sec), 1-methylcyclohexane (74 sec); 5-butyl-5-nonyl acetate (150°, 209 sec), 5-butylnonane (88 sec); 1-adamantyl pivalate (180°, 261 sec), 1-adamantyl neopentyl ether (204 sec), adamantane (47 sec).

Registry No.—**4**, 112-66-3; **5**, 3482-63-1; **7**, 6221-92-7; **8**, 2986-53-0; **10**, 16737-30-7; **13**, 56830-72-9; **15**, 17312-63-9; trichlorosilane, 10025-78-2; 5-*n*-butyl-5-nonanol, 597-93-3; 1-adamantanol, 768-95-6; dodecane, 112-40-3; cyclododecane, 294-62-2; 1-methylcyclohexane, 108-87-2.

References and Notes

(1) Acknowledgment is made to the North Carolina Board of Science and Technology, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Research Corporation for partial support of this work.
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Cuprous Chloride Catalyzed Dimerizations of β-Dicarbonyl Compounds via Their Dicarbanions

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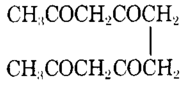
The use of dicarbanions from β-dicarbonyl compounds like β-diketones and β-keto esters in γ-alkylations and γ-acylations has become a common procedure.[1,2] The dicarbanions **2a–c** were investigated in an effort to dimerize them into bisacetylacetones (eq 1).

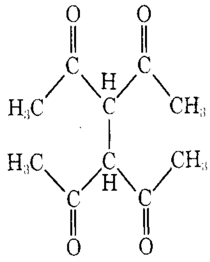
$$\underset{\mathbf{1}}{CH_3COCH_2COCH_3} \longrightarrow \underset{\substack{\mathbf{2a},\ M = M' = Na \\ \mathbf{b},\ M = Na;\ M' = Li \\ \mathbf{c},\ M = M' = Li}}{CH_3COCHMCOCH_2M'} \longrightarrow$$



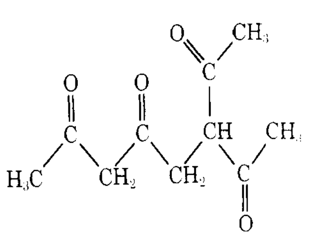
$$\begin{array}{c} CH_3COCH_2COCH_2 \\ | \\ CH_3COCH_2COCH_2 \end{array} \qquad (1)$$

Dimerization of 2,4-pentanedione (**1**) can lead to three possible compounds, **3**, **4**, and **5**.

The 3,3′ dimer or symmetrical tetraacetylethane **3** has been made by the self-condensation of the monoanion of 2,4-pentanedione in an ether solution of iodine.[3,4] The unsymmetrical 1,3′ dimer or 3-acetyloctane-2,5,7-trione, **4**, was obtained by Gritter and Patmore from copper acetylacetonate by a free-radical process.[5a,b] As for the 1,1′ dimer or decane-2,4,7,9-tetrone **5**, there is no record of such a compound in the chemical literature.



3



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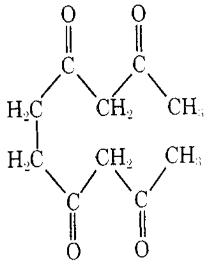
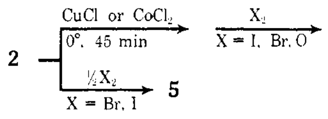


5

Table I provides a representative account of the attempts to obtain **5** by Scheme I. When cuprous chloride or cobaltous chloride was used as a catalyst in the reaction between **2b** and iodine, the reaction proceeded very efficiently (entries 1–5). That the tan solid, mp 62–63°, obtained from the reactions has structure **5** is supported by several pieces of data. For example, this compound is enolic to $FeCl_3$ solution (brown-red color), and its ir and uv spectra are similar to those of **1**. The ^1H NMR spectrum of this solid has four proton centers, namely, at τ 8.02 (singlet) and 7.84 (singlet), $-C(=O)CH_3$ (6 H), 7.45 (singlet), $C(=O)CH_2CH_2C(=O)$ (4 H), 4.64 (singlet), $C(=O)CH=C(=O)$ (2 H), and a broad peak at −4.86 due to enolic protons (2 H). The mass spectrum (70 eV) of this material showed m/e 198 (M^+ ion). Elemental analysis is consistent with the formula $C_{10}H_{14}O_4$ (see Experimental Section).

Scheme I



Dilithioacetylacetone (**2c**, entry 6) did not undergo oxidative dimerization under the same conditions. Since **2c** was generated in liquid ammonia, which was then replaced by THF, traces of ammonia could have interfered rather than **2c** being inherently unreactive. The use of pyridine to solublize the cuprous chloride reduced the reaction period markedly, in addition to rendering the work-up procedure less tedious (entry 5).

The importance of the cuprous chloride or cobaltous chloride catalyst in these reactions as well as the conditions of the reactions is illustrated by entries 6–15. In these cases where the catalyst was not used, the conditions were changed, or other reagents that have been successful in coupling monoanions[3,4,6-9] were used with the dianions, no coupled product **5** could be isolated.

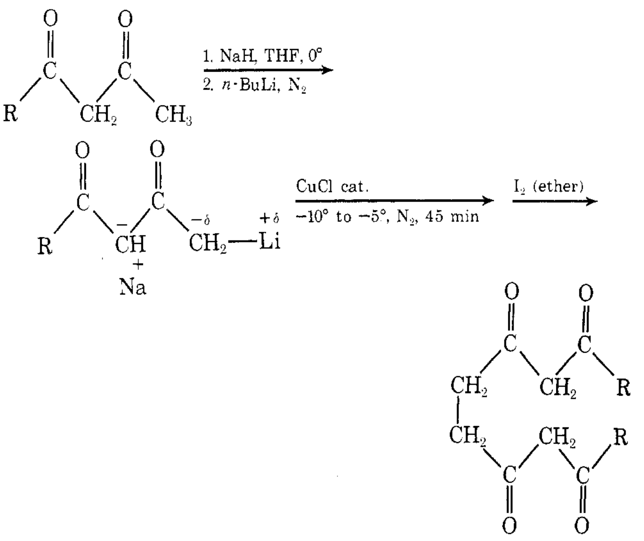
This procedure can be applied to other β-dicarbonyl compounds. As Scheme II illustrates, the method was successfully applied to the syntheses of 1,1′ dimers of benzo-

Table I
Results of the Dimerization Reactions of Acetylacetone via Dianions

No.	Dicarbanion	Conditions	X_2	Mole ratio of dianion:X_2[g]	Catalyst	% yield of 1,1 dimer
1	2b	THF, 0 → 25°, 24 hr, N_2	I_2	2:1	CuCl[a]	35–60
2	2b	THF, 0 → 25°, 24 hr, N_2	I_2	2:1	CuCl[c]	20–45
3	2b	THF, 0 → 25°, 6 hr, N_2	I_2	2:1	CoCl[d]	35
4	2b	THF, 0 → 25°, 22 hr, N_2	I_2	2:1	$CoCl_2$[e]	33
5	2b	THF, 0°, 2 hr, A	I_2	2:1	CuCl[f]	45
6	2a	NH_3, −33°, 1 hr	I_2	2:1		None
7	2a	NH_3, −33°, 1 hr	I_2	2:1	CuCl[a]	None
8	2c	THF, 0 → 25°, 24 hr, N_2	I_2	2:1	CuCl[a]	None
9	2b	THF, 0 → 24°, 24 hr, N_2	I_2	2:1		None
10	2b	THF, −63 → −30°, 0.5 hr, N_2	Br_2	2:1		None
11	2b	THF, 0 → 25°, 20 hr, N_2	Br_2	2:1	CuCl[a]	None
12	2b	THF, 0 → 25°, 24 hr, N_2		1:1[b]	$KMnO_4$	None
13	2b	THF, 0 → 25°, 24 hr, N_2		1:1[b]	$CuCl_2$	None
14	2b	THF, −110 → −50°, 1.5 hr, N_2	O_2	1:2[b]	CuCl	None
15	2b	THF, 0 → 25°, 12 hr, N_2; 63°, 2 hr, N_2			$CoCl_2$	None

[a] Catalytic amount of CuCl, 0.75 g. [b] Ratio of dianion to catalyst. [c] Stoichiometric amounts of CuCl (1:1 and 1:2). [d] Stoichiometric amount of $CoCl_2$ (4:1). [e] Catalytic amount of $CoCl_2$, 0.5 g (3.85 mmol). [f] 25 ml of pyridine added to dianion solution; catalytic amount of CuCl, 0.75 g. [g] All reactions were run on 0.05-molar scale except entry 9, which was run on 0.025-molar basis.

Scheme II



5, R = CH_3
6, R = C_6H_5
7, R = OC_2H_5

ylacetone and ethyl acetoacetate, namely **6** and **7**, in 75 and 50% yields, respectively. However, the sodiolithio dianion of phenylacetone, $PhC\check{H}NaCOCH_2Li$, failed to undergo dimerization by this procedure.

Experimental Section

Infrared spectra were obtained with a Perkin-Elmer 257 grating infrared spectrophotometer using KBr pellets. The ^1H NMR spectra were obtained using a Varian Model A-60D spectrometer and samples dissolved in CCl_4 with Me_4Si as internal standard. The mass spectrum was recorded from a Bell & Howell instrument, Model 21-490.[11]

Melting points were determined using open capillary tubes in a Thomas-Hoover melting point apparatus. The melting points are uncorrected. Elemental analysis of the products was done by Galbraith Laboratories Inc., Knoxville, Tenn.

All the reactions involving organometallic compounds were run in three-necked round-bottom flasks equipped with serum-capped addition funnels in an atmosphere of dry nitrogen. Prior to the introduction of the reagents, the reaction vessel was thoroughly dried with a Bunsen burner flame while being purged with a stream of nitrogen. Tetrahydrofuran (THF) was refluxed over $LiAlH_4$ for 24 hr and distilled in a dry nitrogen atmosphere into vessels containing freshly drawn sodium ribbons. Commercially available anhydrous ether was stored over sodium ribbons. Cuprous chloride was freshly prepared and dried at 70° for 30 min. Anhydrous cobaltous chloride was kept in a vacuum oven at 150° for 24 hr and used immediately. *n*-Butyllithium (2.4 *M* in hexane) from Alfa Inorganics was used directly from the bottle.

Dimerization of 2b Using Cuprous Chloride as Catalyst and Iodine (Entry 1). A typical experimental procedure was as follows. A solution of 2,4-pentanedione (5.0 g, 0.05 mol) in dry THF (20 ml) was added dropwise to a stirred suspension of sodium hydride (1.2 g, 0.05 mol) in 30 ml of THF at 0° in a nitrogen atmosphere. The white sodium salt that was formed in 20 min was then treated with *n*-butyllithium in hexane (2.4 *M* solution) (29.0 ml, 0.05 mol). The *n*-butyllithium was added dropwise from a serum-capped addition funnel over 10–15 min. After the yellow solution had stirred for 15 min, the reaction flask was cooled to −10°. Freshly prepared dry cuprous chloride (0.75 g, 0.0076 mol) was added rapidly to the dianion solution and stirred for 45 min. A dark brown solution resulted. Prior to the addition of cuprous chloride about 30 ml of dry pyridine may be added to **2b** in order to increase the solubility of the inorganic salt (entry 5). A solution of iodine (6.35 g, 0.025 mol) in anhydrous ether (75 ml) was added over 10–15 min. The dark brown reaction mixture slowly acquired a pale yellowish-brown hue. The reaction mixture was stirred for 8–12 hr and allowed to warm to room temperature. It was cooled to 0°, poured into chopped ice (50 g), and acidified with cold concentrated hydrochloric acid to a pH of 2.0. The organic layer was separated and the aqueous phase was extracted with three 35-ml portions of ether in the presence of saturated ammonium chloride solution. The ethereal extract was washed with two 30-ml portions of 10% sodium thiosulfate solution, followed by washing with two 30-ml portions of saturated sodium chloride solution. Any insoluble material was removed by filtration through glass wool. The organic extract was dried over anhydrous Na_2SO_4.

The drying agent was removed by filtration and the filtrate on evaporation in a rotary evaporator at room temperature gave a yellowish-brown syrup (4.8 g). This was recrystallized from cyclohexane and methyl acetate to obtain 1.8–3.0 g (35–60%) of **5**, mp 60–62°, a pale yellow crystalline solid. An analytical sample was prepared by two recrystallizations from cyclohexane using Nuchar. The product was dried under vacuum at room temperature: mp 62–63°; ir (KBr) $\bar{\nu}_{max}$ 2960, 2900, 1670–1530 (broad), 1400, 1280, 1190, 1110, 1010, 905, 795, 760 cm^{-1}; uv λ_{max} (cylohexane) 227 nm (log ε 4.37).

Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.6; H, 7.07. Found: C, 60.36; H, 7.19.

The compound **5** was converted into its dipyrazole derivative, mp 198–200°.

Preparation of 1,6-Dibenzoyl-2,5-diketohexane (6). A solution of benzoylacetone (8.1 g, 0.05 mol) in THF (30 ml) was added dropwise to a stirred suspension of sodium hydride (1.2 g, 0.05 mol) and 75 ml of THF at 0° under a nitrogen atmosphere. A pale yellowish suspension of the monoanion was formed in 15 min.

About 28.0 ml of *n*-butyllithium (2.4 *M* solution in hexane) was then added dropwise over 15 min to form a dark green or greenish-blue solution, presumably the sodiolithio dianion of the β-diketone. The solution was then cooled to −5° and cuprous chloride (0.75 g, 0.0076 mol) was introduced rapidly into the flask. The mixture was stirred for 45 min as it turned dark brownish red. As described earlier, an iodine solution (6.35 g, 0.025 mol) in ether was added and the reaction mixture stirred for 8 hr at room temperature. The usual work-up procedure gave 7.2 g of an orange-yellow syrup which solidified into a yellow mass. This was recrystallized (ether and cyclohexane) to obtain 6.0 g (75%) of a pale yellow crystalline product, mp 83–85°. An analytical sample was obtained by recrystallization from ether at −63° as yellow needles: mp 89–90° [lit.[10] 92–95° (ethanol)]: ir (KBr) $\tilde{\nu}_{max}$ 3020, 1710–1620, 1400, 1290, 750 cm^{-1}; ^{1}H NMR (CCl$_4$) τ 7.21 [$C(=O)CH_2CH_2C(=O)$, 4 H] [whereas for bezoylacetone $-C(=O)CH_3$ is seen as singlet at 7.92], 393 [s, $-C(=O)CH=COH$, 2 H], 2.67 (m) and 2.30 (m) ($-C_6H_5$, 10 H), and −5.5 (hump), enolic protons (2 H); uv λ_{max} (cyclohexane) 315, 248, and 216 nm (log ϵ 4.57, 3.6, and 4.32, respectively).

Anal. Calcd for $C_{20}H_{18}O_4$: C, 74.60; H, 5.59. Found: C, 74.64; H, 5.77.

Preparation of Bis(ethyl acetoacetate) (7). The dianion of ethyl acetoacetate (0.05 mol) was generated by the procedure of Weiler et al. After cooling the yellowish-red solution to −5°, a cuprous chloride (0.75 g) was added and stirred for 45 min to obtain a dark solution. This organocopper reagent was then oxidized as before with iodine solution. The reaction mixture was stirred at 0° for 1–5 hr. The reaction mixture was poured onto chopped ice (30 g) and carefully neutralized with cold dilute 30% hydrochloric acid. The organic phase was separated and the aqueous layer was extracted with three 35-ml portions of ether. The ethereal solution was treated as before to obtain 6.8 g of a yellow-brown syrup.

This was triturated in petroleum ether (bp 35–60°) and ethyl acetate (10:1 v/v) and cooled to −63° (chloroform slush bath) as a white solid formed. The solid was suction filtered and air dried, 3.2 g (50%), mp 40–42°. An analytical sample was obtained by recrystallizations from petroleum ether and absolute ethanol at −63°: mp 47–48°; ir (KBr) $\tilde{\nu}_{max}$ 2990, 1750–1690 cm^{-1}; ^{1}H NMR (CCl$_4$) τ 8.8 (t, $-OCH_2CH_3$, 6 H), 7.20 [s, $C(=O)CH_2CH_2C(=O)$, 4 H], 6.65 [s, $C(=O)CH_2C(=O)$, 4 H], and 5.9 (q, $-OCH_2CH_3$, 4 H).

Anal. Calcd for $C_{12}H_{18}O_6$: C, 55.82; H, 6.98. Found: C, 55.68; H, 7.10.

Generation of Dicarbanions 2a and 2c. The dianions were generated by the procedure of Hauser et al.[1b] from 5.0 g (0.05 mol) of 2,4-pentanedione and 2 molar equiv (0.1 mol) of MNH_2 (M = Na or Li).

Non-Copper-Catalyzed Reactions. The dianions were treated as indicated in Table I, entries 6–15. In each case a viscous oil which could not be crystallized to produce any **5** was obtained. Gas chromatography showed several components, including in several cases some **1**.

Registry No.—**1**, 123-54-6; **2**, 56830-65-0; **3**, 56580-16-6; **4**, 56830-66-1; **5**, 56830-67-2; **6**, 56830-68-3; **7**, 56830-69-4; cuprous chloride, 7758-89-6; benzoylacetone, 93-91-4; ethyl acetoacetate, 141-97-9.

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(11) The authors thank Dr. James Pinson and Leonard Ingram for the mass spectrum.