7a, 50688-77-2; 7b, 98943-71-6; 7d, 98943-72-7; 8a, 98943-73-8; 8b, 98943-74-9; 8c, 85809-29-6; 8d, 98943-75-0; 8g, 98943-76-1; 8h, 98943-77-2; 8i, 98943-78-3; 9a, 614-17-5; 9b, 70772-75-7; 9c, 5705-57-7; 9c-D, 98943-95-4; 9d, 98943-79-4; 9e, 3278-14-6; 9f, 77414-34-7; 10a, 98943-80-7; 10b, 98943-81-8; 10c, 98943-82-9; 11b, 98943-83-0; 11c, 33561-46-5; 11d, 98943-84-1; 11h, 36556-72-6; 12c, 33561-48-7; 12d, 98943-85-2; 13d, 98943-86-3; 18a, 10302-15-5; 19a, 5048-63-5; 19b, 5048-64-6; 21a, 98943-87-4; 22a, 98943-88-5; 22b, 98943-89-6; 23a, 19871-46-6; 24, 98943-90-9; 25, 70686-42-9; 26a, 70650-93-0; 26b, 98943-91-0; 28, 98943-92-1; 29, 98943-93-2; 30, 98943-94-3; AH^-, 14314-91-1; AH_2, 120-12-7; XH, 92-83-1; A^{2-}, 23013-59-4.

(Phosphine)carbonylnitrosylacylcobaltate Complexes as Acyl Transfer Reagents. Acylation of Allylic Halides, Conjugated Enones, and Quinones

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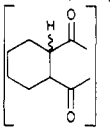
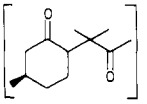
The complex $Co(NO)(CO)_2(PPh_3)$ is an air stable, easily handled crystalline solid, prepared from $Co_2(CO)_8$, sodium nitrite, and triphenylphosphine without isolation of the volatile intermediate $Co(NO)(CO)_3$. Treatment of this complex with organolithium reagents at −40 °C generated unstable acylate complexes $[RCOCo(NO)(CO)(PPh_3)]^-$ which readily transferred the acyl group to allylic halides to produce β,γ-unsaturated ketones, to conjugated ketones to produce 1,4-dicarbonyl compounds, and to quinones to form 4-acylcyclohexadienones.

Reduction of transition-metal carbonyl complexes generates anionic metal carbonyl species that are often potent nucleophiles. Reaction of these "carbonylate" complexes with organic halides or tosylates produces acylmetal complexes many of which are useful acyl transfer reagents in organic synthesis. Thus "Collman's reagent", $Na_2Fe(CO)_4$, reacts with organic halides to give the acylate complex $[RCOFe(CO)_4]^-$ which converts reactive organic halides and tosylates to ketones and which can also be converted to aldehydes and carboxylic acid derivatives.[1,2] Similarly $NaCo(CO)_4$ acylates reactive organic halides and epoxides to give carboxylic acid derivatives.[3,4]

Alternatively, reaction of iron pentacarbonyl with organolithium reagents generates the same acylate complex as that from $Na_2Fe(CO)_4$ and organic halides, $[RCOFe(CO)_4]^-$. This complex has been converted to ketones, conjugated enones,[5] amides,[6] and other carbonyl-containing products[7] by reaction with electrophiles such as organic halides, epoxides, or imines. In contrast, reaction of these acylate iron complexes with electrophiles prone to reaction at oxygen, such as ethyl fluorosulfonate results in O-alkylation of the acyl group, resulting in carbene complex formation.[8]

Nickel carbonyl also forms reactive acylate complexes upon treatment with organolithium reagents. These complexes, generated and used in situ, convert conjugated enones to 1,4-diketones,[9] allylic halides to β,γ-unsaturated ketones,[10] and alkynes to 1,4-diketones,[11] as well as undergo coupling to form α-diketones when treated with acid.[12] In spite of the useful transformations effected by these nickel acylate complexes, they have found little use in synthetic organic chemistry in the 15–20 years of their existence.[13] This is undoubtedly due to the extreme volatility and toxicity of nickel carbonyl and the resulting problems in handling this material. Cobalt nitrosyl tricarbonyl, $Co(NO)(CO)_3$, is isoelectronic with nickel carbonyl and is also a volatile, toxic liquid. However, it readily forms an air-

Table I. Acylation of Conjugated Enones by Cobalt Acylate Complexes 2 (Eq 1)

3	R	R′	R″	yield,[a] %
a	Me	Ph	Me	87
b	*n*-Bu	Ph	Me	78
c	Me	Ph	Ph	58
d	Me	$(Me)_2$	Me	39
e	*n*-Bu	$(Me)_2$	Me	75
f	Me	Me	Me	60
g	*n*-Bu	Me	Me	69
h	Me	$(Me)_2$	$CH{=}CMe_2$ [b]	91
i	Me	$-(CH_2)_4-$		0[c]
j				73[d]
k				47

[a] Reported yields are for isolated, purified products. [b] This species only underwent *mono*acylation. [c] Cyclohexenone was recovered unchanged. [d] Mixture of stereoisomers.

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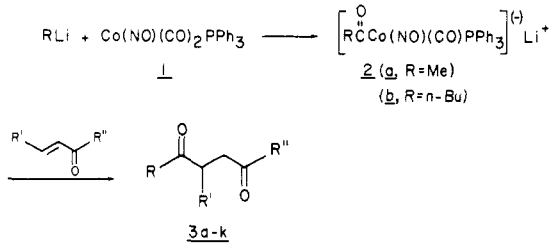
0022-3263/85/1950-4955$01.50/0

stable, nonvolatile, easily handled monotriphenylphosphine adduct, $Co(NO)(CO)_2(PPh_3)$, which can be readily prepared on a large scale and stored in air indefinitely.[14,15] The preparation and reactions of acylate complexes of this species are reported below.

Results and Discussion

The desired $Co(NO)(CO)_2PPh_3$ (1) was prepared on a 35–40-g (0.1 mol) scale in a one-pot procedure by the reaction of dicobalt octacarbonyl with sodium nitrite in aqueous acetic acid,[14] sweeping the volatile $Co(NO)(CO)_3$ into a THF solution of triphenylphosphine with a slow stream of argon and collecting 1 by precipitation with methanol. Treatment of a THF solution of 1 with a variety of organolithium reagents at −40 °C produced a red-brown homogeneous solution. The infrared spectrum of this solution indicated complete conversion of 1 to an acylate complex 2, as evidenced by the complete disappearance of the ν_{CO} (2013, 1982 cm^{-1}) and ν_{NO} (1757 cm^{-1}) bands of 1 and the appearance of new bands at ν_{CO} 1905 cm^{-1} and ν_{NO} at 1645 cm^{-1}, characteristic of *anionic* metal carbonyl nitrosyl complexes,[16] as well as weak bands at ν_{CO} 1584 and 1560 cm^{-1}, tentatively assigned to the acyl group.[17] This species was stable at −40 °C for extended periods but rapidly decomposed upon warming to room temperature. The carbonylate complexes 2 from methyl- and *n*-butyllithium were generally reactive toward α,β-unsaturated ketones, producing 1,4-dicarbonyl compounds in fair-to-good yield (eq 1) (Table I). Thus, benzalacetone (**3a,b**),

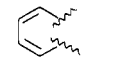
(1)



chalcone (**3c**), mesityl oxide (**3d,e**), and 3-penten-2-one (**3f,g**) underwent clean β-acylation with this acylate reagent. Phorone (**3h**) was cleanly *mono*acylated in high yield, despite the presence of two reactive enone positions. Remarkably, cyclohexenone was inert and was recovered unchanged from the reaction mixture, while both 1-acetylcyclohexene (**3j**) and pulegone (**3k**) were cleanly acylated.

In contrast, conjugated esters such as methyl cinnamate, methyl crotonate, and methyl methacrylate were inert under conditions which resulted in decomposition of the acylate complex. The range of reactive organolithium reagents was limited. Although vinyl-, allyl-, benzyl-, (trimethylsilyl)methyl, and 1-propynyllithium all converted 1 to the corresponding acylate complex 2 (by infrared spectroscopy), these complexes failed to acylate conjugated enones. The acylate complex from phenyllithium acylated benzalacetone in only 8% yield. The remainder was unreacted benzalacetone, biphenyl, and benzil. Cinnamyl chloride (see below) was acylated in low yields by the benzyl and phenyl acylates, but significant amounts of homocoupled products—biphenyl, benzophenone, bi-

Table II. Acylation of Quinones by Cobalt Acylate Complex 2a

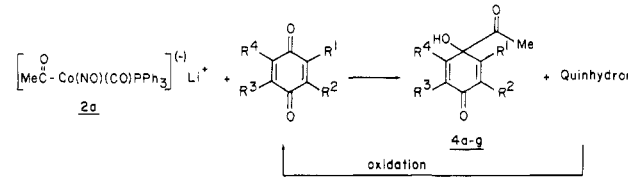
4	R^1	R^2	R^3	R^4	yield,[a] %
a	H	H	H	H	28
b	Me	Me	H	H	25
c	Me	H	Me	H	39
d	H	Me	H	H	25
e	Me	H	H	Me	18[b]
e′	H	Me	Me	H	33[b]
f	Me	Me	Me	Me	29[c]
g	H	H			15

[a] Reported yields are for isolated, purified products. [b] Regioisomers from attack at the two different carbonyl groups. [c] A 19% yield of 4-hydroxy-2,3,4,5,6-pentamethyl-2,4-cyclohexadienone was also obtained.

benzyl, and 1,3-diphenylacetone—were also obtained. Grignard reagents failed to form acylate complexes at all. Rather unreacted 1 was the only species detected by infrared spectroscopy even after several hours of reaction.

In the reactions of cobalt acylate complex **2a** with benzoquinones, electron transfer processes competed with acyl transfer processes (eq 2) (Table II). Acylation occurred

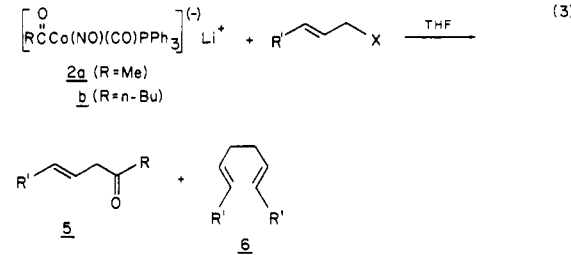
(2)



exclusively at a carbonyl carbon, producing dienones **4a–g** in only modest yield. The remainder of the quinone was converted to the corresponding quinhydrone (isolated and characterized in the case of benzoquinone) and was recovered in quite high yield upon oxidative isolation. Since the recovered quinone could be recycled, this acylation was relatively efficient in terms of the substrate but inefficient in terms of the cobalt acylate complex. The product distribution was insensitive to the relative proportions of starting materials, and the yield of acyl transfer could not be improved by using an excess of either reagent, since electron transfer from **2a** to the quinone inactivated both species toward further acyl transfer. With unsymmetrical quinones, both possible regioisomers were obtained, with attack at the less hindered terminus predominating. With duroquinone, substantial amounts of methyl transfer was noted, even though complete conversion of 1 to **2a** had occurred (IR) and no free methyllithium was detected by the classical Gilman test.[18]

Allylic halides were converted to β,γ-unsaturated ketones by reaction with cobalt acylate complexes **2a,b** (eq 3) (Table III). Allylic bromides suffered competitive reductive coupling and gave substantial yields of biallyls.

(3)



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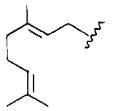
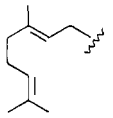
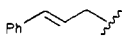
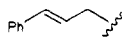
(18) Fieser, L. F.; Fieser, M. "Reagents for Organic Synthesis"; Wiley: New York, 1967; p 417.

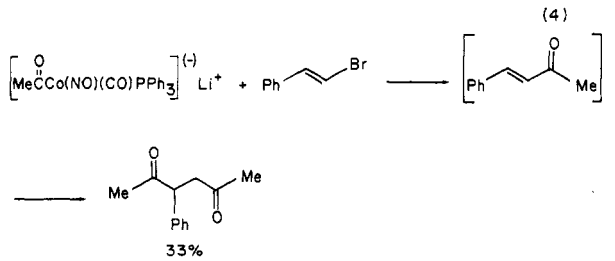
Table III. Acylation of Allylic Halides by Cobalt Acylate Complexes 2a,b

R	allylic halide	X	procedure	yield,[a] % 5	6
Me		Br	A[b]	31	39
			B[c]	66	12
		Cl	A	41	26
			B	69	6
Bu		Br	A	53	39
Me		Br	A	35	*d*
			B	64	*e*
		Cl	A	62	
			B	85	
Bu		Br	A	35	*f*
			B	55	*f*
Me		Br	A	20	59
			B	47	36
		Cl	A	42	43
			B	85	6
Me		Cl	B	51[g]	

[a] Yields are of isolated, purified material. [b] Procedure A refers to reactions run in THF at −20 °C in the absence of any additives. [c] Procedure B refers to reactions run in the presence of 1 equiv of $BF_3{\cdot}OEt_2$/equiv of cobalt complex. [d] Substantial amounts of product resulting from alkylation of the enolate of 5 by cinnamyl bromide were obtained. [e] Substantial amounts of an unidentified byproduct containing cinnamyl groups but no carbonyl groups were obtained. [f] A substantial amount of an unidentified byproduct was obtained. [g] Exclusive bisacylation occurred.

to addition of allylic halide suppressed the reductive coupling substantially perhaps by decreasing the reducing ability of the acylate complex by complexation. In line with this explanation, allylic chlorides, being more difficult to reduce than the corresponding bromides, were acylated in high yield in the presence of $BF_3{\cdot}Et_2O$. Even 2,3-bis(chloromethyl)butadiene underwent reaction, acylating twice to produce the unusual 2,3-bis(acetonyl)butadiene.

Finally, a single example of a vinyl halide was examined. β-Bromostyrene was converted to the corresponding 1,4-diketone, presumably through the initial acylation product, benzalacetone (eq 4). This behavior again parallels that of the corresponding nickel acylate complex $[RCONi(CO)_3]^-Li^+$.[10]



In summary, cobalt acylate complex 2 is readily prepared from an air-stable, easily handled precursor. Its chemistry parallels that of the much more difficult to handle nickel acylate complexes, $[RCONi(CO)_3]Li$, with some minor differences. Complex 2 is slightly less reactive than the corresponding nickel species toward conjugated enones in that it does not acylate conjugated esters whereas nickel acylates do. Complex 2 appears to be a better reducing agent, in that reductive coupling of allylic halides is a serious but controllable competing process with complex 2 but is not observed with $[RCONi(CO)_3]Li$. Finally, β-bromostyrene is diacylated by both species. (The reactions of nickel acylate species with quinones have not been studied.) The ease of preparation and handling of these cobalt acylate complexes should make their chemistry more accessible for application in organic synthesis.

Experimental Section

General Procedures. Melting points were taken with a Mel-Temp apparatus and are uncorrected. Infrared spectra were recorded on a Beckman 4240 spectrometer. ^1H NMR spectra were recorded with a Varian T-60 (60 MHz), IBM WP-270 (270 MHz), or Nicolet NTCFT 1180 (360 MHz) spectrometer with tetramethylsilane as an internal standard. Liquid chromatography was performed with a radial layer chromatographic device (Chromatotron, Harrison Research) with plates of Kieselgel 60 PF 254 silica gel. Elemental analysis were performed by M-H-W Laboratories, Phoenix, AZ.

Materials. THF was distilled from sodium/benzophenone. Methyllithium (Aldrich), *n*-butyllithium (Aldrich), and phenyllithium (Alfa) were standardized by a titration procedure[19] and used as received. All other reagents were distilled or recrystallized as needed.

Preparation of $Co(NO)(CO)_3$.[14] A solution of glacial acetic acid (85 mL) and H_2O (900 mL) was placed in a 2-L, three-neck flask fitted with a $CaCl_2$-filled drying tube, a glass stopper, and a gas inlet tube. Argon was passed through the solution for 0.5 h, and then solid $Co_2(CO)_8$ (25 g, 73 mmol) and $NaNO_2$ (30 g, 430 mmol) were added to the solution. Stirring was continued, and the flask was warmed to 50 °C in an oil bath while an argon purge was maintained. The evolution of red-brown gas began immediately. This gas was condensed with a dry ice/acetone trap and collected in a cooled (−78 °C) Airlessware flask. The argon purge and stirring continued until no colored gas was emitted (7 h). The product was then warmed to room temperature and recollected in another flask at −78 °C after passing through another $CaCl_2$-filling drying tube. The total yield of product was 13.75 g (79 mmol).

Preparation of $Co(NO)(CO)_2(PPh_3)$. A solution of glacial acetic acid (85 mL) and H_2O (1 L) was placed in a 2-L, three-neck, round-bottom flask fitted with a $CaCl_2$-filled drying tube, a glass stopper, and a gas inlet tube. Argon was bubbled through the solution for 0.5 h to degas the system. Then, solid $Co_2(CO)_8$ (25 g, 73 mmol) was added to the solution along with $NaNO_2$ (30 g, 430 mmol). Stirring was continued, and the flask was warmed to 50 °C in an oil bath while a slow argon flow was maintained. The evolution of a red-brown gas began immediately. This was passed through the drying tube and into a precooled (0 °C) solution of THF (400 mL) and PPh_3 (26 g, 99 mmol). When gas evolution ceased, the THF solution was warmed to room temperature and stirred overnight under argon. (Caution, 1 equiv of CO is released.) After 16 h, no $Co(NO)(CO)_3$ was detected by infrared spectroscopy. Methanol (200 mL) was added to the THF solution, and the mixture was concentrated in vacuo to ca. 100 mL. Copious amounts of red-orange crystals precipitated and were removed by suction filtration, washed with cold CH_3OH (3 × 50 mL), and dried in vacuo to give 29.1 g (71 mmol) of product, mp 134.5–136 °C (lit.[15] mp 134–135.5 °C).

General Reaction Conditions. The cobalt carbonylate complex was made as follows. The desired cobalt carbonyl complex was transfered to a dry Airlessware flask equipped with a magnetic stir bar and an argon-filled balloon. An appropriate amount of THF was introduced by syringe to dissolve the sample, and then the solution was cooled to −40 °C in a dry ice/CH_3CN bath. After the solution cooled for 5 min, the required lithium reagent was added by syringe and the reaction was stirred at −40 °C for 0.5–2.0 h as noted. The electrophile was then introduced by syringe if liquid or by dissolving in 1–2 mL of dry THF and then adding if a solid. The reaction mixture was then placed in a freezer with a constant temperature of −20 to −25 °C for the amount of time

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noted. Reactions were monitored by thin-layer chromatography (TLC).

Product Isolation. When the reaction was complete, 10–20 mL of saturated aqueous NH_4Cl was added to the flask at −20 °C and stirred for 2 min. The mixture was then diluted with Et_2O (100 mL), and the contents were transferred to a separatory funnel. The organic layer was washed with H_2O (an additional 30–50 mL added), and then any cobalt carbonyl species were decomposed by the addition of an excess of I_2 in Et_2O. The solution was shaken and allowed to stand 0.5–1.0 h. Excess I_2 was reduced by washing twice with a saturated aqueous solution of $Na_2S_2O_3$. The organic layer was washed twice with water and dried over $MgSO_4$ and the solvent removed in vacuo.

3-Phenyl-2,5-hexanedione (3a).[10] The carbonylate was formed over 2.0 h at −40 °C [705 mg of $Co(NO)(CO)_2(PPh_3)$ (1) (1.73 mmol), 1.07 mL of 1.4 M CH_3Li (1.5 mmol), 10 mL of THF], and then benzalacetone (146 mg, 1.0 mmol) in 1.5 mL of THF was added by syringe. The reaction mixture was warmed to −20 °C and allowed to react 1.5 h. The usual isolation followed by Chromatotron separation (1:1 hexane–Et_2O) gave 165 mg (87%, R_f 0.38) of product as a colorless liquid: ^1H NMR ($CDCl_3$) δ 2.12 (s, 3, CH_3), 2.16 (s, 3, CH_3), 2.57 (dd, J = 18.0, 3.9 Hz, 1, $CHCH_2$), 3.44 (dd, J = 18.0, 10.2 Hz, 1, $CHCH_2$), 4.22 (dd, J = 10.2, 3.8 Hz, 1, $CHCH_2$), 7.25 (m, 5); IR (neat) 3060, 3030, 2910, 1715 (C=O), 1700, 1601, 1493, 1455, 1416, 1396, 1354, 1230, 1214, 1154, 1028, 750, 693 cm^{-1}.

4-Phenyl-2,5-nonanedione (3b).[10] The carbonylate was formed over 2.0 h at −40 °C [626 mg of 1 (1.54 mmol), 590 μL of 2.3 M *n*-BuLi (1.36 mmol), 10 mL of THF], and then benzalacetone (132 mg, 0.90 mmol) in 1.5 mL of THF was added. The reaction mixture was warmed to −22 °C and allowed to react 2.0 h. The usual isolation followed by Chromatotron separation (1:1 hexane–Et_2O) gave 160 mg (78%, R_f 0.53) of product as a colorless oil: ^1H NMR ($CDCl_3$) δ 0.80 (t, J = 7.3 Hz, 3, CH_3), 1.18 (m, 2, CH_2), 1.48 (m, 2, CH_2), 2.16 (s, 3, $COCH_3$), 2.43 (m, 2, $COCH_2$), 2.56 (dd, J = 18.0, 3.8 Hz, 1, $CHCH_2$), 3.45 (dd, J = 18.0, 10.4 Hz, 1, $CHCH_2$), 4.21 (dd, J = 10.4, 3.8 Hz, 1, $CHCH_2$), 7.25 (m, 5); IR (neat) 3055, 3022, 2955, 2930, 2865, 1707 (C=O), 1685, 1598, 1492, 1452, 1395, 1357, 1230, 1161, 1123, 1027, 750, 696 cm^{-1}.

1,3-Diphenyl-1,4-pentanedione (3c).[20] The carbonylate was formed over 0.5 h at −40 °C [650 mg of 1 (1.6 mmol), 1.23 mL of 1.3 M CH_3Li (1.6 mmol), 10 mL of THF], and then chalcone (208 mg, 1.0 mmol) dissolved in 2 mL of THF was added. The reaction mixture was warmed to −20 °C and allowed to react for 11 h. The usual isolation and Chromatotron purification (1:1 hexane–Et_2O) gave 147 mg (58%, R_f 0.46), of product as a colorless oil: ^1H NMR ($CDCl_3$) δ 2.22 (s, 3, CH_3), 3.14 (dd, J = 18.1, 3.7 Hz, 1, $CHCH_2$), 4.02 (dd, J = 18.1, 9.9 Hz, 1, $CHCH_2$), 4.44 (dd, J = 10.1, 3.7 Hz, 1, $CHCH_2$), 7.2–7.6 (m, 8), 7.96 (m, 2); IR (neat) 3060, 3025, 2910, 1720 (C=O), 1686 (ArC=O), 1600, 1584, 1496, 1450, 1396, 1355, 1245, 1160, 1000, 909 cm^{-1}. Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 81.19; H, 6.56.

3,3-Dimethyl-2,5-hexanedione (3d).[10] The carbonylate was formed over 2.0 h at −40 °C [670 mg of 1 (1.64 mmol), 1.07 mL of 1.4 M CH_3Li (1.5 mmol), 10 mL of THF], and then mesityl oxide (115 μL, 1.0 mmol) was added by syringe. The reaction mixture was warmed to −20 °C and allowed to react for 8 h. The usual isolation with Chromatotron separation (2:1 Et_2O–hexane) gave 55 mg (39%, R_f 0.37) of product as a colorless oil: ^1H NMR ($CDCl_3$) δ 1.19 (s, 6, CH_3), 2.11 (s, 3, $COCH_3$), 2.19 (s, 3, $COCH_3$), 2.76 (s, 2, CH_2); IR (neat) 2965, 2930, 2870, 1715 (C=O), 1704, 1620, 1475, 1365, 1170, 1128 cm^{-1}.

4,4-Dimethyl-2,5-nonanedione (3e).[10] The carbonylate was formed over 0.5 h at −40 °C [650 mg of 1 (1.6 mmol), 700 μL of 2.3 M *n*-BuLi (1.6 mmol), 10 mL of THF], then mesityl oxide (114 μL, 1.0 mmol) was added by syringe, and the solution was warmed to −20 °C and allowed to react for 10 h. The usual isolation and Chromatotron separation (1:1 hexane–Et_2O) gave 134 mg (75%, R_f 0.44) of product as a colorless oil: ^1H NMR ($CDCl_3$) δ 0.91 (t, J = 7.3 Hz, 3, CH_2CH_3), 1.18 (s, 6, CH_3), 1.30 (m, 2, CH_2), 1.54 (m, 2, CH_2), 2.10 (s, 3, $COCH_3$), 2.53 (t, J = 7.3 Hz, 2, CH_2CO), 2.76 (s, 2, $COCH_2$); IR (neat) 2960, 2930, 2870, 1710 (C=O), 1465, 1400, 1362, 1186, 1160, 1137, 1119, 1045, 984, 930 cm^{-1}.

(20) Clark, J. H.; Cork, D. G.; Gibbs, H. W. *J. Chem. Soc., Chem. Perkin Trans 1* **1983**, 2253.

3-Methyl-2,5-hexanedione (3f).[10] The carbonylate was made over 2.0 h at −40 °C [650 mg of 1 (1.6 mmol), 1.0 mL of 1.4 M CH_3Li (1.4 mmol), 10 mL of THF], then *trans*-3-penten-2-one (100 μL, 1.0 mmol) was added by syringe, and the solution was warmed to −20 °C for 2.5 h. The usual isolation and Chromatotron purification (1:1 hexane–Et_2O) gave 77 mg (60%, R_f 0.24) of product: ^1H NMR ($CDCl_3$) δ 1.11 (d, J = 7.0 Hz, 3, $CHCH_3$), 2.15 (s, 3, $COCH_3$), 2.23 (s, 3, $COCH_3$), 2.38 (dd, J = 20.3, 3.5 Hz, 1, $CHCH_2$), 2.9–3.1 (m, 3, $CHCH_2$); IR (neat) 2970, 2935, 2880, 1718 (C=O), 1458, 1419, 1397, 1358, 1260, 1160, 1121, 911 cm^{-1}.

4-Methyl-2,5-nonanedione (3g). The carbonylate was formed over 0.5 h [650 mg of 1 (1.6 mmol), 700 μL of 2.3 M *n*-BuLi (1.6 mmol), 10 mL of THF] at −40 °C, then *trans*-3-penten-2-one (98 μL, 1.0 mmol) was added by syringe, and the solution was warmed to −20 °C and allowed to react for 9.5 h. The usual isolation and Chromatotron purification (1:1 hexane–Et_2O) gave 118 mg (69%, R_f 0.42) of product as a colorless oil: ^1H NMR ($CDCl_3$) δ 0.91 (t, J = 7.3 Hz, 3, CH_2CH_3), 1.08 (d, J = 6.7 Hz, 3, $CHCH_3$), 1.31 (m, 2, CH_2), 1.56 (m, 2, CH_2), 2.14 (s, 3, $COCH_3$), 2.38 (m, 1, CH), 2.54 (t, J = 7.3 Hz, 2, CH_2CH_2CO), 2.98 (m, 2, $CHCH_2CO$); IR (neat) 2960, 2930, 2870, 1715 (C=O), 1458, 1398, 1360, 1263, 1170, 1142, 1120, 1064, 1040, 990, 961, 906 cm^{-1}. An analytical sample was obtained by evaporative distillation, 60 °C (0.1 mmHg). Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.25; H, 10.77.

3,3,7-Trimethyl-6-octene-2,5-dione (3h). The carbonylate was made over 1.0 h at −40 °C [650 mg of 1 (1.6 mmol), 1.14 mL of 1.4 M CH_3Li (1.6 mmol), 10 mL of THF], and then phorone (156 μL, 1.0 mmol) was added and the reaction warmed to −20 °C and allowed to react for 23 h. The usual isolation and Chromatotron separation (1:1 hexane–Et_2O) gave 165 mg (91%, R_f 0.41) of product as a colorless oil: ^1H NMR ($CDCl_3$) δ 1.19 (s, 6, $C(CH_3)_2$), 1.87 (d, J = 1.0 Hz, 3, $CH{=}(CH_3)CH_3$), 2.10 (d, J = 1.0 Hz, 3, $CH{=}(CH_3)CH_3$), 2.21 (s, 3, $COCH_3$), 2.77 (s, 3, CH_2), 6.02 (m, 1, =CH); IR (neat) 2965, 2930, 2910, 2865, 1705 (C=O), 1683, 1615, 1470, 1444, 1377, 1352, 1205, 1175, 1140, 1112, 1092, 1040, 1025, 900, 857, 805, 732 cm^{-1}. Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.23; H, 10.06.

1,2-Diacetylcyclohexane (3j). The carbonylate was formed over 0.5 h at −40 °C [650 mg of 1 (1.6 mmol), 1.23 mL of 1.3 M CH_3Li (1.6 mmol), 10 mL of THF], then 1-acetylcyclohexane (128 μL, 1.0 mmol) was added, and the solution was warmed to −20 °C and allowed to react for 24 h. The usual isolation and Chromatotron separation gave 3% recovered enone and two major fractions, corresponding to the two cis and trans isomeric products.

Isomer 1: 54 mg (32%, R_f 0.22); ^1H NMR ($CDCl_3$) δ 1.2–2.2 (m, 8), 2.18 (s, 6, CH_3), 2.75 (m, 2, CH); IR (neat) 2930, 2855, 1705 (C=O), 1650, 1445, 1418, 1351, 1292, 1223, 1159, 1126, 1029, 952, 905, 841 cm^{-1}. Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.57; H, 9.72.

Isomer 2: 69 mg (41%, R_f 0.32); ^1H NMR ($CDCl_3$) δ 1.0–1.25 (m, 2), 1.25–1.4 (m, 2), 1.75–1.9 (m, 2), 2.0–2.2 (m, 2), 2.18 (s, 6, CH_3), 2.7–2.85 (m, 2, CH); IR (neat) 2995, 2930, 2855, 1710 (C=O), 1633, 1448, 1420, 1356, 1295, 1235, 1165, 1110, 960, 882 cm^{-1}. Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.13; H, 9.51.

2-(1,1-Dimethyl-2-oxopropyl)-4(*R*)-methylcyclohexanone (3k). The carbonylate was formed over 0.5 h at −40 °C [705 mg of 1 (1.84 mmol), 1.15 mL of 1.6 M CH_3Li (1.84 mmol), 10 mL of THF], and then (+)-(*R*)-pulegone (98 μL, 0.6 mmol) was added and the reaction warmed to −20 °C and allowed to react for 115 h. The usual isolation and Chromatotron separation (1:1 hexane–Et_2O) gave 55 mg (47%, R_f 0.39) of product as a white crystalline solid: mp 48–50 °C; ^1H NMR ($CDCl_3$) δ 2.93 (m, 1, CHCO), 2.31 (m, 1), 2.24 (s, 3, $COCH_3$), 2.1–1.9 (m, 3), 1.9–1.7 (m, 1), 1.44 (m, 2), 1.20 (s, 3, CH_3), 1.01 (d, J = 7.2 Hz, 3, $CHCH_3$), 1.00 (s, 3, CH_3); IR (KBr) 2950, 2925, 2878, 1692 (C=O), 1472, 1453, 1423, 1364, 1351, 1243, 1231, 1141, 1095, 873 cm^{-1}. Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.42; H, 10.27. Found: C, 73.28; H, 10.23.

1,2-Diphenyl-1,4-pentanedione.[10] The carbonylate was formed over 2 h at −50 °C and then 4 h at −20 °C [650 mg of 1 (1.6 mmol), 900 μL of 1.56 M PhLi (1.4 mmol), 10 mL of THF]. Benzalacetone (202 mg, 0.80 mmol) in 1.5 mL of THF was added, and the reaction was continued for 18 h at −20 °C. The usual isolation and Chromatotron (1:1 hexane–Et_2O) purification gave 17 mg (8.4%, R_f 0.37) of product as a colorless oil: ^1H NMR ($CDCl_3$) δ 2.18 (s, 3, CH_3), 2.75 (dd, J = 17.9, 4.0 Hz, 1, $CHCH_2$), 3.61 (dd, J = 17.9, 10.0 Hz, 1, $CHCH_2$), 5.10 (dd, J = 10.0 4.0 Hz,

1, C*H*CH_2), 7.2–7.5 (m, 8), 7.95 (m, 2); IR (neat) 3060, 3025, 2920, 1738 (C=O), 1684 (Ar C=O), 1600, 1580, 1495, 1455, 1450, 1396, 1355, 1250, 1165, 978, 755, 696 cm^{-1}.

4-Acetyl-4-hydroxy-2,5-cyclohexadienone (4a). The carbonylate was formed over 0.5 h at −40 °C [700 mg of 1 (1.72 mmol), 1.30 mL of 1.3 M CH_3Li (1.7 mmol), 15 mL of THF], and then benzoquinone (151 mg, 1.4 mmol) dissolved in 1.5 mL of THF was added and the reaction warmed to −20 °C and allowed to react for 0.3 h. The usual isolation and Chromatotron purification (1:1 hexane–Et_2O) gave 60 mg (28%, R_f 0.32) of product as an oily solid. An analytical sample was obtained by evaporative distillation, 70 °C (0.2 mmHg): mp 57–58 °C; ^1H NMR ($CDCl_3$) δ 2.29 (s, 3, CH_3), 4.9 (br s, 1, OH), 6.75 (d, J = 8.8 Hz, 2), 6.91 (d, J = 8.8 Hz, 2); IR (neat) 3590, 3410 (OH), 3025, 2920, 1745, 1730 (C=O), 1603, 1505, 1445, 1368, 1230, 1183, 1093, 1040, 1009, 900, 848, 830, 819, 770, 733 cm^{-1}. Anal. Calcd for $C_8H_8O_3$: C, 63.15; H, 5.30. Found: C, 63.37; H, 5.38.

4-Acetyl-2,3-dimethyl-4-hydroxy-2,5-cyclohexadienone (4b). The carbonylate was formed over 0.5 h at −40 °C [407 mg of 1 (1.0 mmol), 770 μL of 1.3 M CH_3Li (1.0 mmol), 10 mL of THF], then 2,3-dimethylbenzoquinone (100 mg, 0.7 mmol) dissolved in 1.5 mL of THF was added, and the temperature was kept at −40 °C for 0.5 h. The usual isolation and Chromatotron separation (1:1 hexane–Et_2O) gave 64 mg (64%) of recovered starting quinone and 32 mg (25%, R_f = 0.32) of product as a white crystalline solid: mp 97.5–98.5 °C; ^1H NMR ($CDCl_3$) δ 2.05 (s, 3, CH_3), 2.11 (s, 3, CH_3), 2.31 (s, 3, $COCH_3$), 5.32 (s, 1, OH), 6.48 (d, J = 8.6 Hz, 1), 6.66 (d, J = 8.6 Hz, 1); IR (neat) 3440 (OH), 2920, 2860, 1750, 1730 (C=O), 1655, 1592, 1485, 1455, 1370, 1286, 1240, 1215, 1190, 1080, 1044, 1010, 900, 850, 808, 768, 730 cm^{-1}. Evaporative distillation gave an analytical sample, 70 °C (0.1 mmHg). Anal. Calcd for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.76; H, 6.81.

4-Acetyl-2,5-dimethyl-4-hydroxy-2,5-cyclohexadienone (4c). The carbonylate was made over 0.5 h at −40 °C [407 mg of 1 (1.0 mmol), 770 μL of 1.3 M CH_3Li (1.0 mmol), 10 mL of THF] and then 2,5-dimethylbenzoquinone (75 mg, 0.55 mmol) in 1.5 mL of THF was added and the solution warmed to −20 °C and allowed to react for 10 h. The usual isolation and Chromatotron purification (1:1 hexane–Et_2O) gave 47 mg (62%) of starting quinone and 39 mg (39%, R_f 0.30) of product as a white solid: mp 118–119 °C; ^1H NMR ($CDCl_3$) δ 2.05 (s, 3, CH_3), 2.13 (s, 3, CH_3), 2.30 (s, 3, $COCH_3$), 5.18 (s, 1, OH), 6.49 (s, 1), 6.71 (s, 1); IR (neat) 3440 (OH), 2950, 2925, 2890, 2860, 1760, 1732 (C=O), 1630, 1592, 1520, 1507, 1465, 1410, 1370, 1240, 1210, 1080, 1040, 1009, 990, 910, 870, 730 cm^{-1}. Anal. Calcd for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.80; H, 6.83.

4-Acetyl-4-hydroxy-2-methyl-2,5-cyclohexadienone (4d). The carbonylate was made over 0.5 h at −40 °C [650 mg of 1 (1.6 mmol), 1.23 mL of 1.3 M CH_3Li (1.6 mmol), 10 mL of THF], then toluquinone (122 mg, 1.0 mmol) dissolved in 1.5 mL of THF was added, and the solution was warmed to −20 °C and allowed to react for 11 h. The usual isolation and Chromatotron purification (1:1 hexane–Et_2O) gave 42 mg (25%, R_f 0.24) of product as a white solid: mp 98–100 °C; ^1H NMR ($CDCl_3$) δ 2.09 (s, 3, CH_3), 2.31 (s, 3, $COCH_3$), 5.42 (s, 1, OH), 6.57 (s, 1, =CH), 6.58 (d, J = 8.4 Hz, 1, =C*H*COH), 6.80 (d, J = 8.4 Hz, 1, =CHCO); IR (neat) 3430 (OH), 2960, 2925, 1756, 1736 (C=O), 1621, 1605, 1596, 1499, 1460, 1435, 1373, 1300, 1220, 1185, 1105, 1014, 910, 861, 819 cm^{-1}. Anal. Calcd for $C_9H_{10}O_3$: C, 65.05; H, 6.06. Found: C, 65.39; H, 6.15.

4-Acetyl-2,6-dimethyl- (4e) and 4-Acetyl-3,5-dimethyl-4-hydroxy-2,5-cyclohexadienone (4e'). The carbonylate was made over 0.5 h at −40 °C [650 mg of 1 (1.6 mmol), 1.23 mL of 1.3 M CH_3Li (1.6 mmol), 10 mL of THF], then 2,6-dimethylbenzoquinone (136 mg, 1.0 mmol) dissolved in 1.5 mL of THF was added, and the solution was warmed to −20 °C and allowed to react for 16 h. The usual isolation and purification gave 71 mg (52%) of starting quinone and 59 mg (33%, R_f 0.26) of product: mp 112–114 °C; ^1H NMR ($CDCl_3$) δ 2.08 (s, 6, CH_3), 2.32 (s, 3, $COCH_3$), 4.77 (s, 1, OH), 6.49 (s, 2); IR (neat) 3470 (OH), 2950, 1748 (C=O), 1605, 1474, 1372, 1320, 1240, 1190, 1180, 1030, 923, 855, 800 cm^{-1}. Anal. Calcd for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.70; H, 6.81.

Also formed was 4-acetyl-3,5-dimethyl-4-hydroxy-2,5-cyclohexadienone (4e'): 32 mg (18%, R_f 0.30): mp 82–84 °C; ^1H NMR ($CDCl_3$) δ 2.23 (s, 6, CH_3), 2.26 (s, 3, $COCH_3$), 4.52 (s, 1, OH), 6.70 (s, 2); IR (neat) 3460 (OH), 2910, 1745 (C=O), 1603, 1487, 1432, 1370, 1322, 1220, 1180, 1026, 904, 850 cm^{-1}. Anal. Calcd for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.69; H, 6.62.

4-Acetyl-4-hydroxy-2,3,5,6-tetramethyl-2,5-cyclohexadienone (4f). The carbonylate was made over 0.5 h at −40 °C [650 mg of 1 (1.6 mmol), 1.14 mL of 1.4 M CH_3Li, 10 mL of THF], and then duroquinone was added (164 mg, 1.0 mmol) and the solution warmed to −20 °C and allowed to react 12 h. The usual isolation and Chromatotron separation (1:1 hexane–Et_2O) gave three fractions.

Fraction 1: 90 mg (55%) of duroquinone. Fraction 2: 61 mg (29%, R_f 0.18) of product; ^1H NMR ($CDCl_3$) δ 2.03 (s, 6, CH_3), 2.10 (s, 6, CH_3), 2.34 (s, 3, $COCH_3$), 4.73 (s, 1, OH); IR (KBr) 3510 (OH), 3000, 2930, 2870, 1740 (C=O), 1575, 1469, 1381, 1370, 1297, 1263, 1225, 1105, 1068, 911, 828 cm^{-1}; mp 147–149 °C (from hexane). Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.22; H, 7.73. Fraction 3: 35 mg (19%, R_f 0.15) of 4-acetyl-2,3,4,5,6-pentamethyl-2,5-cyclohexanedienone; ^1H NMR ($CDCl_3$) δ 1.37 (s, 3, CH_3), 1.84 (s, 6, CH_3), 2.04 (s, 6, CH_3); IR (KBr) 3420 (OH), 2992, 2920, 1662, 1615, 1442, 1374, 1358, 1343, 1281, 1083, 1025, 997, 918, 776 cm^{-1}; mp 138–139 °C (lit. mp 138–140 °C[21]).

4-Acetyl-4-hydroxy-1,4-dihydronaphthalenone (4g). The carbonylate was made over 0.5 h [650 mg of 1 (1.6 mmol), 1.23 mL of 1.3 M CH_3Li (1.6 mmol), 10 mL of THF] at −40 °C, and then naphthoquinone (158 mg, 1.0 mmol) dissolved in 1.5 mL of THF was added. The mixture was warmed to −20 °C and allowed to react for 4.5 h. The usual isolation and Chromatotron separation (1:1 hexane–Et_2O) gave 51 mg (30%) of recovered naphthoquinone and 34 mg (15%, R_f 0.22) of product as a white crystalline solid: mp 132–133 °C; ^1H NMR ($CDCl_3$) δ 2.46 (s, 3, CH_3), 5.94 (s, 1, OH), 6.49 (d, J = 8.0 Hz, 1), 6.94 (d, J = 8.0 Hz, 1), 7.48 (m, 2), 7.74 (d, J = 7.9 Hz, 1), 8.07 (d, J = 9.0 Hz, 1); IR (neat) 3440 (OH), 3060, 1745 (C=O), 1605, 1587, 1478, 1440, 1388, 1370, 1352, 1220, 1146, 1063, 1015, 1000, 928, 900, 820, 770, 755 cm^{-1}. An analytical sample was obtained by evaporative distillation, 95 °C (0.05 mmHg). Anal. Calcd for $C_{12}H_{10}O_3$: C, 71.28; H, 4.98. Found: C, 71.48; H, 5.04.

Methyl *trans*-Geranyl Ketone.[10] The carbonylate was made over 0.5 h at −40 °C [650 mg of 1 (1.6 mmol), 1.14 mL of 1.4 M CH_3Li (1.6 mmol), 10 mL of THF], then *trans*-geranyl bromide (200 μL, 1.0 mmol) was added by syringe, and the reaction was warmed to −20 °C and allowed to react for 22 h. The usual isolation and Chromatotrn separation (1:1 hexane–Et_2O) gave 55 mg (31%, R_f 0.57) of product as a colorless oil: ^1H NMR ($CDCl_3$) δ 1.60 (s, 3, CH_3), 1.63 (s, 3, CH_3), 1.67 (s, 3, CH_3), 2.07 (m, 4, CH_2CH_2), 2.14 (s, 3, $COCH_3$), 3.12 (d, J = 7.2 Hz, 2, =CHC*H*$_2$), 5.08 (m, 1, =CH), 5.32 (m, 1, =CH); IR (neat) 2965, 2920, 2845, 1714 (C=O), 1552, 1445, 1375, 1355, 1155, 1105, 905 cm^{-1}. Also formed in this reaction was 53 mg (39%, R_f 0.82) of bigeranyl (**6a**):[22] ^1H NMR ($CDCl_3$) δ 1.60 (s, 12, CH_3), 1.66 (s, 6, CH_3), 1.9–2.15 (m, 12, CH_2), 4.85–5.20 (m, 4, =CH); IR (neat) 3020, 2962, 2920, 2850, 1446, 1376, 1100, 905 cm^{-1}.

***n*-Butyl *trans*-Geranyl Ketone.**[10] The carbonylate was formed over 0.75 h at −40 °C [650 mg of 1 (1.6 mmol), 700 μL of 2.3 M *n*-BuLi, 10 mL of THF], then *trans*-geranyl bromide (200 μL, 1.0 mmol) was added by syringe, and the reaction was warmed to −20 °C and allowed to react for 21 h. The usual isolation and Chromatotron separation (7:1 hexane–Et_2O) gave 103 mg (53%, R_f 0.42) product as a colorless oil: ^1H NMR ($CDCl_3$) δ 0.90 (t, J = 7.3 Hz, 3, CH_2CH_3), 1.30 (m, 2, CH_2CH_3), 1.55 (m, 2, $CH_2CH_2CH_3$), 1.60 (s, 3, CH_3), 1.63 (s, 3, CH_3), 1.68 (s, 3, CH_3), 2.06 (m, 4, CH_2CH_2), 2.42 (t, J = 7.4 Hz, 2, $COCH_2CH_2$), 3.10 (d, J = 7.2 Hz, 2, =CHC*H*$_2$), 5.08 (m, 1, =CH), 5.32 (m, 1, =CH); IR (neat) 2960, 2920, 2865, 1716 (C=O), 1438, 1406, 1374, 1170, 1120, 1100, 976 cm^{-1}. Also 53 mg (39%, R_f 0.81) of bigeranyl was formed.[22]

Methyl *trans*-Cinnamyl Ketone.[10] The carbonylate was formed over 0.5 h at −40 °C [650 mg of 1 (1.6 mmol), 1.15 mL of 1.3 M CH_3Li (1.5 mmol), 15 mL of THF], then cinnamyl bromide (197 mg, 1.0 mmol) was added, and the solution was

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warmed to −20 °C and allowed to react for 22 h. The usual isolation and Chromatotron separation (1:1 hexane–Et_2O) gave 56 mg (35%, R_f = 0.46) of product as a colorless oil: ^1H NMR ($CDCl_3$) δ 2.21 (s, 3, CH_3), 3.34 (d, J = 7.0 Hz, 2, CH_2), 6.32 (dt, J = 15.9, 7.0 Hz, 1, CH_2CH=), 6.47 (d, J = 15.9 Hz, 1, =CH), 7.2–7.4 (m, 5); IR (neat) 3060, 3030, 2970, 2930, 1716 (C=O), 1677, 1600, 1555, 1497, 1450, 1358, 1157, 962 cm^{-1}. Also formed was 1,6-diphenyl-3-acetyl-1,5-hexadiene: 42 mg (40%, R_f 0.56); ^1H NMR ($CDCl_3$) δ 2.22 (s, 3, $COCH_3$), 2.50 (m, 1, $CHCH_2$), 2.70 (m, 1, $CHCH_2$), 3.41 (m, 1, $CHCH_2$), 6.15 (m, 2, =CH), 6.50 (m, 2, =CH), 7.1–7.4 (m, 10); IR (neat) 3080, 3058, 3022, 2995, 2910, 1712 (C=O), 1598, 1493, 1448, 1351, 1152, 1065, 1022, 960, 736, 684 cm^{-1}.

***n*-Butyl *trans*-Cinnamyl Ketone.**[10] The carbonylate was formed over 0.75 h at −40 °C [650 mg of **1** (1.6 mmol), 700 μL of 2.3 M *n*-BuLi (1.6 mmol), 10 mL of THF], then cinnamyl bromide (197 mg, 1.0 mmol) was added, and the solution was warmed to −20 °C and allowed to react for 21 h. The usual isolation and Chromatotron separation (7:1 hexane–Et_2O) gave 70 mg (35%, R_f 0.31) of product as a colorless oil: ^1H NMR ($CDCl_3$) δ 0.91 (t, J = 7.3 Hz, 3, CH_2CH_3), 1.31 (m, 2, CH_2CH_3), 1.58 (m, 2, $CH_2CH_2CH_3$), 2.49 (t, J = 7.4 Hz, 2, $COCH_2CH_2$), 3.31 (d, J = 6.9 Hz, 2, =$CHCH_2$), 6.32 (dt, J = 16.0, 6.9 Hz, 1, =$CHCH_2$), 6.46 (d, J = 15.9 Hz, 1, CH=$CHCH_2$), 7.2–7.4 (m, 5); IR (neat) 3080, 3055, 3020, 2950, 2920, 2862, 1710 (C=O), 1595, 1492, 1461, 1445, 1400, 1374, 1252, 1118, 1062, 1020, 956, 730, 680 cm^{-1}.

3-Acetylcyclohexene. The carbonylate was formed over 0.5 h at −40 °C [650 mg of **1** (1.6 mmol), 1.14 mL of 1.4 M CH_3Li (1.6 mmol), 10 mL of THF], then 3-bromocyclohexene (116 μL, 1.0 mmol) was added, and the solution was warmed to −20 °C and allowed to react for 24 h. The usual isolation and Chromatotron purification (1:1 Et_2O–hexane) gave two major fractions. The second fraction was 25 mg (20%, R_f 0.50) of product as a colorless oil: ^1H NMR ($CDCl_3$) δ 2.18 (s, 3, CH_3), 1.2–2.4 (m, 6), 3.1 (m, 1, CH), 5.85 (m, 2, CH=CH); IR (neat) 3020, 2930, 2860, 2830, 1710 (C=O), 1642, 1445, 1430, 1354, 1275, 1226, 1164, 1045 cm^{-1}. Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.94. Found: C, 77.18; H, 9.71. The first fraction was 48 mg (59%, R_f 0.80) of 3-(3-cyclohexen-1-yl)cyclohexene (**6e**).[23] ^1H NMR ($CDCl_3$) δ 1.0–2.3 (m, 14), 5.56 (m, 4); IR (neat) 3018, 2925, 2855, 2835, 1650, 1445, 1432, 1338, 1309, 1140, 1129, 1052, 975, 901, 870, 862, 726 cm^{-1}.

Acylation with BF_3·Et_2O and/or Allylic Chlorides. The reactions were performed as with allylic bromides with the exception that if a Lewis acid was used, it was added 10–30 min after alkyllithium addition and the reaction mixture allowed to stir at −40 °C for 10–30 additional min. Then the appropriate allylic halide was introduced. A representative example follows.

4,5-Dimethylene-2,7-octanedione. The carbonylate was made over 20 min at −40 °C [814 mg of **1** (2.0 mmol), 1.25 mL of 1.6 M CH_3Li (2.0 mmol), 10 mL of THF], then 1 equiv of BF_3·Et_2O (240 μL, 2.0 mmol) was added, and the mixture was stirred an additional 10 min. Then 2,3-bis(chloromethyl)-1,3-butadiene (91 mg, 0.6 mmol) was added and the reaction warmed to −20 °C and allowed to react for 7 h. The usual isolation and Chromatotron purification (3:1 Et_2O–hexane) gave 51 mg (51%, R_f 0.29) of product as a white crystalline solid: mp 55–57 °C; ^1H NMR ($CDCl_3$) δ 2.17 (s, 6, $COCH_3$), 3.38 (s, 4, CH_2), 5.16 (s, 2, =CHH), 5.24 (s, 3, =CHH); IR (KBr) 3094, 3000, 2959, 2906, 1820, 1709 (C=O), 1600, 1422, 1399, 1365, 1322, 1172, 1143, 1015, 904 cm^{-1}. Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.33; H, 8.26.

Reaction of β-Bromostyrene with 3. The carbonylate was made over 0.5 h at −40 °C [900 mg of **1** (2.21 mmol), 1.7 mL of 1.3 M CH_3Li (2.2 mmol), 20 mL of THF], then β-bromostyrene (91 μL, 0.7 mmol) was added, and the reaction was warmed to −20 °C for 48 h. The usual isolation and Chromatotron purification (1:1 hexane–Et_2O) gave 48 mg (36%, R_f 0.38) of 3-phenyl-2,5-hexanedione (**3a**) as product, identical in all respects with material made by an alternate procedure.[10]

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Registry No. **1**, 7632-00-0; **3a**, 25234-74-6; **3b**, 25234-75-7; **3c**, 98859-25-7; **3d**, 866-71-7; **3e**, 25234-81-5; **3f**, 4437-50-7; **3g**, 92803-31-1; **3h**, 98859-26-8; *cis*-**3j**, 98859-27-9; *trans*-**3j**, 98859-28-0; **3k**, 98859-29-1; **4a**, 98859-30-4; **4b**, 98859-31-5; **4c**, 98859-32-6; **4d**, 98859-33-7; **4e**, 98859-34-8; **4e'**, 98859-35-9; **4f**, 98859-36-0; **4g**, 98859-37-1; **6a**, 35162-77-7; **6e**, 41585-33-5; $Co(NO)(CO)_3$, 14096-82-3; $Co_2(CO)_8$, 15226-74-1; CH_3Li, 917-54-4; *n*-BuLi, 109-72-8; PhLi, 591-51-5; benzalacetone, 122-57-6; chalcone, 94-41-7; mesityl oxide, 141-79-7; *trans*-3-penten-2-one, 3102-33-8; phorone, 504-20-1; 1-acetylcyclohexene, 932-66-1; (+)-(*R*)-pulegone, 89-82-7; benzoquinone, 106-51-4; 2,3-dimethylbenzoquinone, 526-86-3; 2,5-dimethylbenzoquinone, 137-18-8; toluquinone, 553-97-9; 2,6-dimethylbenzoquinone, 527-61-7; duroquinone, 527-17-3; 4-acetyl-2,3,4,5,6-pentamethyl-2,5-cyclohexadienone, 98874-77-2; naphthoquinone, 130-15-4; *trans*-geranyl bromide, 6138-90-5; methyl *trans*-geranyl ketone, 61692-34-0; *n*-butyl *trans*-geranyl ketone, 98859-38-2; methyl *trans*-cinnamyl ketone, 42762-56-1; *trans*-cinnamyl bromide, 26146-77-0; *n*-butyl *trans*-cinnamyl ketone, 98859-39-3; *trans*-cinnamyl chloride, 21087-29-6; *trans*-geranyl chloride, 5389-87-7; 3-acetylcyclohexene, 29372-98-3; 3-bromocyclohexene, 1521-51-3; 3-chlorocyclohexene, 2441-97-6; 3-(3-cyclohexen-1-yl)cyclohexene, 41585-33-5; 4,5-dimethylene-2,7-octanedione, 98859-40-6; 2,3-bis(chloromethyl-1,3-butadiene), 19869-24-0; β-bromostyrene, 103-64-0; 1,6-diphenyl-3-acetyl-1,5-hexadiene, 98859-41-7.

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Notes

Reductive Debenzylation of 1-Benzylnaphthalene by a Na–K Alloy

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It has been reported that a Na–K alloy, when dissolved in a mixture of glyme–triglyme at 0 °C, is an excellent reagent for cleaving certain carbon–carbon bonds under mild conditions.[1,2] When applied to coal, this blue solution of "solvated electrons" is an excellent reducing medium for converting coal to a pyridine-soluble product.[3]

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