crystals of 2-phenylbenzo[b]thiophene had sublimed to the top of the flask. These were recrystallized from 10 ml of absolute ethanol, giving 110 mg of white plates, mp 170–171°. Another recrystallization raised the melting point to 171.5–172° (lit.[17] mp 171–172°, lit.[15] 172–173°; note also footnote 18).

No rearrangement of 2-phenylbenzo[b]thiophene took place in the absence of an acid catalyst, and the starting material was recovered unchanged.

Preparation of 2-Carboxy-3-phenylbenzo[b]thiophene.—The Grignard reagent was prepared as above from 868 mg (3.0 mmol) of 2-bromo-3-phenylbenzo[b]thiophene and 100 mg (4.0 mg-atoms) of magnesium in 9 ml of dry THF. The nitrogen atmosphere was replaced with dry tank carbon dioxide and the solution was heated at reflux for 25 hr under positive CO_2 pressure. The solution was evaporated at reduced pressure and the residue was treated with 2 ml of concentrated HCl in 15 ml of water. Extraction with two 15-ml portions of diethyl ether followed. The ether solution was extracted with three 10-ml portions of saturated sodium bicarbonate solution, which gave an aqueous suspension of the product sodium salt. The combined bicarbonate layers were acidified with dilute HCl and extracted with three 20-ml portions of ether. The combined ether extracts were dried and evaporated and the remaining yellow powder was recrystallized from 15 ml of 70% aqueous ethanol. A first crop of 394 mg, mp 198–199°, and a second crop of 121 mg were obtained, a total yield of 68%. Recrystallization from 50% aqueous ethanol gave an analytical sample, mp 199.0–199.5°, with prior softening at about 175°: ir (Nujol) 2550 (broad, OH), 1650 (s), 1520 (s), 1485 (m), 1340 (m), 1295 (s), 1250 (m), 1180 (w), 1125 (w), 1080 (m), 1050 (w), 920 (m), 860 (w), 780 (w), 755 (s), 745 (m), 740 (s), 715 (m), and 700 cm^{-1} (s).

Anal. Calcd for $C_{15}H_{10}O_2S$: C, 70.84; H, 3.96; S, 12.61. Found: C, 70.68; H, 4.29; S, 12.49.

Registry No.—VII, 14315-12-9; VIII, 29491-86-9; phenylmercuric bromide, 1192-89-8; tetrachlorothiirane, 22706-41-8; 2,2-dichloro-3,3-diphenylthiirane, 34281-40-8; 2-bromo-2-chloro-3,3-diphenylthiirane, 34281-41-9; 2,2-dibromo-3,3-diphenylthiirane, 34281-42-0; 2-chloro-3-phenylbenzo[b]thiophene, 34281-43-1; 2-bromo-3-phenylbenzo[b]thiophene, 34281-44-2.

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Selective Hydrogenation of α,β-Unsaturated Carbonyl Compounds *via* Hydridoiron Complexes

R. NOYORI,* I. UMEDA, AND T. ISHIGAMI

Department of Chemistry, Nagoya University, Nagoya, Japan

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A reagent generated *in situ* from iron pentacarbonyl and a small amount of base in moist solvents serves as a new, efficient agent for selective hydrogenation of α,β-unsaturated carbonyl compounds (ketones, aldehydes, esters, and lactones, etc.) under mild reaction conditions. The characteristics and the possible mechanisms of the reduction are described.

The reduction of α,β-unsaturated carbonyl compounds (eq 1) has been effected *chemically* by dissolv-

$$RCH{=}CHCOR' \longrightarrow RCH_2CH_2COR' \qquad (1)$$

ing alkali metals such as Li, Na, and K in liquid ammonia (Birch conditions),[1] and amalgamated zinc in hydrochloric acid (Clemmensen conditions).[2] Because such reductions require strongly basic or acidic conditions, which often cause undesired side reactions, their synthetic utility has been restricted. Sodium borohydride also has been employed in certain cases, but lacks general utility.[3] The homogeneous, transition metal catalyzed reduction of unsaturated compounds, most of which proved to involve metal hydride complexes, is the subject of current interest.[4] However, there have so far been few attempts to gain selectivity for homogeneous reduction of α,β-unsaturated carbonyl compounds.[5,6] This paper describes a new, selective reduction of α,β-unsaturated carbonyl compounds by means of iron-based complexes under mild reaction conditions.

Results and Discussion

Treatment of unsaturated carbonyl derivatives with a reagent generated *in situ* from iron pentacarbonyl [$Fe(CO)_5$] and a small amount of NaOH in 95% CH_3OH at 0–60° under nitrogen atmosphere gave the corresponding saturated derivatives in high yield (condition A). A mixture of ether and H_2O (4:1 v/v) which provides a two-layer reaction system may be used in place of 95% CH_3OH (condition B). Besides NaOH, 1,4-diazabicyclo[2.2.2]octane (DABCO) in moist dipolar solvents such as *N*,*N*-dimethylformamide (DMF) or *N*,*N*,*N'*,*N'*,*N''*,*N''*-hexamethylphosphoric triamide (HMPA) gave satisfactory results (condition C). As exemplified in Table I, this reduction method is applicable to a wide variety of α,β-unsaturated carbonyl compounds including ketones, aldehydes, esters, lactones, etc.

The present procedure, within limits of the experiments examined, possesses the following characteristics: (1) overreductions of the ketonic group into >CHOH or $>CH_2$ groups are negligible; (2) ester

(1) (a) A. J. Birch, *Quart. Rev., Chem. Soc.*, **4**, 69 (1950); (b) H. Smith, "Organic Reactions in Liquid Ammonia," Interscience, New York, N. Y., 1963; (c) M. Smith in "Reduction," R. L. Augustine, Ed., Marcel Dekker, New York, N. Y., 1968, p 95.

(2) J. G. St. C. Buchanan and P. D. Woodgate, *Quart. Rev., Chem. Soc.*, **23**, 522 (1969).

(3) (a) W. R. Jackson and A. Zurqiyah, *J. Chem. Soc.*, 5280 (1965); (b) K. Iqbal and W. R. Jackson, *J. Chem. Soc. C*, 616 (1968), and references cited therein.

(4) Reviews: (a) Collected papers presented at the symposium on homogeneous catalysis, Liverpool, U. K., Sept 17 and 18, 1968, in *Discuss. Faraday Soc.*, **46** (1968); (b) M. E. Vol'pin and I. S. Kolomnikov, *Russ. Chem. Rev.*, **38**, 273 (1969).

(5) $Ru(II)Cl_2$ in aqueous HCl exhibited marked selectivity: J. Halpern, J. F. Harrod, and B. R. James, *J. Amer. Chem. Soc.*, **88**, 5150 (1966).

(6) For heterogeneous, *catalytic* hydrogenation systems, see R. L. Augustine, "Catalytic Hydrogenation," Marcel Dekker, New York, N. Y., 1965, p 60.

Table I

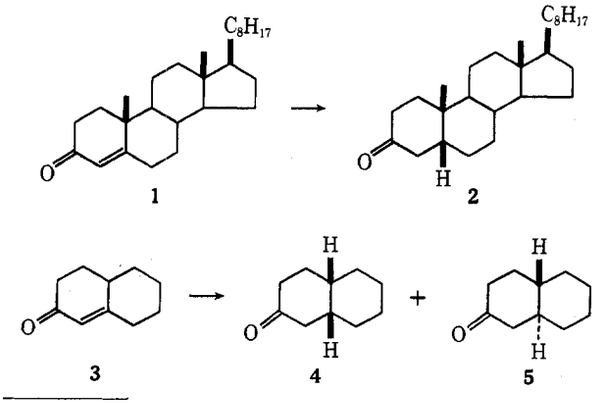
Selective Hydrogenation with Iron Carbonyl

Registry no.	Substrate	Condition[a]	Reaction temp, °C	Reaction time, hr	Product	Yield, %[b]
122-57-6	Benzalacetone	A	20	12	Benzylacetone	>98
		B	20	48		91
		C	20	48		>98
94-41-7	Benzalacetophenone	A	20	12	Benzylacetophenone	>98
		B	20	12		>98
495-41-0	Crotonophenone	A	0	3	Butyrophenone	>98
		B	20	12		>98
		C	20	17		>98
78-94-4	Methyl vinyl ketone	A	0	3	Ethyl methyl ketone	>98
141-79-7	Mesityl oxide	A	60	24	Isobutyl methyl ketone	96
		C	20	36		>98
930-68-7	2-Cyclohexenone	A	20	10	Cyclohexanone	96
		C	20	36		>98
		C[c]	20	20		93
1121-18-2	2-Methyl-2-cyclohexenone	A	60	24	2-Methylcyclohexanone	35[d]
1193-18-6	3-Methyl-2-cyclohexenone	A	60	24	3-Methylcyclohexanone	52[d]
601-57-0	4-Cholesten-3-one	B	20	36	Coprostanone[e]	32[d]
1196-55-0	$\Delta^{1,9}$-2-Octalone	B	20	24	2-Decalones[f]	35[d]
1728-25-2	2-Cyclooctenone	A	20	12	Cyclooctanone	>98
		B	20	18		>98
		C	20	24		>98
4170-30-3	Crotonaldehyde	A	0	2	Butyraldehyde	>98
104-55-2	Cinnamaldehyde	A	20	12	3-Phenylpropionaldehyde	98
103-26-4	Methyl cinnamate	A	20	48	Methyl 3-phenylpropionate	90
624-48-6	Dimethyl maleate	A	0	12	Dimethyl succinate	96
624-49-7	Dimethyl fumarate	A	0	12	Dimethyl succinate	92
108-54-3	5-Hydroxy-2-hexenoic acid δ-lactone	C	60	12	5-Hydroxyhexanoic acid δ-lactone	90
4360-47-8	Cinnamonitrile	A	20	36	3-Phenylpropionitrile	92
7187-01-1	3-(2-Furyl)acrylonitrile	C	60	9	3-(2-Furyl)propionitrile	75

[a] See Experimental Section for details. Under condition C, unless otherwise stated, DMF was used as solvent. [b] Determined by glpc analysis. [c] Moist HMPA was used as solvent. [d] The remainder consisted mainly of the starting material. Side reactions were negligible. [e] Isomeric purity 95%. [f] Cis:trans 37:63.

functions are not reduced; (3) reductive coupling of ketones to pinacols, frequently encountered under Birch conditions, is not observed; (4) no skeletal rearrangements, often promoted under Clemmensen conditions, take place; (5) phenyl and furyl groups are not affected; and (6) the rate of the reduction is profoundly influenced by steric environments around double bonds (competition experiments demonstrated that relative reactivities of 2-cyclohexenone, 2-methyl-2-cyclohexenone, and 3-methyl-2-cyclohexenone are 1.00, 0.10, and 0.017, respectively).[7]

As to the stereochemistry of the reduction, 4-cholesten-3-one (1) was converted selectively into coprostanone (2) having cis stereochemistry at the A/B ring juncture (condition B), whereas $\Delta^{1,9}$-2-octalone (3) was reduced to afford a stereoisomeric mixture of 2-decalones **4** and **5** (37:63 ratio).[8]



The reduction in deuterated solvents serves as a convenient method for specific deuteration at the position β to the carbonyl group.[11] For instance, reduction of crotonophenone under condition A using NaOD–D_2O–CH_3OD gave crude butyrophenone-α,β-d_2. Treatment of the product with CH_3ONa–CH_3OH gave butyrophenone-β-d_1, while work-up with CH_3ONa–CH_3OD afforded butyrophenone-α,α,β-d_3. Deuterium incorporation into the unreacted ketone was not observed.[12]

Noteworthy are the facts observed in the reaction of dimethyl fumarate and maleate in CH_3OD: (1) maleate isomerizes to fumarate during the reduction (2) recovered fumarate contains a considerable amount of deuterium atom, whereas only a slight incorpora-

(7) Isolated double bonds are not hydrogenated, but positionally isomerize slowly. This might offset to some extent the advantages of the present method.

(8) Catalytic reduction of **1** on PdO gave a stereoisomeric mixture, the cis/trans ratio depending on the nature of the solvent used: *e.g.*, 11.5:1 in C_2H_5OH–20% aqueous NaOH and 1.44:1 in C_2H_5OH–3 *N* HCl.[9] Hydrogenation of **3** on 10% Pd–C or PtO_2 yielded a mixture of isomeric decalones in favor of the cis isomer **4**.[10]

(9) S. Nishimura, M. Shimahara, and M. Shiota, *J. Org. Chem.*, **31**, 2394 (1966).

(10) (a) A. Marchant and A. R. Pinder, *J. Chem. Soc.*, 327 (1956); (b) R. L. Augustine, *J. Org. Chem.*, **23**, 1853 (1958).

(11) Previous methods: (a) (Li–ND_3) D. H. Williams, J. M. Wilson, H. Budzikiewicz, and C. Djerassi, *J. Amer. Chem. Soc.*, **85**, 2091 (1963); (b) (Li–$C_3H_7ND_2$) M. Fetizon and J. Gore, *Tetrahedron Lett.*, 471 (1966).

(12) H. W. Whitlock, Jr., C. R. Reich, and R. L. Markezich, *J. Amer. Chem. Soc.*, **92**, 6665 (1970).

TABLE II
REACTION OF DIMETHYL FUMARATE AND MALEATE IN CH_3OD–D_2O[a]

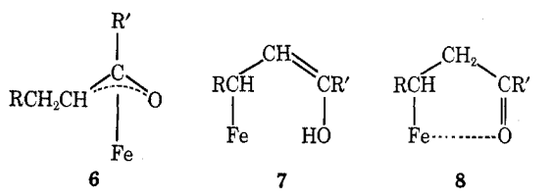
Substrate	Recovered fumarate, %	Recovered maleate, %	Dimethyl succinate, %
Dimethyl fumarate	86 (0.14 D)[b]	0	14 (2.10 D)[c]
Dimethyl maleate	33 (0.22 D)[d]	54 (0.04 D)[e]	13 (2.00 D)[c]

[a] Results of the reaction using 2 equiv of $Fe(CO)_5$ under condition A (0°, 12 hr). Product composition was determined by glpc. Deuterium content of the esters shown in parentheses was obtained by nmr (error <5%). Isotope distribution was determined by mass spectral analysis. [b] 87% d_0, 12% d_1, and 1% d_2. [c] Consists mainly of *meso*- and *dl*-succinate-2,3-d_2: C. R. Childs, Jr., and K. Bloch, *J. Org. Chem.*, **26**, 1630 (1961). [d] 79% d_0, 20% d_1, and 1% d_2. [e] 96% d_0 and 4% d_1.

tion was observed in unreacted maleate (Table II). These phenomena are reminiscent of the recently reported reaction of $HCo(CO)_4$ and dimethyl maleate, where hydrogenation to succinate was claimed to proceed *via* fumarate.[13] In the present case, however, maleate also seems susceptible to the hydrogenation, because (1) reduction of fumarate induced a higher, or at least comparable, extent of deuterium incorporation in the product compared with the case of maleate; (2) apparently both esters were reduced at a comparable rate without an appreciable induction period.

Although the exact nature of the species responsible for the reduction remains unspecified, the reaction most probably proceeds by way of hydridoiron complexes.[14] The present reaction conditions would be expected to produce a complicated mixture of mono-, di-, and trinuclear iron complexes [$H_2Fe(CO)_4$, $H_2Fe_2(CO)_8$, and $H_2Fe_3(CO)_{11}$, respectively], and their salts,[15,16] the composition being subtly influenced by various factors, *e.g.*, kind of solvent and base, ratio of $Fe(CO)_5$ and the base, temperature, and reaction time. The appearance of the characteristic wine-red color suggests the formation of anionic di- and trinuclear complexes ($[HFe_2(CO)_8]^-$ and $[HFe_3(CO)_{11}]^-$),[16] and control experiments demonstrated that these species do reduce 2-cyclohexenone. However, the possibility that feebly colored mononuclear complexes are the major reducing agents could not be excluded. The anionic species is produced according to the stoichiometry $Fe(CO)_5 + 3OH^- \rightarrow [HFe(CO)_4]^- + CO_3^{2-} + H_2O$, and then oxidatively converted to the di- and trinuclear complexes.[15] However, the use of a ratio of $NaOH:Fe(CO)_5$ higher than 1:2 (under condition A) induced significant side reactions and gave decreased yields of the reduction products.[17]

The reaction intermediate might have a π-enolate structure of type **6**.[14] Alternatively, the reduction might proceed *via* the organoiron complexes of type **7**[13] or **8**.[18] However, the s-cis conformation, which facilitates the conjugate addition or the carbonyl chelation, would not be a necessary condition for the reaction since cyclic unsaturated compounds are readily reduced.



6 **7** **8**

Experimental Section

General.—Commercial $Fe(CO)_5$ (Strem Chemicals, Inc.) and CH_3OD (99%, Merck) were used without further purification. Reagent grade CH_3OH, DMF, and HMPA were used after distillation. Ether was purified before use by passing through a column of basic alumina. Benzalacetophenone,[19] crotonophenone,[20] 2-methyl-2-cyclohexenone,[21] $\Delta^{1,9}$-2-octalone,[22] 2-cyclooctenone,[23] 5-hydroxy-2-hexenoic acid δ-lactone,[24] cinnamonitrile,[25] and 3-(2-furyl)acrylonitrile[25] were prepared according to the known procedures. Other starting materials were obtained commercially, and, in most instances, liquid reagents were distilled and solids were recrystallized before use.

Nuclear magnetic resonance (nmr) spectra were taken with a JEOLCO C-60H spectrometer in CCl_4 solution with tetramethylsilane as internal standard. Mass spectra were obtained on a Hitachi RMU 6C mass spectrometer at 70 eV using a heating inlet system. Analytical gas–liquid partition chromatography (glpc) was performed on a Yanagimoto Model G8 instrument with flame ionization detector and nitrogen carrier gas. The columns (3 mm × 2 m) used were 5% diisodecyl phthalate on Celite 545, 5% polyethylene glycol 4000 (with and without $AgNO_3$) on Celite 545, 5% polyethylene glycol succinate on Neopak 1A, 2% silicone OV-17 on Chromosorb W, and 5% silicone SE-30 on Chromosorb W. Yields of the products were determined by cut-and-weigh integration of glpc traces using added standards for correction for detector response differences. Preparative glpc was carried out on a Yanagimoto Model 3D instrument with thermal conductivity detector and a column (5 mm × 1 m) of 5% polyethylene glycol succinate on Neopak 1A using helium carrier gas. Analytical and preparative thin layer chromatography (tlc) was carried out on silica gel plates (Merck silica gel GF_{254}, buffered at pH 7, 0.25-mm and 1.0-mm thickness, respectively).

Procedure.—$Fe(CO)_5$ is toxic, and great care must be exercised in its handling. All reactions and work-ups must be carried out in a well-ventilated hood. All reactions were conducted in a 10-ml round-bottomed flask with a neck and a sidearm to accommodate a three-way stopcock and a rubber serum cap, respectively. Stirring was effected magnetically. Liquid reagents and solutions in the case of solids were transferred with a hypodermic syringe.

The general execution of the present method (condition A) is illustrated by the procedure for the conversion of benzalacetone to benzylacetone. A mixture of $Fe(CO)_5$ (784 mg, 4.0 mmol) and NaOH (80 mg, 2.0 mmol) in a 95:5 v/v mixture of CH_3OH and H_2O (2.0 ml) was flushed with nitrogen and stirred for 5 min at room temperature to ensure the complete depletion of NaOH. To the resulting dark-red solution was added benzalacetone (146 mg, 1.0 mmol) in one portion, and the mixture was allowed to stir at ambient temperature. After a reaction time of 12 hr, the excess reducing agents were decomposed by adding an ethereal solution of I_2 (*Caution:* vigorous foaming occurred), and the mixture was treated with H_2O and extracted with ether. The combined extracts were washed with sodium thiosulfate solution, dried over Na_2SO_4, and concentrated *in vacuo*. The residual oil was subjected to preparative tlc (R_f 0.39, 1:1 *n*-hexane–benzene mixture) to give pure benzylacetone (134 mg, 90% yield; >98% by glpc). The identity was established by comparison of the

(13) P. Taylor and M. Orchin, *J. Organometal. Chem.*, **26**, 389 (1971).
(14) Reduction with $HCo(CO)_4$: R. W. Goetz and M. Orchin, *J. Amer. Chem. Soc.*, **85**, 2782 (1963).
(15) H. W. Sternberg, R. Markby, and I. Wender, *ibid.*, **79**, 6116 (1957), and references cited therein.
(16) J. R. Case and M. C. Whiting, *J. Chem. Soc.*, 4632 (1960).
(17) A reaction aliquot diluted with a 20-fold volume of H_2O showed pH *ca.* 9.
(18) For the related ir complex, see M. McPartlin and R. Mason, *J. Chem. Soc. A*, 2206 (1970).
(19) E. P. Kohler and H. M. Chadwell, "Organic Syntheses, Collect. Vol. I, Wiley, New York, N. Y., 1956, p 78.
(20) R. C. Fuson, R. E. Christ, and G. M. Whitman, *J. Amer. Chem. Soc.*, **58**, 2450 (1936).
(21) E. W. Warnhoff, D. G. Martin, and W. S. Johnson, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 162.
(22) G. Stork, A. Brizzolara, H. Landesman, J. Szmuzkovicz, and R. Terrell, *J. Amer. Chem. Soc.*, **85**, 207 (1963).
(23) E. W. Garbisch, Jr., *J. Org. Chem.*, **30**, 2109 (1965).
(24) R. Kuhn and D. Jerchel, *Ber.*, **76**, 413 (1943).
(25) J. M. Patterson, *Org. Syn.*, **40**, 46 (1960).

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_2-$CH_2COC_6H_5$ 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 $(C_2H_5)_3$-NH^+–$[HFe_3(CO)_{11}]^-$ (546 mg, 1.0 mmol)[16] in CH_3OH (2.0 ml) at room temperature for 6 hr afforded cyclohexanone in 23% yield.

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

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

An Improved Synthesis of Indenes[1]

WILLIAM E. PARHAM* AND DAVID C. EGBERG

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

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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.

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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