spectral data (ir and nmr) and retention time of glpc with those of an authentic sample.

Under condition B, a heterogeneous mixture of ether (1.6 ml) and H_2O (0.4 ml) was used instead of 95% CH_3OH. Condition C refers to the use of DMF (or HMPA)–H_2O mixture (98:2 v/v, 2.0 ml) containing DABCO (224 mg, 2.0 mmol). Unless otherwise stated, the reaction scale and the procedure were as above described. The progress of the reaction was conveniently monitored by glpc or tlc. In general, volatile products were purified by distillation and preparative glpc, whereas nonvolatile materials were isolated in pure state by preparative tlc. The structure was confirmed by comparison of the retention times of glpc and the spectral data (ir, nmr, uv, and mass) with those of authentic specimen. Isomeric purity of coprostanone (**2**) (95%) derived from 4-cholesten-3-one (**1**) was determined according to the standard procedure[26] after converting the whole ketonic products into the 2,4-dinitrophenylhydrazones.

Reduction of 2-Cyclohexenones.—The rates of hydrogenation were compared individually and competitively. When 2-cyclohexenone, 2-methyl-2-cyclohexenone, and 3-methyl-2-cyclohexenone were treated separately with 4 equiv of $Fe(CO)_5$ under condition A at 20°, the corresponding saturated ketones were formed. Yields of cyclohexanone, 2-methylcyclohexanone, and 3-methylcyclohexanone were 43, 3.8, and 1.0% after 30 min, and 96, 15, and 22% after 12 hr, respectively. Although 2-methyl-2-cyclohexenone was reduced more rapidly than 3-methyl-2-cyclohexenone at the early stage of the reaction, the final yield of 2-methylcyclohexanone was lower than that of 3-methylcyclohexanone.

Reaction under condition A using 2-cyclohexenone (10 mg, 0.11 mmol), 2-methyl-2-cyclohexenone (112 mg, 1.0 mmol), $Fe(CO)_5$ (796 mg, 4.1 mmol), NaOH (80 mg, 2.0 mmol), and 95% CH_3OH (2.0 ml) was performed at 20°. A similar competition experiment was conducted using 2-cyclohexenone (10 mg, 0.11 mmol), 3-methyl-2-cyclohexenone (330 mg, 3.0 mmol), $Fe(CO)_5$ (268 mg, 1.3 mmol), NaOH (25 mg, 0.63 mmol), and 95% CH_3OH (6.0 ml). The reaction aliquot was taken up at appropriate intervals and analyzed by glpc. Yields of the reduction products were plotted against reaction time, and the competition figure, 2-cyclohexenone:2-methyl-2-cyclohexenone:3-methyl-2-cyclohexenone = 1.00:0.10:0.017, was obtained from the slope of the traces (conversion <30%).

Preparation of Deuteriobutyrophenones.—To a solution prepared by dissolving Na (35 mg, 1.5 mg-atoms) in a mixture of CH_3OD (1.5 ml) and D_2O (0.075 ml) was added $Fe(CO)_5$ (588 mg, 3.0 mmol), and the mixture was stirred for 5 min at room temperature and then cooled to 0°. Crotonophenone (100 mg, 0.69 mmol) was added in one portion, and the mixture was stirred at 0° for 3 hr. After quenching with an ethereal solution of I_2, the mixture was treated with aqueous sodium thiosulfate solution and extracted with ether. Concentration of the extracts *in vacuo* followed by preparative tlc (R_f 0.29 after two developments with 1:1 *n*-hexane–benzene mixture) gave pure butyrophenone (85 mg, 82% yield). The nmr indicated that the major component was $CH_3CHDCHDCOC_6H_5$: δ 0.98 (d, J = 6.7 Hz, 3 H, CH_3), 1.3–2.0 (m, 1 H, β-CH), 2.6–3.0 (m, 1 H, α-CH), and 7.1–8.0 (m, 5 H, C_6H_5). Crotonophenone recovered from the incomplete reaction (tlc R_f 0.15 after two developments with 1:1 *n*-hexane–benzene mixture) did not contain deuterium atom, as confirmed by nmr and mass analyses.

Butyrophenone-α,β-d_2 above prepared (26 mg, 0.17 mmol) was treated with 0.1 *N* CH_3ONa in CH_3OD (0.17 ml) at room temperature for 3 hr. The reaction mixture was directly chromatographed on a silica gel plate to afford butyrophenone-α,α,β-d_3 (24 mg, 92% recovery). Mass spectral analysis using $CH_3CH_2CH_2COC_6H_5$ and $CH_3CH_2CD_2COC_6H_5$ (86% d_2 and 14% d_1) as reference indicated the composition of 3% d_4, 81% d_3, 15% d_2, and 1% d_1: nmr δ 0.98 (d, J = 6.7 Hz, 3 H, CH_3), 1.3–2.0 (m, 1 H, β-CH), 2.6–3.0 (m, 0.04 H, α-CH), and 7.1–8.0 (m, 5 H, C_6H_5). Butyrophenone-β-d_1 was obtained in a similar fashion using 0.1 *N* CH_3ONa in CH_3OH: mass spectrum 3% d_2, 92% d_1, and 5% d_0; nmr δ 0.98 (d, J = 6.7 Hz, 3 H, CH_3), 1.3–2.0 (m, 1 H, β-CH), 2.6–3.0 (d, J = 6.7 Hz, 2 H, α-CH_2), and 7.1–8.0 (m, 5 H, C_6H_5).

Reaction of Dimethyl Maleate and Fumarate in Deuterated Solvent.—$Fe(CO)_5$ (590 mg, 3.0 mmol) was added to a solution prepared by dissolving Na (35 mg, 1.5 mg-atoms) in CH_3OD (3.0 ml)–D_2O (0.18 ml), and the mixture was stirred at ambient temperature for 5 min. To the resulting dark-red solution kept at 0° was added dimethyl maleate (or fumarate) (224 mg, 1.5 mmol) in one portion, and the mixture was stirred at 0° for 12 hr. The reaction mixture was subjected directly to bulb-to-bulb distillation. The ester fraction obtained at 25° (1 mm) was dissolved in $CDCl_3$, dried by passing through a short column of Na_2SO_4, and analyzed by nmr to determine the deuterium content of succinate. The isotope distribution of succinate could not be specified by mass spectral analysis. Isotope exchange of succinate during the reaction and the work-up proved to be negligible. Samples of maleate and fumarate for mass and nmr analyses were obtained by preparative glpc (5% polyethylene glycol succinate on Neopak 1A, 95°). The results are summarized in Table II.

Reduction of 2-Cyclohexenone with Polynuclear Hydridoiron Complexes.—Treatment of $Fe_2(CO)_9$ (369 mg, 1.0 mmol) with KOH (172 mg, 3.1 mmol) in CH_3OH (2.0 ml) at 20° for 1.5 hr gave a mixture of dinuclear complexes, $[HFe_2(CO)_8]^-$ and $[Fe_2(CO)_8]^{2-}$.[16] 2-Cyclohexenone (98 mg, 1.0 mmol) was added in one portion, and the mixture was stirred at 20° for 6 hr. Glpc analysis of the aliquot quenched by ethereal solution of I_2 indicated the formation of cyclohexanone in 56% yield.

Treatment of 2-cyclohexanone (98 mg, 1.0 mmol) with $(C_2H_5)_3NH^+$–$[HFe_3(CO)_{11}]^-$ (546 mg, 1.0 mmol)[16] in CH_3OH (2.0 ml) at room temperature for 6 hr afforded cyclohexanone in 23% yield.

Registry No.—Iron pentacarbonyl, 13463-40-6.

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[26] F. J. McQuillin, W. O. Ord, and P. L. Simpson, *J. Chem. Soc.*, 5996 (1963).

An Improved Synthesis of Indenes[1]

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Diols of type **2** or ethers of type **3** are prepared in high yield from readily available *o*-bromobenzyl alcohol and are converted to indenes of type **4** by action of protonic acids such as sulfuric acid in glacial acetic acid, *p*-toluenesulfonic acid in hot glacial acetic acid, polyphosphoric acid, or Lewis acids such as boron trifluoride etherate in refluxing benzene. Boron trifluoride etherate is the current acid of choice for the cyclic ketones studied (C_7, C_8, C_9, C_{12}), and high yields of indenes (49–73%) of type **4** are prepared conveniently and without isolation of intermediates. The reaction gives 3-phenylindene when acetophenone is employed. Under certain conditions indan formation has been noted as a side product.

We wish to report a new synthesis of indenes which is illustrated by the synthesis of 6,7,8,9,10-pentahydro-5*H*-cyclohept[*a*]indene (**4**) as shown in Scheme I.

The procedure involves addition of alkyllithium (2 equiv) to the 2-bromobenzyl alcohol in an appropriate nonprotonic solvent such as tetrahydrofuran and hexane. The temperature of addition is not critical; however, the reaction is exothermic and is usually

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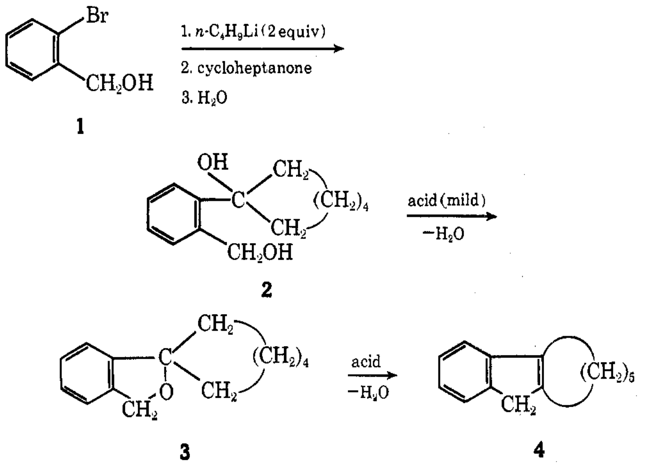
[1] Supported by U. S. Army Medical Research and Development Command, DADA-17-70-C-0008.

SCHEME I

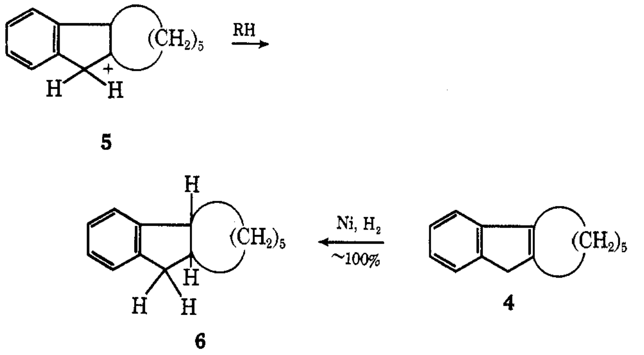


effected in the cold. The ketone, in solution of an inert solvent such as hexane, is added at a rate sufficient to control the exothermic reaction (cooling −10 to −20° is recommended). The intermediate diol **2** can be isolated by conventional methods, or the crude diol can be used without purification for direct conversion to the cyclic ether **3** or to the indene **4** by action of appropriate acid. All acids studied (hot formic acid, *p*-toluenesulfonic acid in acetic acid, sulfuric acid in acetic acid, and boron trifluoride etherate in benzene) effect rapid conversion of diol **2** to cyclic ether **3**; formic acid is the reagent of choice of those studied when isolation of the ether is desired (74% yield of **3**).

Optimum reaction conditions (acid, time, temperature) vary for the conversion to each indene and either the diol **2** or the cyclic ether **3** can be employed; more conveniently the crude diol can be converted directly to indene in essentially a *one-pot* reaction without isolation of intermediates. Boron trifluoride etherate in boiling benzene is currently the acid of choice for the cyclic ketones employed (C_7, C_8, C_9, C_{12}) and the yield of indenes of type **4** has consistently been 49–73%.

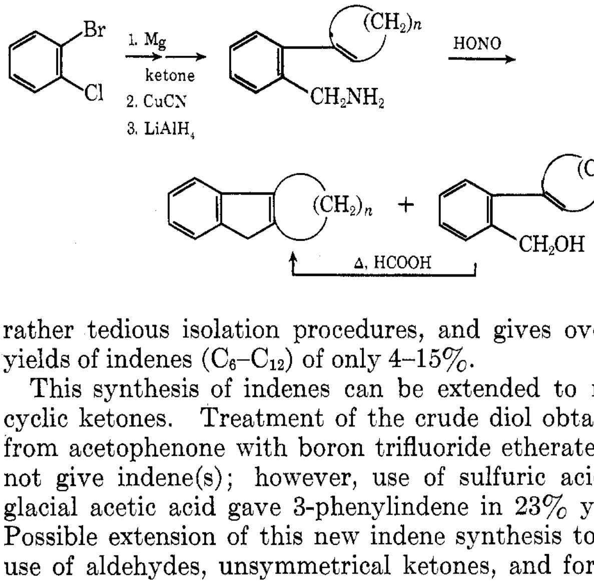
Conversion of diols of type **2** into indenes of type **4** is also practical using sulfuric acid in glacial acetic acid; however, such reactions are accompanied by more tar formation and the yield of indenes is lower (generally 23–38%). Reaction of the diol **2** with polyphosphoric acid (22–31°) gave a mixture of indene **4** (30%) and reduced indene **6** (26%). Indan **6** was observed as a by-product in all acid systems studied; however, its formation was decreased by decreasing the concentration of the reacting diol **2**. The indan **6** was assumed to be formed by hydride transfer involving an intermediate carbonium ion **5**; the structure of **6** was established by its independent synthesis from **4** (Scheme II). Indene **4** does not give rise to indan **6** in polyphosphoric acid or boron trifluoride etherate in benzene; thus, it was established that the by-product indans do not originate from the indenes as they are formed. Reaction of **2** (1.23 mmol) with *p*-toluenesulfonic acid (0.28 mmol) in hot glacial acetic acid proceeded slowly (after 3 hr, 51% conversion to **3**, 40% conversion to 4) but cleanly, and this procedure may prove to be a suitable alternative to use of boron trifluoride etherate in benzene.

SCHEME II



Fused indenes of type **4** are of particular interest to us as intermediates for the preparation of metacyclophanes by addition of halocarbenes with subsequent ring expansion of the derived cyclopropanes.[2] The present method for the preparation of such indenes is superior to that previously reported[3] since the preparation can be carried out rapidly, fewer steps are involved and intermediates need not be isolated or purified. The alternative method[3] starting with *o*-bromochlorobenzene (Scheme III) involves six steps, requires rather tedious isolation procedures, and gives overall yields of indenes (C_6–C_{12}) of only 4–15%.

SCHEME III



This synthesis of indenes can be extended to noncyclic ketones. Treatment of the crude diol obtained from acetophenone with boron trifluoride etherate did not give indene(s); however, use of sulfuric acid in glacial acetic acid gave 3-phenylindene in 23% yield. Possible extension of this new indene synthesis to the use of aldehydes, unsymmetrical ketones, and for the preparation of polycyclic indenes is the subject of further study.

Experimental Section

Methyl *o*-Bromobenzoate.—Esterification of *o*-bromobenzoic acid using molecular sieves was fashioned after the method used by Harrison and coworkers[4] for the synthesis of methyl nonanoate. The yield of pure methyl *o*-bromobenzoate was 91%. The yield was 80–84% when molecular sieves were not employed.

***o*-Bromobenzyl alcohol** was prepared (93% yield) by reduction of methyl *o*-bromobenzoate (0.462 mol) with lithium aluminum hydride, mp 78.5–80.5° (lit.[5] mp 80°).

1-(*o*-Hydroxymethylphenyl)cycloheptanol (2).—Dry *o*-bromobenzyl alcohol (10.00 g, 0.0535 mol) was added to a flame-dried 500-ml three-neck round-bottom flask, equipped with an addition funnel, alcohol thermometer, nitrogen inlet, and mechanical

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[2] (a) W. E. Parham, *Rec. Chem. Progr.*, **29**, (1968); (b) W. E. Parham, D. R. Johnson, C. T. Hughes, M. K. Meilahn, and J. K. Rinehart, *J. Org. Chem.*, **35**, 1048 (1970).

[3] W. E. Parham, C. D. Wright, and D. A. Bolon, *J. Amer. Chem. Soc.*, **83**, 1751 (1961).

[4] L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Vol. I, Wiley, New York, N. Y., 1967, p 705.

[5] C. Mettler, *Ber.*, **39**, 2938 (1906).

stirrer. Tetrahydrofuran (40 ml, distilled from $LiAlH_4$) and 10 ml of hexane (stored over sodium) was added and the solution was cooled to −15° in a Dry Ice–aqueous isopropyl alcohol bath under positive nitrogen pressure. Recently standardized[6] *n*-butyllithium (Alpha) (55 ml, 0.123 mol, 15% molar excess) was slowly added over a 75-min period, forming a thick white precipitate, and the mixture was stirred for an additional 2 hr under nitrogen at −10 to −20°. Cycloheptanone (Aldrich) (9.00 g, 0.080 mol, 15% molar excess based on dilithium salt and excess *n*-butyllithium) in 25 ml of hexane was added to the cold slurry over a 30-min period while maintaining the temperature between −10 and −20°, and a large portion of the white precipitate vanished. The mixture was stirred at −15° for another 2 hr and then was allowed to warm to room temperature and stirred under nitrogen for an additional 16 hr. The clear reaction solution was hydrolyzed (80 ml of saturated aqueous NH_4Cl) and the two phases were separated. The aqueous layer was extracted with two 50 ml-portions of ether and the combined organic extracts were washed with 50 ml of water, dried (Na_2SO_4), filtered, and the solvent removed (rotary evaporation) to a yellow oil (15.29 g). Benzyl alcohol and unreacted cycloheptanone were distilled at 55–88° (10 mm) from the crude diol with a short path column to give 4.04 g of distillate (18 mol % benzyl alcohol and 82% cycloheptanone by nmr). After removal of unreacted ketone and benzyl alcohol, the distillation flask contained 10.55 g (90% yield) of crude diol which crystallized upon cooling to room temperature (22°). The solid material was dissolved in 90 ml of petroleum ether (bp 60–70°) and cooled to −25° with the formation of pink needles (8.30 g, mp 61–64.5°, 71% yield). The mother liquor was concentrated to 2.15 g of red oil which showed the presence of additional dialcohol by nmr spectroscopy.

An analytical sample of **2** was prepared by recrystallizing the diol (0.50 g) two times from petroleum ether to give 0.34 g of small, white needles, mp 62.5–64°, which showed the following spectral properties: ir (neat) 3620–3100 cm^{-1} (broad and strong, associated OH); uv max (95% C_2H_5OH) 211 mμ (log ε 3.94), 254 (sh, 2.20), 259 (2.30), 265 (sh, 2.24), 270 (sh, 2.03); nmr ($DCCl_3$) (with areas relative to 20 protons) τ 2.54–2.86 (m, 4.0, aromatic H), 5.16 (s, 2.0, benzylic CH_2O), 6.36 (s, 2.1, alcohol OH) (disappeared when D_2O added to sample), 7.67–8.57 (two broad peaks, 11.9, aliphatic CH_2).

Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15. Found: C, 76.51; H, 9.03.

Spiro[cycloheptane-1,1′(3′*H*)-isobenzofuran] (Cyclic Ether Intermediate 3).—The crude diol **2** (14.82 g) obtained from *o*-bromobenzyl alcohol (0.0535 mol) as described above which still contained benzyl alcohol and cycloheptanone was added to 65 ml of 88% formic acid (Baker) and heated at the reflux temperature for 80 min. The solution turned deep red and a yellow oil separated on the surface. The reaction mixture was then added with stirring to 250 ml of ice water and the resulting aqueous mixture was extracted with two 100-ml portions of petroleum ether and one 100-ml portion of benzene. The combined organic extracts were washed with 100 ml of water, 100 ml of saturated aqueous sodium bicarbonate, and another 100 ml of water in succession and then dried ($MgSO_4$). The mixture was filtered and the solvent was removed (rotary evaporator) to give a yellow oil (15.41 g). Glpc analysis (5 ft × 0.25 in., 20% DC710 on Chromosorb W, 60–80 mesh, 190°, 60 ml/min He) and nmr analysis of the crude oil showed the presence of the pentahydrocyclohept[*a*]indene (**4**, retention time 14 min 24 sec), benzyl formate, unreacted cycloheptanone, and cyclic ether (retention time 11 min 36 sec). No *o*-bromobenzylformate was observed, indicating complete reaction of *o*-bromobenzyl alcohol with *n*-butyllithium.

The crude oil was subjected to fractional distillation through a short path column. The first fraction (3.02 g) distilled between 45 and 70° (8 mm) and was shown to be composed of benzyl formate and cycloheptanone by glpc analysis (retention times compared with authentic samples on the column described above). The second fraction (8.67 g) distilled at 79° (0.05 mm) and was shown by glpc analysis (internal standard heptadecane) to be 8 wt % indene **4** (0.69 g, 7.0% yield) and 92% cyclic ether **6** (7.98 g, 74% yield). The distillation flask contained 1.344 g of a red viscous oil which contained additional pentahydrocyclohept[*a*]indene and cyclic ether by glpc analysis.

The cyclic ether was purified by preparative glpc and exhibited the following properties: refractive index $n^{27}\text{D}$ 1.5412; ir (neat) 1035 cm^{-1} (CO); uv max (95% C_2H_5OH) 209 mμ (sh, log ε 3.98), 234 (sh, 2.90), 257 (sh, 2.79), 262 (2.92), 269 (2.90), 278 (sh, 2.26); nmr ($DCCl_3$) (with areas relative to 18 protons) τ 2.73–2.90 (with intense peak at 2.79) (m, 4.0, aromatic H), 4.96 (s, 1.9 benzylic CH_2O–), 7.87–8.60 (two broad peaks, 12.1, aliphatic CH_2); mass spectrum *m/e* 202 (molecular ion).

Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.16; H, 9.00.

Direct Conversion of *o*-Bromobenzyl Alcohol to Indenes of Type 4. A. Use of Boron Trifluoride Etherate. 6,7,8,9,10-Pentahydro-5*H*-cyclohept[*a*]indene (4).—Crude 1-(*o*-hydroxymethylphenyl)cycloheptanol (**2**, 4.15 g, 0.0189 mol), obtained as described above, subsequent to removal of benzyl alcohol and cycloheptanone, was added to 175 ml of benzene contained in a 250-ml three-neck flask equipped with a magnetic stirrer, condenser, and nitrogen inlet. Distilled boron trifluoride etherate (2.68 g, 0.0189 mol) was added, and glpc analysis (5 ft × 0.25 in., 20% DC 710 on 60–80 mesh Chromosorb W, 210°, 60 ml/min He) showed the immediate presence of ether **3**. The reaction mixture was heated to the reflux temperature and after 7 hr (solution turned dark red) at that temperature gplc showed complete conversion to the pentahydrocyclohept[*a*]indene with no indan by-product observed. The reaction was hydrolyzed by adding the red benzene solution to 175 ml of ice water and shaking the mixture thoroughly in a separatory funnel (red color changed to light yellow upon hydrolysis). The layers were separated and the benzene layer was washed with a 150-ml portion of saturated aqueous sodium bicarbonate followed by 150 ml of water, dried ($MgSO_4$), and filtered, and the solvent was removed by rotary evaporation to yield 4.101 g of an orange oil (less tar formation than with H_2SO_4). The oil was chromatographed over 120 g of 80–200 mesh alumina (Matheson Coleman and Bell) by elution with 300 ml of petroleum ether to give a pale yellow oil which solidified on standing (2.726 g, mp 35–46°, 70% yield from *o*-bromobenzyl alcohol). Glpc analysis showed only trace impurities and the nmr spectrum was essentially that of the pure compound. The solid was crystallized from ethanol–water to give white needles (1.389 g, mp 48–50°). The mother liquor was concentrated, crystallized from absolute ethanol and recrystallized from ethanol–water to give desired indene (0.399 g, mp 49–51°). The mother liquors were concentrated to an oil which was chromatographed over silica gel (60 g) with petroleum ether and then crystallized from ethanol–water to give additional indene (0.145 g, mp 49–51.5°) which was combined with the above in the same melting point range to give pentahydrocyclohept[*a*]indene (1.933 g, 50% yield from *o*-bromobenzyl alcohol, lit.[3] mp 50.5–51.5°).

B. 6,7,8,9,10,11-Hexahydro-5*H*-cyclooct[*a*]indene.—*o*-Bromobenzyl alcohol (0.0535 mol) was treated with *n*-butyllithium (0.123 mol) and cyclooctanone (10.08 g, 0.080 mol, 15% molar excess) essentially as described for cycloheptanone above. The crude diol (9.52 g, 76% yield) obtained subsequent to removal of benzyl alcohol and cyclooctanone was treated with boron trifluoride etherate (5.77 g, 0.0407 mol) in hot benzene (407 ml) as described in A above. After 4 hr nmr spectroscopy indicated complete conversion. The solution was diluted with water (100 ml), washed with aqueous sodium bicarbonate, dried ($MgSO_4$), and concentrated to give 8.23 g of yellow oil. The oil was distilled through a short path column, and a center cut (4.86 g, 46% yield from *o*-bromobenzyl alcohol) was collected. Glpc analysis of this product (5 ft × 0.25 in., 20% DC 710 of 60–80 mesh Chromosorb W, 198°, 60 ml/min He, 10 min 24 sec retention time) showed it to be 99% pure hexahydrocyclooct[*a*]indene, $n^{25}\text{D}$ 1.5760 (lit.[7] $n^{25}\text{D}$ 1.5784). The ir and nmr spectra of this product were identical with those of an authentic sample.[7]

C. 6,7,8,9,10,11,12-Heptahydro-5*H*-cyclonona[*a*]indene.—The product (8.53 g) obtained from *o*-bromobenzyl alcohol (7.60 g, 0.041 mol) and cyclonanone (6.00 g, 0.043 mol) as described above, obtained subsequent to removal of benzyl alcohol and cyclonanone, was treated with boron trifluoride etherate (4.87 g, 0.034 mol) in hot benzene (343 ml). The reaction was monitored by nmr (prolonged heating was found to reduce the yield of indene) and was complete after refluxing for 6.5 hr. The mixture was quenched by pouring the reaction mixture into a separatory funnel containing 350 ml of ice water (vigorous shaking). The layers were separated and the aqueous layer was washed with two

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[6] H. Gilman and A. H. Haubein, *J. Amer. Chem. Soc.*, **66**, 1515 (1944).

[7] W. E. Parham and J. K. Rinehart, *ibid.*, **89**, 5668 (1967).

50-ml portions of ether. The combined organic layers were washed with four 100-ml portions of water and two 100-ml portions of saturated aqueous sodium bicarbonate. The solution was dried ($MgSO_4$) and filtered, and the solvent was removed by rotary evaporation to a light orange oil (8.17 g) which was primarily desired indene by nmr. The indene was distilled at 96–97° (0.025 mm) through a short path column to give 5.12 g (59% yield) of a light yellow oil, $n^{19}\mathrm{D}$ 1.5769, which was 97% pure by glpc analysis (5 ft × 0.25 in., 20% DC 710 on Chromosorb W 60–80 mesh, 220°, 60 ml/min He, 5 min retention time). The analytical sample was prepared by using preparative glpc.

The distilled indene showed the following spectral properties: ir (neat) 1628 (w, ν C=C), 1609 (w), 1468 (s), 1445 (m), 1395 (m), 760 (s) and 720 cm^{-1} (s); uv max (95% C_2H_5OH) 207 mμ (log ϵ 4.25), 220 (sh, 4.08), 226 (sh, (3.92), 260 (4.12), 266 (sh, 4.08), 270 (sh) (4.02), 286 (sh, 3.16); nmr (20% CCl_4) (with areas relative to 20 protons); τ 2.61–3.16 (with intense peak at 2.89) (m, 3.9, aromatic H), 6.84 (s, 1.9, CH_2 in indene 5 position), 7.27–7.59 (m, 3.7 benzylic CH_2), 7.84–9.24 (with intense peak at 8.53) (m, 10.5, bridge aliphatic CH_2).

Anal. Calcd for $C_{16}H_{20}$: C, 90.50; H, 9.50. Found: C, 90.59; H, 9.78.

D. Use of Sulfuric Acid in Glacial Acetic Acid. 6,7,8,9,10-Pentahydro-5*H*-cyclohept[*a*]indene (4).—The crude alcohol (4.15 g, 0.0189 mol) obtained as described in A above was added to 145 ml of glacial acetic acid (low concentration decreases indane by-product formation) containing concentrated sulfuric acid (1.48 g, 0.015 mol). The reaction was heated to reflux and monitored by nmr (disappearance of $-CH_2O$). After 16 hr, sodium acetate trihydrate (4.1 g, 0.03 mol) was added to neutralize the sulfuric acid. Acetic acid (100 ml) was removed (rotary evaporator) and 100 ml of water was added to the dark oil. The remaining acetic acid in the resulting mixture was neutralized with 10% aqueous sodium hydroxide. The suspension was extracted with two 200-ml portions of petroleum ether and one 200-ml portion of benzene. The combined organic extracts were washed with 300 ml of water, dried ($MgSO_4$), and filtered, and the solvent was removed by rotary evaporation to a black oil (2.34 g). The oil was chromatographed over 80 g of 80–200 mesh alumina (Matheson Coleman and Bell) with 200 ml of petroleum ether as eluent to give a yellow oil (1.50 g, 39% yield from *o*-bromobenzyl alcohol) which was essentially pure pentahydrocyclohept[*a*]indene by nmr spectroscopy. Glpc analysis showed only desired indene with no indan side product present. The oil was crystallized from ethanol (−25°) to give white needles (0.658 g, mp 49.5–51.5°). The mother liquor was concentrated and crystallized from ethanol and then recrystallized from ethanol–water to give white needles (0.248 g, mp 49–51°). The combined mother liquors were concentrated to an oil which was chromatographed over 60 g of 100–200 mesh silica gel. The resulting oil (0.189 g) was crystallized from ethanol–water to white needles (0.091 g, mp 49–51.5°) which were combined with the above in the same melting point range to give pure indene (0.997 g, mp 49–51.5, 26% yield from *o*-bromobenzyl alcohol, lit.[4] mp 50.5–51.5°).

6,7,8,9,10,11,12,13,14,15-Decahydro-5*H*-cyclododec[*a*]indene.—The reaction of *o*-bromobenzyl alcohol (0.0535 mol) and cyclododecanone was carried out as described in B above. The acidic solution (H_2SO_4 in acetic acid) was heated for 22 hr and the crude product (7.20 g) was chromatographed to give 4.62 g (35% yield from *o*-bromobenzyl alcohol) of essentially pure (glpc) decahydrocyclododec[*a*]indene as an oil which crystallized. There was obtained from the oil 3.58 g (26% yield) of decahydrocyclododec[*a*]indene, mp 49–52° (lit.[7] mp 53.5–55°). The ir and nmr spectra were identical with those of an authentic sample.[7]

3-Phenylindene.—The reaction of *o*-bromobenzyl alcohol (0.0535 mol) with acetophenone was carried out as described for other ketones. The crude solid diol (10.85 g) showed only minor impurities (nmr) but was not further characterized. The product was treated first with boron trifluoride etherate (total of 10.10 g, 0.71 mol) for 24 hr in boiling benzene; however, the nmr spectrum of the only product (9.51 g) showed no indene and was consistent with the corresponding cyclic ether. The crude ether was treated with sulfuric acid (3.54 g, 0.036 mol) in hot (reflux temperature) glacial acetic acid (455 ml) for 12 hr as described above. The brown oil (7.16 g) thus obtained was distilled, bp 93–99° (0.03 mm), through a short path column to give 3.62 g (35.2% yield) of a light yellow oil. Glpc analysis (5 ft × 0.25 in., 20% DC 710 on Chromosorb W 60–80 mesh, 210°, 60 ml/min He) with internal standard *n*-octadecane showed the distillate to contain 65.5 wt % (2.37 g, 23%) yield of 3-phenylindene (retention time 6 min 10 sec).

A pure sample of 3-phenylindene was obtained by preparative glpc and had the following properties: refractive index $n^{25}\mathrm{D}$ 1.6308 (lit. $n^{20}\mathrm{D}$ 1.6320,[8] $n^{24}\mathrm{D}$ 1.6313,[9] $n^{18}\mathrm{D}$ 1.6357[10]); uv max (95% C_2H_5OH) 204 mμ (log ϵ 4.52), 228 (4.33), 257 (sh, 3.89), 282 (sh, 3.27), 293 (2.87); nmr ($DCCl_3$) (with areas relative to 12 protons) τ 2.22–2.86 (complex multiplet, 9.0, aromatic H), triplet centered at 3.40 (J = 2 Hz, 1.0 proton in 2 position), doublet centered at 6.51 (J = 2 Hz, 2.0 protons in 1 position).

Reaction of 3 with Sulfuric Acid in Formic Acid. Isolation of Indene and By-product Indan.—The cyclic ether **3** (6.53 g, 0.0323 mol) and 52 ml of 88% formic acid (Baker) were added to a 100-ml round-bottom flask equipped with a condenser and magnetic stirrer. Concentrated sulfuric acid (5.9 g, 0.60 mol) was added and the mixture was heated to reflux temperature (reaction mixture turned red). After 30 min at reflux temperature the reaction was quenched by adding it to 75 ml of ice water with stirring. The aqueous mixture was extracted with two 100-ml portions of petroleum ether and one 100-ml portion of benzene. The combined organic extracts were washed with 100 ml of water, 100 ml of saturated aqueous sodium bicarbonate, and 100 ml of water in succession and then dried ($MgSO_4$) and filtered. The solvent was removed by rotary evaporation to 6.31 g of orange oil which showed primarily desired indene and no unreacted ether (benzylic CH_2O) by nmr spectroscopy. The crude oil was chromatographed (fraction analyzed by tlc every 125 ml) over 200 g of 100–200 mesh silica gel (Matheson Coleman and Bell) with petroleum ether as eluent. The first 1.3 l. of eluent were concentrated (rotary evaporation) to a colorless oil (0.259 g, 4.3% yield). The oil was purified by preparative glpc and showed the following properties: refractive index $n^{26}\mathrm{D}$ 1.5459; ir (neat), 3050 (w), 3000 (w), 2900 (s), 2832 (s), 1480 (m), 1460 (m), 1440 (w), 1020 (w), 740 cm^{-1} (s); uv max (95% C_2H_5OH) 209 mμ (log ϵ 3.94), 212 (3.94), 217 (sh, 3.87), 253 (sh, 2.77), 260 (2.99), 266 (3.16), 273 (3.21); nmr (5% w/v $DCCl_3$) (with areas relative to 18 protons) τ 2.80 (s, 4.0, aromatic H), 6.43–7.80 (complex, 4.4, benzylic CH_2 and methine CH), 7.80–8.90 (complex, 9.6, bridge CH_2); mass spectrum *m/e* 186 (parent peak, 58% of base peak), P − 57 (base peak).

This product was identical with that obtained (97% yield) by reduction (absorption of 1 molar equiv of hydrogen) of pentahydrocyclohept[*a*]indene (absolute ethanol, Raney nickel, 22°, 24 hr, 45 psi).

Anal. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74. Found: C, 90.52; H, 9.68.

The next 1.9 l. of eluent were concentrated to 2.40 g (40% yield) of yellow oil which crystallized to a solid (mp 44–51°) which yielded white needles of **4** (1.80 g, 30% yield, mp 50.5–52°, lit.[3] mp 50.5–51.5°) upon recrystallization from an ethanol and water mixture at −22°.

Conversion of Pure 1-(*o*-Hydroxymethylphenyl)cycloheptanol (2) to 6,7,8,9,10-Pentahydro-5*H*-cyclohept[*a*]indene. With Polyphosphoric Acid.—A sample of **2** (0.500 g, 2.27 mmol) was added to 9.5 g of polyphosphoric acid (9.5 g, City Chemical) at 22°. The mixture turned dark and the temperature rose to 31°. After 20 min the reaction was hydrolyzed (25 ml ice water). Analysis of the oil (0.428 g), obtained subsequent to washing, drying, and solvent removal, by glpc (5 ft × 0.25 in., DC 710 on Chromosorb W, 60–80 mesh, 210°, 60 ml/min He) with *n*-heptadecane as an internal standard showed the product to contain 29 wt % (0.12 g, 30% yield) of **4** and 26 wt % (0.11 g, 26% yield) of reduced pentahydrocyclohept[*a*]indene (the indan **6**).

With Boron Trifluoride Etherate.—The reaction was carried out as described above in section A using 1.73 mmol of **2** and 1.73 mmol of boron trifluoride etherate in 9 ml of benzene. The reaction progress was followed by glpc analysis (see section A) using *n*-heptadecane as an internal standard (the relative response[11] factors of the cyclic ether **3** and the indene **4** were determined with pure samples). Glpc analysis showed the following prior to reflux: immediately after mixing, **3** (80%), **4** (10%); after 2.5 hr, **3** (88%), **4** (10%). The mixture was heated

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to reflux and glpc analysis showed, after 15 min, **3** (60%), **4** (36%), indan **6** (0%); after 2 hr, **3** (14%), **4** (70%), **6** (6%); after 3 hr, **3** (10%), **4** (73%), **6** (7%); after 6 hr, **3** (0%), **4** (68%), **6** (7%).

Additional boron trifluoride etherate (0.260 g, 1.82 mmol) was added to the refluxing solution. Glpc analysis showed a steady decrease in **4** to 18% yield after 13.5 hr with no detectable increase in the amount of indan formation.

With *p*-Toluenesulfonic Acid in Glacial Acetic Acid.—1-(*o*-Hydroxymethylphenyl)cycloheptanol (**2**) (0.270 g, 1.23 mmol), *p*-toluenesulfonic acid monohydrate (0.0534, 0.281 mmol), an internal standard *n*-heptadecane (0.0563 g), and 8 ml of glacial acetic acid were added to a 50-ml two-neck round-bottom flask equipped with magnetic stirrer, condenser, and nitrogen inlet. The solution was heated to reflux temperature and the reaction process was followed by glpc analysis (5 ft × 0.25 in. 20% DC 710 on 60–80 mesh Chromosorb W, 210°, 60 ml/min He) with the following results: after 1 hr, **3** (68%), **4** (31%); after 3 hr, **3** (51%), **4** (40%). No indan by-product (**6**) was observed by glpc.

Reaction with Sulfuric Acid in Glacial Acetic Acid.—Concentrated sulfuric acid (0.09 g, 0.92 mmol) was added to a solution of *o*-(1-cycloheptanol) benzyl alcohol **2** (0.135 g, 0.610 mmol), *n*-heptadecane (0.0563 g) (internal standard) and 8 ml of acetic acid at the reflux temperature. Glpc analysis (5 ft 0.25 in. 20% DC 710 on 60–80 mesh Chromosorb W, 210°, 60 ml/min He) showed, after 5 hr, **3** (20%), **4** (60%); after 17 hr, **3** (0%), **4** (73%). None of the side product **6** was detected by glpc.

Registry No.—**2**, 34219-85-7; **3**, 32921-59-8; **4**, 34219-87-9; **6**, 34219-89-1; 6,7,8,9,10,11,12-heptahydro-5*H*-cyclonone[*a*]indene, 34219-88-0; 3-phenylindene, 1961-97-3

Homogeneous Hydrogen-Transfer Reactions Catalyzed by Tricarbonylchromium Complexes. Hydrogenation of Trienes[1]

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Hydrogenating 1,3,5-cycloheptatriene with methyl benzoate-Cr(CO)$_3$ yields a mixture of 1,3-cycloheptadiene and cycloheptene. The formation of 1,3- instead of 1,4-cycloheptadiene is in contrast to the results obtained with acyclic conjugated trienes. Deuteration experiments rule out 1,6 addition and support a mechanism involving 1,4 reduction followed by rapid isomerization of 1,4- to 1,3-cycloheptadiene (1,3-hydrogen-deuterium shift). Catalytic hydrogenation of *trans*-1,3,5-hexatriene with methyl benzoate-Cr(CO$_3$) yields *cis*-1,4-hexadiene as the most important intermediate, the product expected from 1,4 addition. Hydrogenation of *cis*-1,3,5-hexatriene gives mainly cyclohexene. This product is derived from 1,3-cyclohexadiene formed by thermal cyclization of the cis hexatriene.

The homogeneous hydrogenation of unsaturated compounds continues to be the subject of intensive investigation. A high degree of selectivity is probably the most important practical characteristic of homogeneous hydrogenation catalysts.[3] Our studies of the catalytic activity of arene–Cr(CO)$_3$ complexes have demonstrated a selectivity approaching 100% in the hydrogenation of 1,3 and 1,4 dienes to monoenes.[4] Selectivity, kinetic, and deuterium tracer studies[4c,5] have provided ample evidence for 1,4 addition of hydrogen as the dominant mechanism of reduction catalyzed by these arene–Cr(CO)$_3$ complexes. With 1,4 dienes and monoenes, double-bond isomerization by 1,3-hydrogen shift was indicated.[5b]

Hydrogenation of methyl β-eleostearate (*all-trans*-9,11,13-octadecatrienoate) with these complexes yielded the diene products expected from 1,4 addition (*trans*-9,*cis*-12- and *cis*-10,*trans*-13-octadecadienoates).[6] With α-eleostearate (*cis*-9,*trans*-11,*trans*-13-octadecatrienoate) stereoselective 1,4 reduction producing up to 60% linoleate (*cis*-9,*cis*-12-octadecadienoate) was observed, but concurrent isomerization to β-eleostearate yielded also the corresponding cis,trans-1,4-diene products. This paper reports an extension of these studies to the hydrogenation of 1,3,5-cycloheptatriene and 1,3,5-hexatriene.

Results and Discussion

1,3,5-Cycloheptatriene.—Hydrogenations and deuterations were catalyzed by methyl benzoate–Cr(CO)$_3$ as in earlier work.[4c,5] Figure 1 plots results of kinetic runs with H$_2$ and D$_2$. 1,3-Cycloheptadiene was the main initial product detected by glc. Cycloheptene was formed in only minor amounts at 160°, but at 175° it was formed in significant amounts after 1,3-cycloheptadiene reached a maximum concentration of 80%. On the basis of previous work,[5] no significant kinetic isotopic effect would be expected. Identification of 1,3-cycloheptadiene by glc was confirmed by uv and ^{1}H nmr analyses of the hydrogenation products. That there was no 1,4-cycloheptadiene in the products was demonstrated by the absence of resonance corresponding to the α,α-methylene proton (C=CCH$_2$C=C) on C-3 (τ 7.20).

The formation of 1,3- instead of 1,4-cycloheptadiene

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