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Synthesis of α-Diketones by Direct, Low-Temperature, in Situ Nucleophilic Acylation of Esters by Acyllithium Reagents

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Addition of *n*-, *sec*-, or *tert*-butyllithium to a CO-saturated solution of an ester, $R'CO_2R''$ in a solvent system of 4:4:1 (by volume) THF/Et_2O/pentane at −110 °C (or at −135 °C in 3:1 (by volume) Me_2O/THF), followed by hydrolysis with saturated aqueous NH_4Cl, results in the formation of α-diketones, BuC(O)C(O)R′, yellow liquids, in good yield. Similar reactions with diethyl succinate gave in one instance both t-$BuC(O)C(O)CH_2CH_2CO_2Et$ and t-$BuC(O)C(O)CH_2CH_2C(O)C(O)Bu$-$t$. The monoacylation product of dimethyl oxalate, t-$BuC(O)C(O)CO_2Me$, readily formed a crystalline hydrate, t-$BuC(O)C(OH)_2CO_2Me$.

Introduction

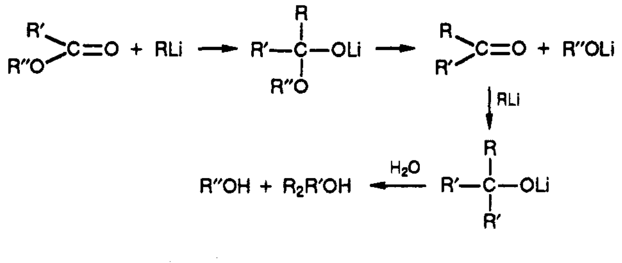
Several years ago, in a series of preliminary communications,[1-10] we reported the direct nucleophilic acylation of a variety of organic electrophiles by acyllithium reagents, RC(O)Li. The latter, for effective utilization in synthesis, had to be generated at low temperatures (−135 °C to −110 °C) in the presence of the organic electrophile. Accounts of the history of nucleophilic acylation and of our own studies relating to the development of acyllithiums as useful synthetic reagents have been given in review articles[11-14] and will not be repeated here. It is sufficient to point out that at such low temperatures the addition of the alkyllithium to C≡O (to give RC(O)Li) in many cases is faster than the reaction of the organolithium with the electrophilic substrate that is present in this in situ procedure. Also, again in many cases, the reaction of the RC(O)Li thus formed with the electrophilic substrate to give the desired acylation product is faster than any other processes that might consume the RC(O)Li. Good evidence has been provided by Nudelman and co-workers that the reaction of aryllithium reagents with carbon monoxide is a single-electron-transfer process,[15] and this makes the high rate of RLi/CO reactions at very low temperatures understandable.

Among the diverse reactions of acyllithium reagents, those with esters, which give α-diketones in high yield (eq 1), proceed particularly well. In view of the continuing

$$RLi + CO + R'CO_2R'' \xrightarrow{-110\ ^\circ C} RC(O){-}C(O)R' + R''OLi \quad (1)$$

interest in the synthesis of α-diketones,[16] we give full details of the work previously communicated and of further studies on this topic.

Scheme I



It will be noted that all of the nucleophilic ester acylations were carried out using *n*-, *sec*-, and *tert*-butyllithium. It was convenient to do so since they could be purchased. However, as demonstrated in our nucleophilic acylation of chlorosilanes,[1] other alkyllithium reagents (with the exception of CH_3Li) serve well in nucleophilic acylation chemistry. Such reactions of aryllithium reagents will be discussed in a later paper.

Results and Discussion

The reaction of organolithium reagents with carboxylic acid esters generally gives a mixture of a tertiary carbinol and a ketone (after hydrolytic workup, Scheme I).[17] The best yields of ketone are obtained when the organolithium reagent is added at low temperature to an excess of the ester, conditions which minimize the RLi/ketone reaction. In view of the very low temperatures required for the successful utilization of acyllithium reagents, we felt that an α-diketone synthesis by reactions of acyllithium reagents with ketones had a good chance of success. This turned out to be so. The procedure is a very simple one. A solution of the ester in a 4:4:1 (by volume) mixture of tetrahydrofuran (THF), diethyl ether, and pentane is cooled to −110 °C while carbon monoxide is bubbled through the solution. (Alternatively, the reaction can be carried out at −135 °C in a solvent system consisting of three parts by volume of dimethyl ether and one part of THF.) The CO stream is continued through the solution at these low temperatures for about 30 min. Subsequently,

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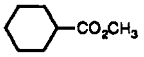
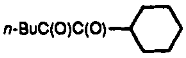
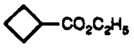
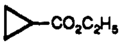
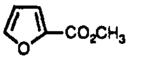
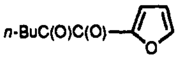
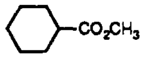
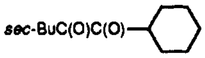
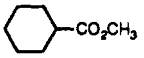
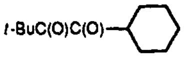
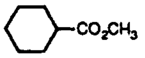
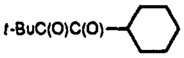
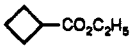
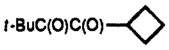
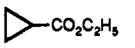
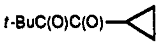
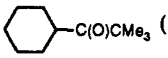
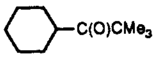
Table I. Synthesis of α-Dicarbonyl Compounds by Nucleophilic Acylation of Esters

R in RLi	ester	ester/RLi ratio	reaction temp, °C	1,2-diketone	(% yield)
n-Bu	$CH_3CO_2CH_3$	2	−110 °C	*n*-BuC(O)C(O)CH$_3$	(71)
n-Bu	$C_2H_5CO_2CH_3$	2	−110 °C	*n*-BuC(O)C(O)C$_2$H$_5$	(67)
n-Bu	*n*-$C_3H_7CO_2CH_3$	2	−110 °C	*n*-BuC(O)C(O)C$_3$H$_7$-n	(66)
n-Bu	*n*-$C_5H_{11}CO_2C_2H_5$	2	−110 °C	*n*-BuC(O)C(O)C$_5$H$_{11}$-n	(79)
n-Bu	*n*-$C_5H_{11}CO_2C_2H_5$	2	−78 °C	*n*-BuC(O)C(O)C$_5$H$_{11}$-n	(51)
n-Bu	$Me_3CCO_2CH_3$	2	−110 °C	*n*-BuC(O)C(O)CMe$_3$	(80)
n-Bu	$C_6H_5CO_2CH_3$	2	−110 °C	*n*-BuC(O)C(O)C$_6$H$_5$	(68)
n-Bu	*n*-$C_5H_{11}CO_2CH_3$	1	−110 °C	*n*-BuC(O)C(O)C$_5$H$_{12}$-n	(83)
n-Bu		2	−110 °C		(83)
n-Bu		1	−110 °C		(72)
n-Bu		1	−110 °C		(67)
n-Bu		1	−110 °C		(66)
sec-Bu	$Me_3CCO_2CH_3$	2	−110 °C	*sec*-BuC(O)C(O)CMe$_3$	(74)
sec-Bu	$Me_3CCO_2CH_3$	1	−110 °C	*sec*-BuC(O)C(O)CMe$_3$	(75)
sec-Bu	$C_2H_5CO_2CH_3$	1	−110 °C	*sec*-BuC(O)C(O)C$_2$H$_5$	(76)
sec-Bu		1	−110 °C		(46)
sec-Bu	$C_6H_5CO_2CH_3$	1	−110 °C	*sec*-BuC(O)C(O)C$_6$H$_5$	(65)
t-Bu	$C_6H_5CO_2CH_3$	2	−110 °C	*t*-BuC(O)C(O)C$_6$H$_5$	(53)[a]
t-Bu	$C_6H_5CO_2CH_3$	1	−110 °C	*t*-BuC(O)C(O)C$_6$H$_5$	(75)[b]
t-Bu	$C_6H_5CO_2CH_3$	1	−135 °C	*t*-BuC(O)C(O)C$_6$H$_5$	(88)
t-Bu	$C_2H_5CO_2CH_3$	1	−110 °C	*t*-BuC(O)C(O)C$_2$H$_5$	(77)
t-Bu	n-$C_6H_{13}CO_2C_2H_5$	2	−110 °C	*t*-BuC(O)C(O)C$_6$H$_{13}$-n	(70)
t-Bu		2	−110 °C		(77)[c]
t-Bu		1	−110 °C		(85)[d]
t-Bu		1	−110 °C		(80)
t-Bu		1	−110 °C		(60)

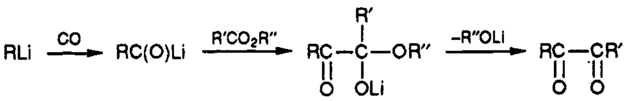
[a] Also C$_6$H$_5$C(O)CMe$_3$ (27%). [b] Also C$_6$H$_5$C(O)CMe$_3$ (9%). [c] Also  (13%). [d] Also  (3%).

the alkyllithium reagent solution is added very slowly, at a constant rate, by means of a syringe pump. Upon completion of the addition, the reaction mixture is stirred for 2 h at the low temperature. During the alkyllithium addition, the reaction solution becomes orangish in color, and when the addition is complete, it is orange-red. The reaction mixture then is allowed to warm to room temperature in a stream of CO. This results in a further color change to light orange. Hydrolytic workup (saturated aqueous NH_4Cl) then gives a yellow organic layer from which the α-diketone product, generally a bright yellow liquid, can be isolated by fractional distillation or by gas chromatography (GLC).

Initially, the reactant stoichiometry used was 2 molar equiv of ester to 1 of the alkyllithium reagent; the reaction temperature used was −110 °C. In many such reactions the yields of α-diketones obtained were quite satisfactory, in the 65–80% range. However, in some cases the byproduct (i.e., the product of RLi addition to the substrate) yield was comparable to or exceeded that of the desired α-diketone. For instance, the addition of *t*-BuLi to 2 molar equiv of methyl propionate in the presence of CO in 4:4:1 THF/Et$_2$O/C$_5$H$_{12}$ at −110 °C resulted in the formation of *t*-BuC(O)C(O)C$_2$H$_5$ in 21% yield as well as *t*-BuC(O)C(OH)(CH$_2$CH$_3$)(Bu-*t*) in 18% yield. The latter resulted from the reaction of *t*-BuC(O)Li with CH$_3$CH$_2$C(O)Bu-*t*, the product of the reaction of *t*-BuLi with methyl propionate. It was clear that under those conditions the *t*-BuLi/ester reaction was not suppressed nor was nucleophilic attack at the ethyl *tert*-butyl ketone byproduct disfavored. A change in experimental conditions solved this problem very nicely.

Experiments in which the direct in situ nucleophilic acylation of aldehydes and reactive ketones was studied in greater detail had shown that optimum results were obtained when a 1:1 RLi/electrophile stoichiometry was used and the reaction temperature was lowered to −135 °C.[4] This required a change in the reaction solvent to three parts by volume of dimethyl ether and one of THF in order to have a stirrable system. For the nucleophilic acylation of esters a change to a 1:1 RLi/ester stoichiometry (still at −110 °C) in some cases had dramatic effects. With the *t*-BuLi/CO/C$_2$H$_5$CO$_2$CH$_3$ reaction a 1:1 reactant stoichiometry resulted in a *t*-BuC(O)C(O)C$_2$H$_5$ yield of 77% and the byproduct yield was suppressed to less than 5%. The case of the *t*-BuLi/CO/C$_6$H$_5$CO$_2$CH$_3$ reaction also is illustrative. When the original 1:1 *t*-BuLi/CO/2 C$_6$H$_5$CO$_2$CH$_3$ at −100 °C conditions were used, the yield of *t*-BuC(O)C(O)C$_6$H$_5$ was 53%. When a 1:1 stoichiometry was used at −110 °C, the product yield was increased to 75%, and a 1:1 stoichiometry at −135 °C gave *t*-BuC(O)C(O)C$_6$H$_5$ in 88% yield. Table I lists the results of the RLi + CO + ester reactions carried out during the course of this study. It is readily apparent that an excellent synthesis of α-diketones is in hand. Most of these reactions were carried out on a small (~10 mmol) scale, and the product usually was isolated by gas chromatography. However, these reactions may be carried out with good success on a larger, preparative scale as illustrated by the preparation of 9 g of *n*-C$_4$H$_9$C(O)C(O)CH(CH$_3$)$_2$ (in 74%

Scheme II



yield) by the in situ reaction of n-C_4H_9Li, CO, and $(CH_3)_2CHCO_2CH_3$ at −100 °C.[18] The nucleophilic acylations of monoesters carried out in this study are summarized in Table I.

The suggested reaction course of the RLi/CO/ester reaction is shown in Scheme II. To confirm this, the in situ reaction of *tert*-butyllithium, CO, and ethyl acetate was carried out at −110 °C, and then trimethylchlorosilane was added to the reaction mixture before it was warmed to room temperature. This served to trap the t-BuC(O)C$(CH_3)(OC_2H_5)$(OLi) intermediate, giving t-Bu(O)C$(CH_3)(OC_2H_5)(OSiMe_3)$ in 87% yield. This experiment demonstrates that the loss of lithium alkoxide to form the α-diketone occurs only at higher temperatures.

Experiments in which the electrophile was a diester also were carried out. Alkyllithium/CO/diethyl succinate reactions, using a 1:1 $RLi/C_2H_5O_2CCH_2CH_2CO_2C_2H_5$ ratio at −110 °C gave $RC(O)C(O)CH_2CH_2CO_2C_2H_5$, an interesting functional ester, in fair yield (R = n-Bu, 64%; *sec*-Bu, 40%; t-Bu, 40%). In the reaction in which t-BuLi was used there was a second product of higher GLC retention time, a viscous yellow liquid (51% yield) which was identified as the diaddition product, t-BuC(O)C(O)CH_2CH_2C(O)C(O)Bu-t.

Of particular interest was the reaction of the t-BuLi/CO reagent with dimethyl oxalate, carried out using 1:1 t-BuLi/$(CO_2Me)_2$ stoichiometry at −110 °C with hydrolytic workup. The product, collected by preparative GLC, was a yellow liquid. This, however, changed to a white crystalline solid, mp 60 °C, on exposure to the laboratory air. When a benzene solution of the white solid was heated at reflux using a Dean-Stark trap the solution turned yellow. The yellow liquid could be isolated again by GLC of this solution. Analytical and spectroscopic data established that the yellow liquid was 1 and that the white solid was

t-BuC(O)C(O)C(O)OCH_3
1

its hydrate 2. The central C═O group of 1 would be expected to be very electrophilic as a result of the electronic effects of the adjacent acyl and ester groups. Like

t-BuC(O)C$(OH)_2$C(O)OCH_3
2

other very electrophilic carbonyl compounds such as chloral and glyoxal, 1 would be expected to form a hydrate on exposure to moisture. Since such hydration reactions are equilibrium processes, dehydration of 2 to give the tricarbonyl compound 1 is not surprising. In the t-BuLi/CO/dimethyl oxalate reaction 3 would be expected

t-BuC(O)C(OLi)(OCH_3)C(O)OCH_3
3

to be the initial product whose decomposition would give the tricarbonyl product 1. This intermediate could be intercepted by adding Me_3SiCl to the reaction mixture while it was still at −110 °C, giving 4 in good yield. The

t-BuC(O)C$(OSiMe_3)(OCH_3)$C(O)OCH_3
4

crude but fairly pure product could be identified on the basis of its IR and ^1H NMR spectra, but on attempted purification by GLC it decomposed in part to the yellow tricarbonyl compound 1.

Methyl pyruvate, $CH_3C(O)CO_2CH_3$, was a special case. Its acetyl group is activated by the adjacent ester group, and the t-BuLi/CO in situ reagent (1:1 stoichiometry at −110 °C) acylated the carbonyl function of the acetyl group, giving, after hydrolytic workup, 5, in 40% yield. In

t-BuC(O)C(CH_3)(OH)C(O)OCH_3
5

t-BuC(O)C$(CH_3)(OSiMe_3)$C(O)OCH_3
6

this case also, the initially formed product was intercepted with Me_3SiCl at −110 °C, giving 6 in 53% yield. No improvement in yield could be effected by carrying this reaction out at −135 °C; 5 was obtained in 48% yield. A similar reaction sequence using *sec*-BuLi resulted in formation of 7 in 41% yield.

sec-BuC(O)C$(CH_3)(OSiMe_3)$C(O)OCH_3
7

Diethyl carbonate was found to be sufficiently reactive to compete with CO for the alkyllithium reagent as it was being added to the CO-saturated $(EtO)_2C{=}O$ solution. The only products that could be isolated were the respective RC(O)C(O)OEt compounds in such reactions of n-, *sec*-, and *tert*-butyllithium.

The reaction of a thioester, $CH_3C(O)SEt$, with the t-BuLi/CO in situ reagent at −110 °C paralleled that of $CH_3C(O)OEt$, giving the diketone, t-BuC(O)C(O)CH_3 in 67% yield. In this case, EtSLi is lost from the initially formed product, t-BuC(O)C(OLi)(CH_3)(SEt). A similar reaction course was observed in the reaction of *N*,*N*-dimethylpivaloylamide with the n-BuLi/CO in situ reagent at −110 °C. In this reaction Me_2NLi was eliminated from the initially formed product and t-BuC(O)C(O)Bu-n was the final product that was produced in 57% yield. Although the nucleophilic acylation of RC(O)SR′ and RC(O)NR'_2 compounds was successful, the method of choice for the preparation of α-diketones by nucleophilic acylation is the one in which esters are the starting materials used.

Experimental Section

General Comments. ***All reactions* involving the use of CO were carried out in a good hood; *CO is toxic*, so due caution *should be exercised*.** All glassware was flame-dried prior to use under a stream of prepurified nitrogen. Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketyl, and pentane was distilled from lithium aluminum hydride prior to use. Dimethyl ether (Matheson) was passed through a drying tower of Drierite and condensed directly into the reaction flask. Carbon monoxide (Matheson) was used directly as received. n-Butyllithium (Alfa/Ventron, in hexane) and *tert*-butyllithium (Aldrich, in pentane) were used as received. *sec*-Butyllithium (Alfa/Ventron) was purchased as a solution in cyclohexane. However, cyclohexane freezes at the reaction temperature that was used, so cyclohexane was removed by trap-to-trap distillation (1.0 mmHg) at room temperature and replaced with pentane. All alkyllithium solutions were assayed prior to use by the Gilman method. Addition of alkyllithium solutions was effected with a syringe pump (Orion Research, Inc., Model 341 A). Melting points were uncorrected.

Total-immersion-type, low-temperature pentane thermometers (Kesler) were used to measure the temperature in the partial immersion mode. The readings usually are 7–8 °C higher compared to the actual temperature under our reaction conditions. The temperatures reported here all are corrected by subtracting 7 °C from the thermometer readings.

Proton NMR spectra were obtained using either JEOL FX-90Q (90-MHz) or Bruker WM-250 (250-MHz) spectrometers, with samples in $CDCl_3$ solution. They are reported in δ units, referenced to internal, residual $CHCl_3$ at 7.24 ppm downfield from tetramethylsilane. Infrared spectra were obtained using a Per-

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[18] For a preparative-scale synthesis of 3-hydroxy-2,2,3-trimethyloctan-4-one by the in situ reaction of n-butyllithium, CO, and pinacolone at −110 °C, see: Hui, R. C.; Seyferth, D. *Org. Synth.* **1990**, *69*, 114.

kin-Elmer Model 283B grating infrared spectrometer. Analytical gas chromatography was carried out using a Perkin-Elmer 5754 Research chromatograph equipped with a 6 ft × $^1/_4$ in. 15% SE-30 on Chromosorb P column and a Gow Mac 550P Model chromatograph with a similar column. The program used for the separation of the compounds was 100–275 °C, heating at 6 °C/min. Yields by GLC were obtained using the internal standard method (C_8–C_{12}). Analyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark.

Nucleophilic Acylation of Monoesters. (A) Small-Scale Procedure at −110 °C. Undecane-5,6-dione. A 500-mL, three-necked, round-bottomed flask equipped with a mechanical stirrer, a Claisen adapter (that was fitted with a low-temperature thermometer and a gas outlet tube), and a no-air stopper which held a gas dispersion tube (which was connected to a CO cylinder) was flushed well with dry N_2 and charged with 130 mL each of dry THF and diethyl ether, 40 mL of pentane, and 1.08 g (7.50 mmol) of ethyl hexanoate. This solution was cooled to −110 °C with the aid of a liquid nitrogen filled Dewar flask, and while the temperature was maintained at this temperature (± a few degrees) by appropriate raising or lowering of the Dewar flask, gaseous CO was bubbled through the solution for about 30 min. While the admission of CO was continued, 3.10 mL of a 2.39 N solution of *n*-butyllithium in hexane (7.41 mmol) was added, with stirring, at a controlled rate of about 0.5 mmol/min through a syringe needle that was connected by polyethylene tubing to an Orion Research, Inc., Model 341 A syringe pump. The tip of the syringe needle was held about 1 in. above the surface of the ester solution. After the addition had been completed, the orange to orange-red reaction mixture was stirred at −110 °C for 2 h while the stream of CO was continued. The mixture then was allowed slowly to warm to rt. During this time the color of the reaction mixture changed gradually from orange to light orange. Hydrolysis of this mixture with 75 mL of cold, saturated aqueous NH_4Cl solution, followed by separation of layers and washing of the aqueous layer with two portions of diethyl ether, gave a yellow combined organic solution. This was dried ($MgSO_4$), filtered, and distilled at reduced pressure (9-in. Vigreux column) to remove the solvents and other low-boiling material. Examination of the residue by GLC (6 ft × 0.25 in. SE-30 silicone rubber gum on Chromosorb P, 100–275 °C at 6 °C per min, decane internal standard) showed the presence of the title ketone in 83% yield.

Reactions in which the ester/RLi ratio was 2 were carried out in the same manner. In most cases, lower α-diketone yields were obtained compared to those of the 1:1 reactions.

(B) Large-Scale Procedures at −110 °C. 2-Methyl-3,4-octane-3,4-dione and Octane-3,4-dione. Addition (at 0.67 mL per min) of 30.4 mL of a 2.53 N solution of *n*-butyllithium in hexane (76.9 mmol) to 7.85 g (77.0 mmol) of methyl isobutyrate in a solvent mixture of 400 mL each of THF and diethyl ether and 100 mL of pentane (in a 2-L flask equipped as described above) at −110 °C was carried out by the procedure described above. After a 2-h reaction time at −110 °C, the mixture was allowed to warm to rt and hydrolyzed with 300 mL of saturated aqueous NH_4Cl. The dried organic phase was distilled to remove solvents. The residue was fractionally distilled (7-cm vacuum-jacketed Vigreux column) to give 8.92 g (74%) of 2-methyloctane-3,4-dione, bp 65–67 °C (20 Torr), 97% pure by GLC.

In such larger scale reactions, use of a syringe pump is convenient but not necessary. For instance, in a reaction of 71 mmol of *n*-BuLi with a CO-saturated solution of 90 mmol of methyl propionate in 350 mL each of THF and Et_2O and 85 mL of pentane at −110 °C, the lithium reagent solution was added by syringe, with the dropwise addition being controlled by hand at a rate of about 0.4 mL per min. Otherwise, the procedure was as that described above. Octane-3,4-dione (6.72 g, bp 66–69 °C (19 Torr)) was obtained in 66% isolated yield.

(C) Procedure at −135 °C. 3,3-Dimethyl-1-phenylbutane-1,2-dione. Essentially the same procedure as in A was used, except that a solvent system that is fluid at −135 °C was required. An about 3:1 (by volume) mixture of dimethyl ether (bp −24.9 °C) and THF, which had served well in earlier low-temperature reactions in these laboratories,[19] was used.

Following the procedure outlined in A above, *tert*-butyllithium (pentane solution, 1.68 N, 9.1 mL, 15.3 mmol) was added at a rate of 0.35 mL/min to a solution of methyl benzoate (2.09 g, 15.4 mmol) in 70 mL of THF and about 220 mL of Me_2O at −135 °C. (The temperature was maintained by means of a liquid nitrogen filled Dewar flask as in A.) The addition of the *t*-BuLi resulted in an orange-red solution, the color of which persisted at −135 °C throughout the 2-h reaction period. Warming the reaction mixture to rt gave an orange solution. The CO stream was stopped at about −30 °C while the Me_2O was distilling. Hydrolysis with 75 mL of saturated aqueous NH_4Cl resulted in a yellow organic phase. This was dried and distilled, and the residue was analyzed by GLC. The product was present in 88% yield.

In a similar reaction carried out at −110 °C using a 1:1 *t*-BuLi/$C_6H_5CO_2CH_3$ stoichiometry, the yield of the diketone was 75% and another product, $(CH_3)_3C(O)C_6H_5$, also was present in 9% yield. The latter resulted from the reaction of *t*-BuLi with methyl benzoate. The yield of the monoketone was increased to 27% and that of the 1,2-diketone decreased to 53% when a 1:2 *t*-BuLi/methyl benzoate stoichiometry was used in a reaction carried out at −110 °C.

Product Characterization. The pure α-diketones prepared in this study are yellow liquids. Their refractive indices, C, H analyses, ^{1}H NMR spectra, and characteristic IR ν (C=O) are collected in Table II.

Nucleophilic Acylation of Ethyl Acetate. Me_3SiCl Quench. 2-Ethoxy-4,4-dimethyl-2-(trimethylsiloxy)pentan-3-one. The procedure in A above was followed in the addition of 17.2 mmol of *t*-BuLi in pentane to a CO-saturated solution of 1.49 g (16.9 mmol) of ethyl acetate in 4:4:1 THF/Et_2O/pentane at −110 °C. Upon completion of the reaction, trimethylchlorosilane (5.60 g, 51.2 mmol) was added by syringe to the reaction mixture while it was still at −110 °C. Slow warming to rt was followed by filtration and evaporation of solvents at reduced pressure. GLC analysis (*n*-nonane internal standard) showed the presence of the title compound in 87% yield.

^{1}H NMR (90 MHz, $CDCl_3$): δ 0.19 (s, 9 H, Me_3Si), 1.15 (t, J = 7 Hz, 3 H, OCH_2CH_3), 1.22 (s, 9 H, Me_eC), 1.44 (s, 3 H, C-(OEt)CH_3), 3.30 (m, 2 H, OCH_2CH_3). IR (neat, NaCl): 1709 (s), ν (C=O) cm^{-1}. Anal. Calcd for $C_{12}H_{26}O_3Si$: C, 58.49; H, 10.63. Found: C, 58.87; H, 10.68.

Nucleophilic Acylation of Diesters. (a) With Diethyl Succinate. Ethyl 4,5-Dioxononanoate. The general procedure used in the RLi/CO/R′CO_2R″ reactions at −110 °C was applied to the reaction of 9.7 mmol of *n*-BuLi in hexane with 1.71 g (9.8 mmol) of $EtO_2CCH_2CH_2CO_2Et$ in 4:4:1 THF/Et_2O/pentane that was being kept saturated with CO. A sample of the product was isolated from the concentrated organic phase by GLC as a yellow liquid and identified as *n*-BuC(O)C(O)$CH_2CH_2CO_2Et$, n^{20}_D 1.4400. GLC yield determination (*n*-octane internal standard): 64%.

Ethyl 6-Methyl-4,5-dioxooctanoate. A similar reaction using *sec*-BuLi (11.7 mmol) and 2.02 g (11.6 mmol) of diethyl succinate gave the diketo ester, a yellow liquid, n^{25}_D 1.4457, in 40% yield.

Ethyl 6,6-Dimethyl-4,5-dioxoheptanoate. A reaction in which 9.7 mmol of *t*-BuLi in pentane and 9.7 mmol of diethyl succinate were used in the same procedure gave an organic phase that was too viscous to permit analysis by GLC. Accordingly, it was trap-to-trap distilled in high vacuum to give a clear yellow liquid distillate. GLC analysis of the latter (*n*-decane internal standard) showed the presence of a small amount of diethyl succinate and two other compounds. These, both yellow liquids, were collected by GLC and identified as the title diketo ester, n^{20}_D 1.4357, present in 40% yield, and the diaddition product, *t*-BuC(O)C(O)CH_2CH_2C(O)C(O)Bu-$_t$, a viscous yellow liquid, in 51% yield.

(b) With Dimethyl Oxalate. Methyl 4,4-Dimethyl-3-oxo-2,2-dihydroxypentanoate. The usual procedure was used in the addition of 5.2 mL of 1.74 N *t*-BuLi (9.0 mmol) to 1.08 g (9.1 mmol) of dimethyl oxalate in CO-saturated 4:4:1 THF/Et_2O/pentane (300 mL total) at −110 °C. The crude product obtained after solvent removal crystallized on exposure to laboratory air to form needles, mp 60.0 °C, 1.076 g. Alternatively, preparative GLC of the crude product gave a yellow liquid, exposure of which to the laboratory air resulted in crystallization to give colorless needles. According to its NMR spectra and analysis this product was $(CH_3)_3CC(O)C(OH)_2C(O)OCH_3$.

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[19] Seyferth, D.; Mueller, D. C.; Armbrecht, F. M., Jr. *Organomet. Chem. Synth.* **1970/71**, *1*, 3.

Table II. Characterizing Data for α-Diketones Prepared in This Study

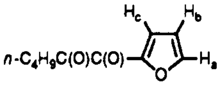
α-diketone	n^{20}_D	anal. calcd (found), %		^{1}H NMR, δ, ppm (* = CDCl$_3$, ≠ = CCl$_4$, # = C$_6$D$_6$, φ = CD$_2$Cl$_2$)	ν(CO), cm^{-1} (thin film)
		carbon	hydrogen		
n-$C_4H_9C(O)C(O)CH_3$	1.4134 (lit.[a] 1.4138)			*0.89 (t, J = 6.8 Hz, 3 H, CH_3 or n-Bu) 0.9–1.5 (m, 4 H, $CH_3C\mathit{H}_2C\mathit{H}_2CH_2$) 2.31 (s, 3 H, $C(O)CH_3$) 2.72 (t, 7.3 Hz, $C(O)CH_2$)	1720
n-$C_4H_9C(O)C(O)C_2H_5$	1.4191	67.57 (67.57)	9.92 (9.99)	≠0.8–1.4 (m, 10 H, alkyl H) 2.2–2.6 (m, 4 H, both $C(O)CH_2$)	1700
n-$C_4H_9C(O)C(O)C_3H_7$-n	1.4221 (n^{24}_D) (lit.[b] 1.4229)			*0.9–1.64 (m, 12 H, alkyl H) 2.70 (t, J = 6.83 Hz, 4 H, both $C(O)CH_2$)	1705
n-$C_4H_9C(O)C(O)C_5H_{11}$-n	1.4318	71.70 (71.91)	10.94 (10.96)	≠0.8–1.5 (m, 16 H, alkyl H) 2.49 (t, J = 7.3 Hz, 4 H, both $C(O)CH_2$	1710
n-$C_4H_9C(O)C(O)C(CH_3)_3$	1.4261	70.55 (70.84)	10.66 (10.64)	≠1.0–1.7 (m, 16 H, alkyl H, with s at 1.2 for t-Bu) 2.55 (t, J = 7.0 Hz, 2 H, $CH_2C(O)$)	1710
n-$C_4H_9C(O)C(O)C_6H_5$	1.5156			φ0.93 (t, J = 6.5 Hz, 3 H, CH_3 of n-Bu) 1.20–1.82 (m, 4 H, $CH_3C\mathit{H}_2C\mathit{H}_2CH_2$) 2.87 (t, J = 7.0 Hz, 2 H, $CH_2C(O)$) 7.40–7.67 and 7.74–8.01 (m, 3 H and 2 H, resp, Ph)	1710, 1672
n-$C_4H_9C(O)C(O)C_6H_{11}$-c	1.4601	73.43 (73.16)	10.27 (10.20)	*0.85–1.78 (m, 17 H, alkyl H) 2.86 (t, J = 7.0 Hz), 2 H, $CH_2C(O)$) 3.11 (m, 1 H, CH of C_6H_{11})	1705
n-$C_4H_9C(O)C(O)C_4H_7$-c	1.4515	71.39 (71.28)	9.59 (9.53)	*0.88 (t, J = 7.0 Hz, 3 H, CH_3 or n-Bu) 1.15–2.29 (m, 10 H, ring and butyl H) 2.71 (t, J = 7.0 Hz), 2 H, $C\mathit{H}_2C(O)$)	1704
n-$C_4H_9C(O)C(O)C_3H_5$-c	1.4469	70.10 (70.00)	9.15 (9.21)	*0.89–1.82 (m, 12 H, ring and butyl H) 2.60–2.86 (m, 3 H, CH of C_3H_5 and $C\mathit{H}_2C(O)$)	1700
		66.66 (66.33)	6.71 (6.78)	*0.91 (t, J = 6.8 Hz, 3 H, CH_3 or n-Bu) 1.38–1.62 (m, 4 H, $CH_3C\mathit{H}_2C\mathit{H}_2CH_2$) 2.89 (t, J = 7.1 Hz, 2 H, $CH_2C(O)$) 6.58 (dd, J_{ab} = 2.9 Hz, J_{bc} = 1.0 Hz, 1 H, H_b) 7.61 (d, 1 H, H_a) 7.72 (d, 1 H, H_c)	1708, 1655
$C_2H_5(CH_3)CHC(O)C(O)C_2H_5$		67.57 (67.15)	9.92 (9.81)	*0.86 (t, J = 7.4 Hz, 3 H, $CHCH_2C\mathit{H}_3$) 1.1 (m, 6 H, $C(O)CH_2C\mathit{H}_3$ and $CHC\mathit{H}_3$) 1.4–1.7 (m, 2 H, $CHC\mathit{H}_2CH_3$) 3.2 (m, 1 H, $C(O)C\mathit{H}$)	1710
$C_2H_5(CH_3)CHC(O)C(O)C(CH_3)_3$	1.4195	70.55 (70.84)	10.66 (10.64)	*0.89 (t, J = 7.4 Hz, 3 H, $CHCH_2C\mathit{H}_3$) 1.04 (d, J = 7.1 hz, 3 H, $C\mathit{H}_3CH$) 1.22 (s, 9 H, $C(C\mathit{H}_3)_3$) 1.3–1.7 (2 H, m, $CH_3C\mathit{H}_2CH$) 3.0 (m, 1 H, $C(O)C\mathit{H}$)	1710
$C_2H_5(CH_3)CHC(O)C(O)C_6H_{11}$-c	1.4540	73.43 (73.51)	10.27 (10.36)	*0.57–185 (m, 18 H, alkyl H) 3.0–3.31 (m, 2 H, $C\mathit{H}C(O)C(O)C\mathit{H}$)	1707
$C_2H_5(CH_3)CHC(O)C(O)C_6H_5$	1.5118	75.76 (75.59)	7.42 (7.34)	*0.80–2.12 (m, 8 H, alkyl H) 3.35 (m, 1 H, $C_2H_5C\mathit{H}$) 7.35–7.92 (m, 5 H, C_6H_5)	1705, 1640
$(CH_3)_3CC(O)C(O)C_6H_5$	1.5092 (lit.[c] 1.5086)			φ1.29 (s, 9 H, $C(C\mathit{H}_3)_3$) 7.5–7.9 (m, 5 H, $C_6\mathit{H}_5$)	1705, 1675
$(CH_3)_3CC(O)C(O)C_2H_5$	1.4249	67.57 (67.49)	9.92 (9.93)	*1.07 (t, J = 7.33 Hz, 3 H, $C\mathit{H}_3CH_2C(O)$) 1.22 (s, 9 H, $C(C\mathit{H}_3)_3$) 2.67 (q, J = 7.33 hz, $CH_3C\mathit{H}_2C(O)$)	1700
$(CH_3)_3CC(O)C(O)C_6H_{13}$-$n$		72.68 (72.63)	11.18 (11.09)	*0.7–2.2 (m, 20 H, alkyl H) incl 1.22 (s, $C(C\mathit{H}_3)_3$) 2.60 (t, J = 6.5 Hz, 2 H, $C\mathit{H}_2C(O)$)	1700
$(CH_3)_3CC(O)C(O)C_6H_{11}$-c		73.43 (73.52)	10.27 (10.23)	*1.09 (s, 9 H, $C(CH\mathit{H}_3)_3$) 1.2–2.0 (m, 10 H, ring CH_2) 2.80 (m, 1 H, $C\mathit{H}C(O)$)	1700
$(CH_3)_3CC(O)C(O)C_4H_7$-c	1.4398	71.39 (71.21)	9.59 (9.68)	*1.21 (s, 9 H, $C(CH_3)_3$) 1.85–2.30 (m, 6 H, ring CH_2) 3.57 (m, 1 H, $C\mathit{H}C(O)$)	1697
$(CH_3)_3CC(O)C(O)C_3H_5$-c		70.10 (70.17)	9.15 (9.16)	*0.95–1.13 (m, 4 H, ring CH_2) 1.23 (s, 9 H, $C(C\mathit{H}_3)_3$) 2.09 (m, 1 H, $C\mathit{H}C(O)$)	1690
n-$C_4H_9C(O)C(O)CH_2CH_2CO_2C_2H_5$	1.4400	61.66 (61.62)	8.47 (8.57)	0.79–1.50 (m, 12 H, $OCH_2C\mathit{H}_3$ and C_4H_9) 2.48–3.11 (m, 6 H, $C(O)CH_2CH_2C(O)$ and $C(O)C\mathit{H}_2CH_3$) 4.10 (q, J = 7.0 Hz, 2 H, $OC\mathit{H}_2$)	1736 (ester), 1716
$C_2H_5(CH_3)CHC(O)C(O)CH_2CH_2$-$CO_2C_2H_5$	1.4457	61.66 (62.02)	8.47 (8.57)	*0.78–1.59 (m, 12 H, $OCH_2C\mathit{H}_3$ and C_4H_9) 2.61–3.12 (m, 4 H, $C(O)CH_2CH_2C(O)$) 3.31–3.52 (m, 1 H, $C_2H_5C\mathit{H}$) 4.12 (q, J = 7.0 Hz, 2 H, $OC\mathit{H}_2CH_3$)	1738 (ester), 1717 1717
$(CH_3)_3CC(O)C(O)CH_2CH_2CO_2C_2H_5$	1.4357	61.66 (61.74)	8.47 (8.65)	*1.22 (m, 12 H, $C(C\mathit{H}_3)_3$ and $OCH_2C\mathit{H}_3$) 2.53–2.90 (2, 4 H, $C(O)CH_2CH_2C(O)$) 4.12 (q, J = 7.0 Hz, $OC\mathit{H}_2CH_3$)	1733 (ester), 1717

Table II (Continued)

α-diketone	$n^{20}{}_D$	anal. calcd (found), %		^{1}H NMR, δ, ppm (* = $CDCl_3$, ≠ = CCl_4, # = C_6D_6, ϕ = CD_2Cl_2)	ν(CO), cm^{-1} (thin film)
		carbon	hydrogen		
$(CH_3)_3C(O)C(O)CH_2CH_2C(O)$-$C(O)C(CH_3)_3$		66.12 (65.87)	8.72 (8.74)	*1.24 (s, 18 H, $C(CH_3)_3$) 2.98 (s, 4 H, $C(O)CH_2CH_2C(O)$) [^{13}C NMR in $CDCl_3$: 26.0 ($C(CH_3)_3$), 31.9 (CH_2), 42.2 ($C(CH_3)_3$), 200.2 ($C(O)C(CH_3)_3$), 206.6 ($C(O)CH_2$)]	1700

[a] Tischenko, I. G.; Akhrem, A. A.; Nazarov, I. N. *J. Gen. Chem. USSR* **1959**, *29*, 795. [b] Cuivigny, T. *Ann. Chim.* (*Paris*) **1956**, ser. 13 (1), 475. [c] Fuson, R. C.; Gray, H.; Gouza, J. J. *J. Am. Chem. Soc.* **1939**, *61*, 1937.

^{1}H NMR ($CDCl_3$): δ 1.23 (s, 9 H, *t*-Bu), 3.82 (s, 3 H, OCH_3), 5.05 (s, 2 H, OH). Addition of D_2O washed out the 5.05 ppm signal. ^{13}C {^{1}H} NMR ($CDCl_3$): δ_C 27.05 ($(CH_3)_3C$), 42.90 ($(CH_3)_3C$), 53.25 (OCH_3), 92.10 ($C(OH)_2$), 169.69 ($C(O)OCH_3$), 208.10 ($(CH_3)_3CC(O)$). IR (Nujol): 3420 (s, br), 3340 (s, br) (OH), 1750 (s), 1710 (s) (ν(C=O)) cm^{-1}. Anal. Calcd for $C_8H_{14}O_5$: C, 50.52; H, 7.42. Found: C, 50.82; H, 7.48.

Methyl 4,4-Dimethyl-2,3-dioxopentanoate. In another experiment, crystals of this hydrate (0.1 g) were placed in a 50-mL flask topped with a condenser and a Dean Stark trap to remove water. Benzene (20 mL) was added, and the solution was heated to reflux. After 15 min the initially colorless solution became yellow. After 3 h of reflux the benzene was distilled and the yellow liquid residue was purified by GLC and found to be the title tricarbonyl compound.

IR (thin film): no OH bands; 1765 (s), 1735 (s), 1710 (s) (ν(C=O) cm^{-1}. ^{1}H NMR (C_6D_6): δ 1.02 (s, 9 H, *t*-Bu), 3.14 (s, 3 H, OCH_3). ^{13}C {^{1}H} NMR ($CDCl_3$): δ_C 25.30 ($(CH_3)_3C$), 42.50 ($(CH_3)C$), 52.44 (OCH_3), 161.77 ($C(O)OCH_3$), 184.33 ($C(O)C(O)OCH_3$), 205.88 ($(CH_3)_3CC(O)$). Anal. Calcd for $C_8H_{12}O_4$: C, 55.81; H, 7.02. Found: C, 55.95; H, 7.14.

Exposure of this yellow liquid to moist air gave white crystals of the hydrate (IR).

Methyl 4,4-Dimethyl-3-oxo-2-methoxy-2-(trimethylsiloxy)pentanoate. When such a *t*-BuLi/CO/dimethyl oxalate reaction as carried out at −110 °C and the reaction mixture was quenched with an excess of trimethylchlorosilane, the crude product, identified as the title compound by ^{1}H NMR spectroscopy, was isolated in 94% yield.

^{1}H NMR ($CDCl_3$): δ 0.21 (s, 9 H, Me_3Si), 1.21 (s, 9 H, *t*-Bu), 3.33 (s, 3 H, $C(O)C(OCH_3)C(O)$), 3.75 (s, 3 H, CO_2CH_3).

However, this product could not be purified by GLC since this converted it in part to *t*-$BuC(O)C(O)CO_2CH_3$.

Nucleophilic Acylation of Methyl Pyruvate. Methyl 2,4,4-Trimethyl-3-oxo-2-hydroxypentanoate. The usual procedure was followed in the addition (0.43 mmol/min) of 5.1 mL of 1.78 N *t*-BuLi in pentane (9.0 mmol) to 0.82 mL (9.0 mmol) of $CH_3C(O)CO_2CH_3$ in CO-saturated 4:4:1 THF/Et_2O/pentane at −110 °C. The usual workup, followed by GLC analysis, showed two products to be present: *t*-BuC(O)CH(OH)Bu-*t* (16%) and *t*-$BuC(O)C(CH_3)(OH)CO_2CH_3$, $n^{20}{}_D$ 1.4366, in 40% yield.

^{1}H NMR ($CDCl_3$): δ 1.20 (s, 9 H, *t*-Bu), 1.56 (s, 3 H, CCH_3), 3.77 (s, 3 H, CH_3), 4.08 (s, 1 H, OH). IR (thin film): 1740 (s), 1710 (s), ν(C=O) cm^{-1}. Anal. Calcd for $C_9H_{16}O_4$: C, 57.43; H, 8.57. Found: C, 57.39; H, 8.53.

Methyl 2,4,4-Trimethyl-3-oxo-2-(trimethylsiloxy)pentanoate. In a similar experiment (same scale), in the workup, an excess of trimethylchlorosilane was added at −110 °C to the reaction mixture. Using a nonhydrolytic workup (filtration, distillation of volatiles), the title compound $n^{20}{}_D$ 1.4292, was isolated by GLC. The product yield was 53% by GLC.

^{1}H NMR ($CDCl_3$): δ 0.18 (s, 9 H, Me_3Si), 1.21 (s, 9 H, $C(CH_3)_3$), 1.55 (s, 3 H, CCH_3); 3.70 (s, OCH_3). IR (thin film): 1750 (ester C=O), 1710 (s) cm^{-1}. Anal. Calcd for $C_{11}H_{24}O_4$: C, 55.35; H, 9.29. Found: C, 55.78; H, 9.41.

Nucleophilic Acylation of Diethyl Carbonate. Ethyl 3,3-Dimethyl-2-oxobutanoate. The usual procedure was used in the addition of 5.0 mL of 1.8 N *t*-BuLi in pentane (9.0 mmol) at the rate of 0.43 mmol/min to 1.2 mL (10.0 mmol) of $(EtO)_2CO$ in CO-saturated 4:4:1 THF/Et_2O/pentane. The title oxo ester, present in 49% yield, was isolated by GLC.

^{1}H NMR ($CDCl_3$): δ 1.23 (s, 9 H, *t*-Bu), 1.33 (t, J = 7.3 Hz, 3 H, OCH_2CH_3), 4.33 (q, J = 7.3 Hz, OCH_2CH_3). This is in agreement with the ^{1}H NMR reported for this compound by Crandall et al.[20] IR (thin film): 1735 (ester), 1720 (sh, *t*-BuC(O)) cm^{-1}.

A similar reaction in which *sec*-BuLi was used gave *sec*-$BuC(O)CO_2Et$ in 30% yield.

^{1}H NMR ($CDCl_3$): δ 0.90 (t, J = 7.5 Hz, 3 H, CH_3CH_2C), 1.12 (d, J = 6.9 Hz, 3 H, CH_3CEt), 1.35 (t, J = 7.2 Hz, 3 H, OCH_2CH_3), 1.38–1.80 (m, 2 H, CH_3CH_2C), 3.06–3.19 (m, 1 H, CHC(O)), 4.32 (q, J = 7.2 Hz, 2 H, OCH_2CH_3).

Nucleophilic Acylation of *S*-Ethyl Thioacetate. 2,2-Dimethyloctane-3,4-dione. The standard in situ procedure was used in the addition of 3.90 mL of 2.40 N *t*-BuLi in pentane (9.36 mmol) to 1.0 mL (9.37 mmol) of $CH_3C(O)SEt$ in CO-saturated 4:4:1 THF/Et_2O/pentane at −110 °C. Hydrolysis of the yellow reaction mixture gave a bright yellow organic phase. GLC analysis of the concentrated organic phase showed the presence of the title diketone in 67% yield. The IR spectrum of this product was identical with that of an authentic sample prepared using the *t*-BuLi/CO/$CH_3CO_2CH_3$ reaction.

Nucleophilic Acylation of *N*,*N*-DimethylPivaloylamide. 2,2-Dimethyloctane 3,4-dione. The standard in situ procedure was used in the reaction of 11.0 mmol of *n*-BuLi in hexane with 1.49 g (11.5 mmol) of *t*-$BuC(O)NMe_2$ in a solvent mixture of 250 mL of pentane and 50 mL of THF at −110 °C. The usual workup was followed by GLC analysis of the concentrated organic phase. *t*-BuC(O)C(O)Bu-*n* was present in 57% yield. It was identified by comparison of its IR and ^{1}H NMR spectra with those of an authentic sample.

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