TABLE II
HYDROGENATION OF CYCLOOCTENE WITH SOLUBLE HYDROGENATION CATALYSTS AS A FUNCTION OF Li/Co RATIO AND CATALYST LEVEL[a]

Entry	Li/Co[b]	Catalyst level, mol %	Time, min	% conversion
1	1.7	0.3	90	8
2	4.0	0.3	30	100
3	5.6	0.3	20	99
4	6.0	0.3	20	100
5	9.9	0.3	90	16
6	5.6	0.05	90	0
7	5.6	0.1	30	93
8	5.6	0.3	20	99
9	4.7[c]	0.3	90	98

[a] Hydrogen pressure 50 psi, 50°. [b] Molar ratio. [c] *n*-Butyllithium–nickel octoate cocatalysts.

with 0.05 mol % catalyst may be due to loss of catalyst by oxidation or other impurities.

Transition metal salts other than cobalt 2-ethylhexanoate may be used as cocatalysts in the hydrogenation of olefins. Nickel 2-ethylhexanoate–*n*-butyllithium hydrogenation catalyst is less active than its cobalt counterpart (Table II, entry 9).

A number of alkyl- or aryllithiums have been used in place of *n*-butyllithium as cocatalysts with cobalt 2-ethylhexanoate in the hydrogenation of olefins. Comparative data at 50°, 50 psi of hydrogen pressure, Li/Co = 4.0, are listed in Table III. Similar reactivity is observed with aromatic and primary and secondary alkyllithiums. Hydrogenation activity is diminished significantly if cyclopentyllithium is used as the cocatalyst, but this may reflect the unknown purity of cyclopentyllithium.

TABLE III
HYDROGENATION OF OLEFINS WITH SOLUBLE HYDROGENATION CATALYSTS AS A FUNCTION OF LITHIUM SOURCE[a]

Lithium source	Olefin	Time, min	% conversion
n-Butyllithium	*cis*-Pentene-2	20	100
Ethyllithium	Cyclooctene	10	100
sec-Butyllithium	Cyclooctene	10	100
Cyclopentyllithium	Cyclooctene	90	63
Phenyllithium	Hexene-1	10	100

[a] Hydrogen pressure 50 psi, Li/Co = 4.0, 50°, 0.3 mol % catalyst.

Cycloolefins may be selectively reduced in the presence of their 1-methyl counterparts. Cyclohexene in a 50% mixture of cyclohexene and 1-methylcyclohexene is quantitatively reduced in 10 min while 18% reduction of 1-methylcyclohexene occurs. A *n*-butyllithium–cobalt 2-ethylhexanoate catalyst was used having a Li/Co of 6.0 at a 0.2 mol % catalyst level at 50°, 50 psi of hydrogen pressure. In an analogous experiment with a 50% mixture of cycloheptene and 1-methylcycloheptene, cycloheptene is quantitatively reduced in 10 min while 25% reduction of the 1-methyl derivative occurs. The selectivity is not absolute and higher ratios of Li/Co may show improved selectivity.

An active soluble lithium-based hydrogenation catalyst system has been discussed in terms of several reaction parameters. This catalyst system is as active as aluminum-based systems at convenient catalyst concentrations and offers as an advantage the ease of handling of organolithiums compared with other hydrogenation catalysts such as alkylaluminums.

Experimental Section

Materials.—Aryl- and alkyllithium reagents were purchased from the Foote Chemical Co. A solution of cobalt 2-ethylhexanoate in cyclohexane was purchased from the Harshaw Chemical Co. and nickel 2-ethylhexanoate was purchased from K & K Laboratories. The olefins were purchased from either the Eastman Kodak Co. or the Aldrich Chemical Co. and were distilled and stored over molecular sieves prior to use. Solvents were passed through molecular sieves. All reactions and reagent transfers were carried out under a dry nitrogen atmosphere.

Catalyst Preparation.—A 0.285 *M* solution of catalyst (molarity based upon the amount of lithium) was prepared by adding 14.1 g of cobalt 2-ethylhexanoate solution (12.0% cobalt, w/w) over a period of 90 min to a solution of 0.0854 mol of *n*-butyllithium in 287 ml of cyclohexane; Li/Co = 3.0. Other ratios were prepared in the same manner.

Olefin Hydrogenation.—In a typical example, cycloheptene (44.9 g) was dissolved in 1500 ml of cyclohexane and placed with 0.5 mol % of a *n*-butyllithium–cobalt 2-ethylhexanoate catalyst having a lithium/cobalt ratio of 3.0:1 in a 2-l. reactor thermostated at 50°. The reactor was kept at a constant hydrogen pressure of 50 psi throughout the hydrogenation. Aliquots of the reaction mixture were withdrawn periodically, and the per cent conversion was determined by measuring the amounts of cycloheptane and cycloheptene using a F & M Dual Flame Model 810 gas chromatograph with an activated alumina column at 200°.

Registry No.—Cyclooctene, 931-88-4; cyclohexene, 110-83-8; cycloheptene, 628-92-2; 1-methylcyclohexene, 591-49-1; *cis*-pentene-2, 627-20-3; hexene-1, 592-41-6; 2-methylpentene-2, 625-27-4; *trans*-pentene-2, 646-04-8; styrene, 100-42-5; 2,3-dimethylbutene-2, 563-79-1; *n*-butyllithium, 109-72-8; cobalt 2-ethylhexanoate, 136-52-7; nickel octanoate, 4995-91-9; ethyllithium, 811-49-4; *sec*-butyllithium, 598-30-1; cyclopentyllithium, 23473-12-3; phenyllithium, 591-51-5.

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The Deconjugation of Isophorone[1]

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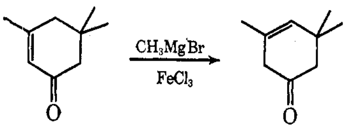
We were interested in an efficient procedure for the deconjugation of isophorone (**1**) to β-phorone (**2**) in connection with our recent synthesis of an allenic sesquiterpene.[2] While Kharasch and Tawney[3] have described a procedure for accomplishing this transformation, we found that the results were disappointingly erratic, giving sometimes large amounts of viscous, black material and sometimes a mixture of two crystalline products.

[1] Supported by NIH Training Grant 5RO1 GM00834-09.

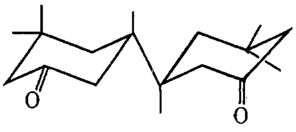
[2] J. Meinwald and L. Hendry, *Tetrahedron Lett.*, 1657 (1969).

[3] M. S. Kharasch and P. O. Tawney, *J. Amer. Chem. Soc.*, **63**, 2308 (1941).

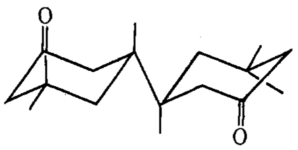
The crystalline by-products (mp 124 and 163°) were recognized from spectral evidence to result from reductive dimerization; their properties are well accounted for on the basis of formulas **3** and **4**, although we were unable to decide which isomer corresponds to the racemic mixture **3** and which to the meso form **4**. Earlier workers[4,5] have described these reductive dimers from the sodium or lithium metal reductions of **1**. In our case, reductive dimerization seems to be brought about by the presence of excess magnesium metal in the methylmagnesium bromide reagent used to bring about the desired deconjugation.



1 **2**



3



4

On the basis of many experiments, we find that high yields of **2** are obtained when no excess of magnesium is present in the Grignard reagent, when the isophorone is added very rapidly to this reagent, and when other precautions noted in the Experimental Section are observed.

Experimental Section

All melting points and boiling points are uncorrected. Infrared spectra were taken on a Perkin-Elmer 257 grating infrared spectrophotometer. The nuclear magnetic resonance spectra were obtained on Varian Associates A-60 and A-60A instruments. Mass spectra were taken on an Associated Electrical Industries MS-902 mass spectrometer.[6]

β-Phorone (2).—To a stirred solution of 51.5 g of Mallinckrodt Grignard magnesium in 300 ml of ether in a 3-l. flask, 200 g of cooled methyl bromide in 300 ml of ether was added. The dropwise addition was carried out over a 3-hr period, keeping the mixture under nitrogen and just below reflux temperature with an ice bath. When all of the magnesium was dissolved, 4 g of anhydrous ferric chloride in 100 ml of ether was added dropwise over 15 min. A solution of 207 g of distilled isophorone (1) [bp ~90° (10 mm)] in 300 ml of ether was added with rapid stirring over a 25-min interval. This step is dangerous and requires adequate venting of methane; moreover, the reaction mixture should not be allowed to cool, since large amounts of polymer are formed under those conditions. The reaction mixture was refluxed for 1 hr and poured into a 6-l. separatory funnel containing 50 g of ammonium chloride and 100 g of ice. After dropwise addition of 120 ml of glacial acetic acid, the mixture was shaken, and the aqueous phase was extracted twice with ether. The combined ether extract was washed with water, 5% aqueous sodium bicarbonate, and again with water. The ether was dried with anhydrous magnesium sulfate and filtered. Evaporation of the solvent and two distillations of the product using a Vigreux column gave 150 g of 96% pure β-phorone (2) [bp ~70° (10 mm)]; the purity was tested by gas chromatography on a 4% SE-30 column at 135°. The yield of β-phorone was 73%; however, reconjugation to isophorone (1) occurred at room temperature. This process was slowed by rapid distillation of the products and subsequent refrigeration.

Isophorone Dimers 3 and 4.—To a suspension of 25 g of magnesium in a 2-l. flask containing 200 ml of ether was added 100 g of cooled methyl bromide in 300 ml of ether. The system was flushed with nitrogen and 2 g of anhydrous ferric chloride in 50 ml of ether was added. (Specks of magnesium metal were visible in the mixture.) A solution of 125 g of isophorone (1) in 150 ml of ether was added carefully over a 1-hr period. A viscous material formed while refluxing for 1 hr which made stirring very difficult. Ice and 60 ml of acetic acid were used to hydrolyze the reaction mixture. After washing with water, 5% aqueous sodium bicarbonate, and water again, the ether layer was dried with anhydrous magnesium sulfate. Evaporation of the solvent yielded a semisolid viscous residue. The oil partially dissolved in pentane yielding 8.5 g of a crystalline dimeric species, mp 163°. Fractional crystallization in pentane yielded 15 g of a more soluble dimeric species, mp 123–124°. The total yield of dimer was about 20%; however, other experiments under varying conditions produced as much as 50% yield of dimers. Spectral data for both isomers were indistinguishable.

The dimer, mp 163°, had the following spectra: mass spectrum (70 eV) *m/e* 278.2239 ($C_{18}H_{30}O_2$ requires 278.2246), 263.2000 ($C_{17}H_{27}O_2$ requires 263.2010), 245.1875 ($C_{17}H_{25}O_2$ requires 245.1905), 263 $\xrightarrow{m^*\ 228.1}$ 245, 139 ($M - C_9H_{15}O$); nmr ($CDCl_3$) δ 1.05 (s, 6 H), 1.10 (s, 12 H), 1.27, 1.51, 1.70, 1.94 (AB quartet, $J_{AB} \sim 14$ cps, 4 H), 1.94, 2.18, 2.30, 2.54 (AB quartet, $J_{AB} \sim 14$ ops, 4 H), 2.18 (s, 4 H); nmr (pyridine) δ 0.99 (s, 18 H), 1.20, 1.43, 1.72, 1.95 (AB quartet, $J \sim 14$ cps, 4 H), 1.95, 2.18, 2.37, 2.60 (AB quartet, $J \sim 14$ cps, 4 H), 2.18 (s, 4 H); ir (CH_2Cl_2) 5.86 μ.

The dimer, mp 123–124°, had the following spectra: mass spectrum (70 eV) *m/e* 278, 263, 245, 263 $\xrightarrow{m^*\ 228.1}$ 245, 139; nmr ($CDCl_3$) δ 1.09 (s, 18 H), 1.28, 1.52, 1.71, 1.95 (AB quartet, $J \sim 14$ cps, 4 H), 1.92, 2.15, 2.31, 2.54 (AB quartet, $J \sim 14$ ops, 4 H), 2.18 (s, 4 H); nmr (pyridine) δ 0.99 (s, 18 H), 1.18, 1.42, 1.65, 1.89 (AB quartet, $J \sim 14$ cps, 4 H), 1.92, 2.16, 2.34, 2.58 (AB quartet, $J \sim 14$ cps, 4 H), 2.18 (s, 4 H); ir (CH_2Cl_2) 5.86 μ.

Registry No.—**1**, 78-59-1; **3**, 28192-72-5; **4**, 4994-12-1.

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A New Synthesis of Symmetrical Diaroylmethanes

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Sieglitz and Horn[2] prepared a series of symmetrical β-diketones by the reaction of vinyl acetate with the appropriate acid chloride in the presence of aluminum chloride. This method suffers from the disadvantage that appreciable amounts of unsymmetrical diketones, $RCOCH_2COCH_3$, are also formed. Rothman and Moore[3] have reported a route to β-diketones [$(RCO)_2CH_2$; R = alkyl] starting from isopropenyl esters. Recently, we described the preparation of symmetrical and unsymmetrical diaroylmethanes containing the pentafluorophenyl group.[4] We now report a simple general method for the preparation of symmetrical diaroylmethanes.

Vinyl esters of benzoic acids (Table I), prepared in

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