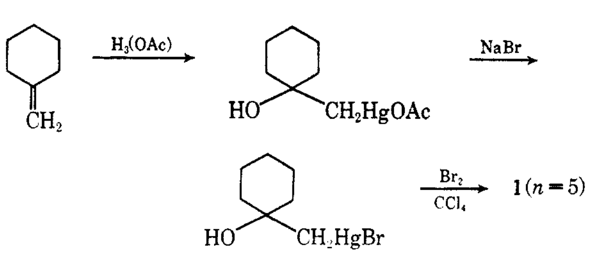
synthesis of 1-bromomethyl-1-cyclohexanol (**1**, $n = 5$) was attempted. The obvious synthetic approaches to the latter, *via* methylenecyclohexane and hypobromous acid, and methylenecyclohexane epoxide and 48% aqueous hydrogen bromide were reported by Traynham and Pascual[3] to yield the isomeric compound **2**, mp 82–83° (eq 2). Thus an alternative synthesis was



(2)

2

sought. The sequence is outlined in eq 3. The product isolated, **1** ($n = 5$), was found to melt at 82–83°.



(3)

3

The reported[3] product **2** (whose structure was primarily determined by qualitative organic analysis) was synthesized from methylenecyclohexane epoxide and hydrogen bromide[3] and found to be identical with **1** (n = 5) [mixture melting point, ir and nmr spectra (singlet, τ 6.63, two bromomethyl hydrogens; ten ring hydro-

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[10] The mass spectrum was determined by Mr. Jack R. Barnes using a Varian M-66 mass spectrometer.

[11] The diol tenaciously retained a trace of benzene, and a satisfactory analysis was obtained only after prolonged drying *in vacuo*.

(1) A. J. Sisti, *J. Org. Chem.*, **33**, 453 (1968).

(2) A. J. Sisti, *Tetrahedron Lett.*, 5327 (1967).

(3) J. G. Traynham and O. Pascual, *Tetrahedron*, **7**, 165 (1959).