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, -CHC**H**$_3$), 1.2 (s, 6, C(C**H**$_3$)$_2$), 3.2 (broad s, 2, **OH**), and 3.97 (m, 1, C**H**CH$_3$).

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$_3$)$_2$N), 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.

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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*.

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

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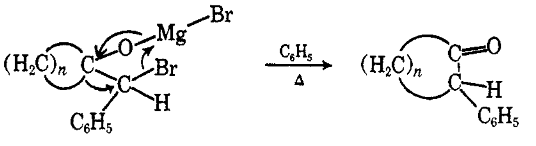
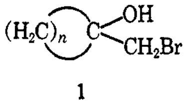
Two previous manuscripts reported a simple new method of ring enlargement, namely, the decomposition of the magnesium salts of 1-(α-bromobenzyl)-1-cycloalkanols[1] and 2-(α-bromobenzyl)-2-norbornanol[2] (eq 1). In order to investigate the synthetic generality of the method, the synthesis of compounds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



$n = 4–7$

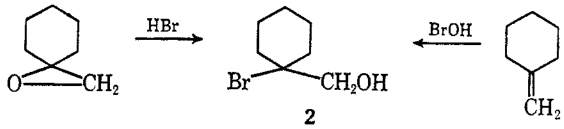
(1)



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



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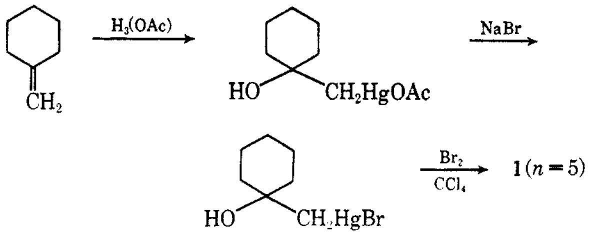
(2)



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

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

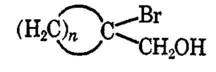
[3] J. G. Traynham and O. Pascual, *Tetrahedron*, **7**, 165 (1959).

gens at 8.50)]. The structural assignment for **3** was based on elemental analysis, infrared spectroscopy (KBr pellet, hydroxyl absorption at 3350 cm^{-1}), and reduction with sodium borohydride[4] to 1-methylcyclohexanol as ascertained from the nmr spectrum (singlet, τ 8.9, methyl group hydrogens and ten ring hydrogens at 8.65). Attempted acylations of **1** (n = 5) with acetic anhydride–pyridine at room temperature for periods of 1 and 3 days were fruitless. Only starting material was isolated. This observation, coupled with the synthesis (eq 3), strongly indicate the structure represented by **1** (n = 5) to be correct for all *three* synthetic methods (eq 2 and 3) and not **2**.

Additional evidence was obtained from studies directed toward the synthesis of **2**, first, by way of the lithium aluminum hydride reduction of methyl 1-bromocyclohexanecarboxylate (eq 4). Distillation yielded a small amount of **2** (nmr spectrum, singlet, τ 6.30, two hydroxymethyl hydrogens) mixed with **4** (nmr spectrum, doublet, τ 6.58–6.65) and mainly a nondistillable polymeric residue. Attempted purification of the mixture (vpc, distillation, and column chromatography) were unsuccessful owing to the expected lability of **2**.[5] The presence of **2** in the mixture was determined from the nmr spectrum, as well as from the reaction with alcoholic silver nitrate (instantaneous precipitation of silver bromide) resulting in the production of cyclohexanecarboxaldehyde. The synthesis *via* the reduction of the ester was abandoned. It was then reasoned that the cleavage reaction of methylenecyclohexane epoxide with hydrogen bromide (eq 2) should not only produce **1** (n = 5) as the major product, but also **2**. After isolation of **1** (n = 5), the residue was distilled, yielding an oil (nmr spectrum, singlets, τ 6.30 and 6.63, 80 and 20%, respectively) that consisted mainly of **2** contaminated with **1** (n = 5). Two additional distillations[5] were self-defeating for they resulted in the enrichment of the oil in **1** (n = 5) not **2** (nmr spectrum, singlets, τ 6.63 and 6.30, approximately equal amounts). The presence of **1** (n = 5) in the oil was verified by seeding with pure **1** (n = 5) followed by the addition of petroleum ether (bp 30–60°) to complete the crystallization. Reexamination of the nmr spectrum of the oil which was produced after filtration and removal of the solvent revealed 90–95% purity of **2** (singlet, τ 6.30, 90–95%; singlet, 6.63, 5–10%). The latter gave an excellent analysis, an *instantaneous* precipitate of silver bromide, and an instantaneous decoloration with potassium permanganate. Similarly, treatment of this oil with alcoholic silver nitrate yielded cyclohexanecarboxaldehyde.

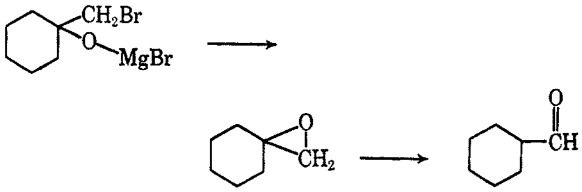
4 + **2** (4)

Since the study of Traynham and Pascual[3] also included the reactions of methylenecyclobutane, methylenecyclopentane, and methylenecycloheptane with hypobromous acid, as well as the cleavage of the corresponding epoxides with hydrogen bromide, all their structural assignments for the products **5** are highly suspect.



5, n = 3–6

With the correct structural assignment, **1** (n = 5), one could now perform a meaningful experiment directed toward ring enlargement. When a benzene solution of **1** (n = 5) was treated with an equivalent amount of isopropylmagnesium bromide, there was obtained a 40% conversion into cyclohexanecarboxaldehyde; no cycloheptanone was detected (vpc). The results are in accord with the studies and conclusions of Geissman and Akawie[6] that primary halides do not rearrange unless a good migrating group is present and that secondary and tertiary halides rearrange when an alkyl or aryl group is involved. Thus, the production of cyclohexanecarboxaldehyde can be envisaged as being formed from rearrangement of the epoxide[6] (eq 5).



(5)

Experimental Section[7]

Preparation of 1-Hydroxycyclohexyl-1-methylmercuric Bromide (3).—To 240 ml of 50% aqueous acetone was added 40 g (0.125 mol) of mercuric acetate followed by the slow addition of 12 g (0.125 mol) of methylenecyclohexane (Columbia Chemicals Co.). After being stirred 5 min at room temperature, 120 ml of 1 *N* sodium hydroxide solution containing 25 g of sodium bromide was added; the reaction mixture was stirred at ice-bath temperature for 1 hr. The solid which precipitated was filtered and recrystallized from ethyl acetate yielding 42 g (0.107 mol) of a solid (86%): mp 114.5–115°; ir, 3350 cm^{-1} (KBr pellet).

Anal. Calcd for $C_7H_{13}BrHgO$: C, 21.35; H, 3.33. Found: C, 21.61; H, 3.53.

The product **3** was then reduced with sodium borohydride according to the procedure of Brown,[4] and the isolated product (bp 152–155°), dissolved in carbon tetrachloride, gave the following nmr signals: singlet, τ 8.90, methyl group; ten ring hydrogens, 8.65.

Preparation of 1-Bromomethyl-1-cyclohexanol (1, n = 5).—Into a flask was placed 200 ml of anhydrous carbon tetrachloride and 9.8 g (0.025 mol) of **3**. To the mixture was added, over a 4-hr period, 4 g of bromine (washed with concentrated sulfuric acid followed by distillation from phosphorous pentoxide) dissolved in 50 ml of carbon tetrachloride. The reaction mixture was stirred overnight at room temperature. The theoretical amount of mercuric bromide was filtered off, and the carbon tetrachloride was washed with water, a 5% sodium carbonate solution, and water and dried over magnesium sulfate. After removal of the carbon tetrachloride under vacuum, and after recrystallization of the residue from petroleum ether (bp 30–60°), there was obtained 4.4 g (0.023 mol) of product, mp 82–83° (92%). The infrared spectrum in carbon tetrachloride showed a sharp absorption at ν 3550 cm^{-1} and a weak broad absorption

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[4] H. C. Brown and P. Geoghegan, Jr., *J. Amer. Chem. Soc.*, **89**, 1522 (1967).

[5] Each distillation produced considerable amounts of polymeric material, undoubtedly due to the decomposition of **2** which possesses an expected extremely labile bromine.

[6] T. A. Geissman and R. I. Akawie, *J. Amer. Chem. Soc.*, **73**, 1993 (1951).

[7] All melting points and boiling points are uncorrected. Microanalyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich. Infrared spectra were determined with a Perkin-Elmer Spectrocord infrared spectrophotometer. Nmr spectra were determined with a Varian A-60 instrument.

at 3400 cm^{-1}. The nmr spectrum revealed a singlet at τ 6.63 (two hydrogens) and ten ring hydrogens at 8.50.

Anal. Calcd for $C_7H_{13}BrO$: C, 43.54; H, 6.78. Found: C, 43.63; H, 6.78.

The above bromination was carried out in pyridine yielding similar results.

Treatment of methylenecyclohexane epoxide (0.6 mol) (K & K Chemical Co.) with 48% aqueous hydrogen bromide according to the procedure of Traynham[3] produced a solid which, when recrystallized from petroleum ether, melted at 82–83° (60%). The product was shown to be identical with **1** (n = 5) (from the bromination of **3**), mixture melting point and infrared and nmr spectra identical (CCl_4). After removal of the petroleum ether vacuum distillation of the residue, bp 50–51° (0.15 mm), yielded a colorless oil: nmr spectrum (CCl_4), singlet τ 6.30 (80%), singlet, 6.63 (20%). Two redistillations, bp 41–42° (0.08 mm), yielded a viscous oil: nmr spectrum (CCl_4), singlets, τ 6.30 and 6.63 in equal amounts. The oil was treated with a few crystals of **1** (n = 5) and petroleum ether, cooled, and filtered. The petroleum ether was then removed under vacuum. The nmr spectrum (CCl_4) of the residual oil now revealed singlets at τ 6.30 (90–95%) and 6.63 (5–10%): ir, ν^{film} 3400 cm^{-1} broad).

Anal. Calcd for $C_7H_{13}BrO$: C, 43.54; H, 6.78. Found: C, 43.80; H, 6.93.

Treatment of the oil with excess alcoholic silver nitrate at room temperature for 2 hr followed by dilution with water and extraction with ether yielded, after drying and removal of the ether, cyclohexanecarboxaldehyde which was characterized as the 2,4-dinitrophenylhydrazone, mp 170–171° (ethanol) (lit.[8] mp 172–173°).

Reduction of Methyl 1-Bromocyclohexanecarboxylate.—Into a flask was placed 100 ml of anhydrous ether and 2.5 g (0.066 mole) of pulverized lithium aluminum hydride. The mixture was cooled to 0° and the dropwise addition of 20 g (0.09 mol) of methyl 1-bromocyclohexanecarboxylate[9] dissolved in 25 ml of ether was commenced. The reaction mixture was stirred for an additional hour at 0°. Decomposition was effected with water followed by the addition of a 10% solution of sulfuric acid. The ether layer was separated, washed with water, and dried over magnesium sulfate. Removal of the ether followed by distillation of the residue yielded 5 g of a colorless oil, bp 55° (0.55 mm), and a large amount of nondistillable material. The nmr spectrum (CCl_4) of the oil showed a singlet at τ 6.30 due to two hydroxymethyl hydrogens (2) and a doublet at τ 6.58–6.65 (4). Treatment of the oil with alcoholic silver nitrate produced an instantaneous precipitate of silver bromide. Dilution of the reaction mixture with water was followed by extraction with ether. After drying the ether with magnesium sulfate, the removal of the ether left an oil which was converted into its 2,4-dinitrophenylhydrazone, mp 170–171° (ethanol) (lit.[8] mp 172–173°) for cyclohexanecarboxaldehyde.

The Reaction of 1 (n = 5) with Isopropylmagnesium Bromide.—To 21 g (0.11 mol) of **1** (n = 5) dissolved in 300 ml of anhydrous benzene was added, dropwise, an equivalent of isopropylmagnesium bromide (prepared from 16 g (0.13 mol) of isopropyl bromide, 75 ml of ether, and 3.2 g of magnesium) at room temperature. The reaction mixture was refluxed for 8 hr. It was then poured into a saturated solution of ammonium chloride, and the organic layer was separated and washed with water, a 10% sodium carbonate solution, and water, and finally the organic layer was dried over magnesium sulfate. The solvent was subsequently removed under vacuum. Examination of the residue by vpc revealed no cycloheptanone. Distillation afforded 5 g (0.045 mol, 40%) of cyclohexanecarboxaldehyde, bp 49–50° (30 mm) [lit.[8] bp 50–53° (20 mm)]. The 2,4-dinitrophenylhydrazone melted at 172–173° (lit.[8] mp 172–173°). A large amount of decomposition resulted during distillation with the production of polymeric material.

Registry No.—**1** (n = 5), 17299-10-4; **2**, 17299-11-5; **3**, 17299-12-6; **4**, 100-49-2; reduction product of **3**, 590-67-0.

Acknowledgment.—I am grateful to Mr. B. Waxman for helpful discussions during this project and to Mr. T. Kolesar for the nmr spectra.

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[8] M. Stiles and A. J. Sisti, *J. Org. Chem.*, **25**, 1691 (1960).

[9] W. J. Bailey and R. Baylouny, *ibid.*, **81**, 2126 (1959).

The Reaction of Phenyl Derivatives of Transition Metals with Acetylene

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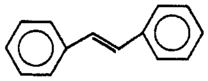
Numerous examples of the reaction of acetylenes with transition metal carbonyls and their derivatives are known,[1] but there appear to be only a few examples of the reaction of alkyl (or aryl) transition metal complexes with acetylenes. Tsutsui, Herwig, Metlesics, and Zeiss have investigated the reaction of various aryl- and alkylchromium compounds and other transition metal alkyls with disubstituted acetylenes.[2] In some reactions they found the formation of compounds containing two acetylene units and an alkyl or aryl group from the metal, as well as the cyclotrimerization product of the acetylenes, hexasubstituted benzene. For example, triphenyl- and triethylchromium reacted smoothly with diphenylacetylene in tetrahydrofuran (THF) to give 1,2,3,4-tetraphenylnaphthalene and -benzene, respectively, in addition to hexaphenylbenzene. Diethylnickel and diphenylacetylene gave tetraphenylcyclohexadiene and hexaphenylbenzene. However, for the reaction of triphenylchromium with a monosubstituted acetylene or acetylene itself, they reported that the triarylchromium was rapidly decomposed by acetylenic hydrogen and the acetylene was polymerized under the conditions they used. The fate of the phenyl group was not determined.[2b] This type of sensitivity toward acidic hydrogen of acetylene seems to be general in other alkyl or acyl transition metal compounds,[3,4] and only a few examples were reported about the reaction of acylmetal carbonyls with acetylene or monosubstituted acetylenes.[5]

In this paper we wish to report the formation of all-*trans*-1,6-diphenyl-1,3,5-hexatriene by the reaction of triphenylchromium with acetylene in THF at low temperature. A large excess of acetylene was bubbled into a THF solution containing triphenylchromium as its tetrahydrofuranate at −70°, and the reaction mixture was slowly warmed with stirring. After the ordinary treatment, the following products were obtained: all-*trans*-1,6-diphenyl-1,3,5-hexatriene (**4**), *trans,trans*-1,4-diphenyl-1,3-butadiene (**3**), biphenyl



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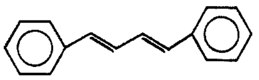

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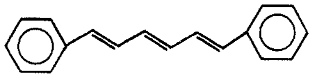

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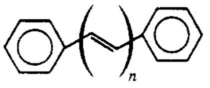

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[1] M. A. Bennett, *Chem. Rev.*, **62**, 611 (1962).

[2] (a) M. Tsutsui and H. Zeiss, *J. Amer. Chem. Soc.*, **81**, 6090 (1959); (b) W. Herwig, W. Metlesics, and H. Zeiss, *ibid.*, **81**, 6203 (1959).

[3] R. F. Heck, *ibid.*, **86**, 2819 (1964).

[4] A. Nakamura, *Mem. Inst. Sci. Ind. Res., Osaka Univ.*, **19**, 81 (1962); *Chem. Abstr.*, **59**, 8786 (1963).

[5] Y. Sawa, I. Hashimoto, M. Ryang, and S. Tsutsumi, *J. Org. Chem.*, **33**, 2159 (1968).