Registry No.—**1**, 5089-33-8; **2a**, 54120-39-7; **3a**, 41992-38-5; **3b**, 42077-73-6; **3c**, 41992-39-6; **4a**, 54120-40-0; **4b**, 54120-41-1; **4c**, 3454-24-8; **5**, 54120-42-2; **7a**, 54120-43-3; **7b**, 54120-44-4; **7c**, 54120-45-5; **8a**, 54120-46-6; **8b**, 54181-91-8; **8c**, 54120-47-7; **10**, 1137-41-3; **11**, 54120-48-8; **12**, 54120-49-9; **13**, 54120-50-2; 1,3-dicyanobenzene, 626-17-5; 3,5-dicyanopyridine, 1195-58-0; 4,4′-dicyanobiphenyl, 1591-30-6; *p*-bromoaniline, 106-40-1; chlorotrimethylsilane, 75-77-4; dichlorodiphenylsilane, 80-10-4; dichloromethylphenylsilane, 149-74-6; dichlorodimethylsilane, 75-78-5.

References and Notes

(1) Taken in part from the Ph.D. Dissertation of J. R. Pratt, University of Southern Mississippi, 1974.
(2) W. Broser and W. Harrer, *Angew. Chem.*, **77**, 1139 (1965); *Angew. Chem., Int. Ed. Engl.*, **4**, 1081 (1965).
(3) D. R. M. Walton, *J. Chem. Soc. C*, 1706 (1966).
(4) G. Greber, *J. Prakt. Chem.*, **313**, 461 (1971).
(5) F. S. Kipping and N. W. Cusa, *J. Chem. Soc.*, 1088 (1935).
(6) J. R. Pratt and S. F. Thames, *Synthesis*, **4**, 223 (1973).
(7) F. C. Schaefer, "Chemistry of the Cyano Groups", Z. Rappoport, Ed., Interscience, New York, N.Y., 1970, p 276.
(8) The crude material displayed a broad carboxylic dimer stretch at 2950 cm^{-1} and a strong acid carbonyl stretch at 1630 cm^{-1}. Both absorptions disappeared after recrystallization from acetone in the presence of dilute base.
(9) Redistilled from $LiAlH_4$ or CaH_2 under nitrogen and stored over molecular sieves.
(10) Stored over sodium ribbon.
(11) F. H. Pinkerton, Dissertation, University of Southern Mississippi, 1971, p 173.

Dipole Stabilized Carbanions. Reactions of Benzoate Esters with Lithium 2,2,6,6-Tetramethylpiperidide

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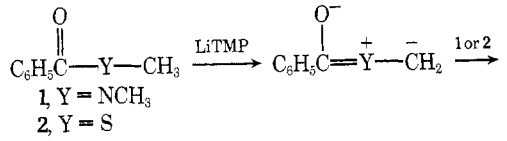
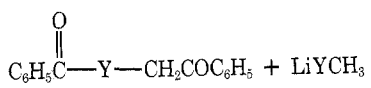
The reactions of benzyl benzoate (**3**), allyl benzoate (**5**), and vinyl benzoate (**12**) with lithium 2,2,6,6-tetramethylpiperidide at −78° in tetrahydrofuran give, respectively, benzoin benzoate (**4**), α-benzoyl allyl benzoate (**6**) and α-benzoyl-β-methyl vinyl benzoate (**7**), and α-benzoyl vinyl benzoate (**13**) via formation of a carbanion adjacent to oxygen followed by nucleophilic attack of the anion on the starting ester. However, methyl, ethyl, and the propyl and butyl benzoates, **15** and **17–22**, in the presence of the same base lose an ortho proton from the ring to provide, after benzoylation, the *o*-benzoylbenzoates **16** and **23–28** in a synthetically useful reaction. Related proton abstractions lead to substitution of benzophenone ortho to the carbonyl and to benzoylation of benzyl β,β-diphenylacrylate adjacent to the carbonyl group. It does not appear that the potential dipole stabilization of the ester function is sufficient, under these conditions and in the absence of additional stabilization, to direct proton abstraction to the carbon adjacent to oxygen.

The novel abstraction of a proton from the methyl groups of *N,N*-dimethylbenzamide and methyl thiobenzoate by lithium 2,2,6,6-tetramethylpiperidide (LiTMP) to generate the transient nitrogen- and sulfur-substituted dipole-stabilized carbanions **1** and **2** has been communicated.[1] Our interest in the possible generality of such species



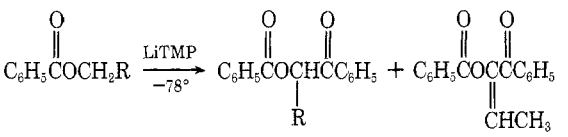
1, Y = NCH_3
2, Y = S



as well as their synthetic potential[2] prompted investigation of the reaction of benzoate esters with LiTMP. The present report establishes that formally dipole stabilized carbanions can be produced by abstraction of a proton from benzoate esters which have additional activation provided by unsaturation. In the absence of such activation, removal of an ortho proton occurs and the ultimate product is an *o*-benzoylbenzoate.

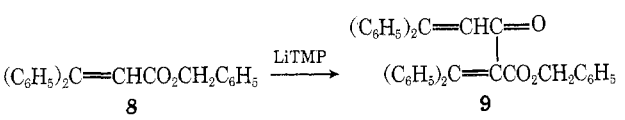
Results and Discussion

Benzyl Benzoate, Allyl Benzoate, and Vinyl Benzoate. The reaction of benzyl benzoate (**3**) with LiTMP[3] in tetrahydrofuran at −78° for 10 min provides benzoin benzoate (**4**) in 65% yield (77% conversion). A similar reaction of allyl benzoate (**5**) gives α-benzoyl allyl benzoate (**6**) and α-benzoyl-β-methyl vinyl benzoate (**7**) in a 4:1 ratio in 53% yield (75% conversion). The structural assignments for **6** and **7** are based on spectral and analytical properties. It appeared possible that **7** was produced by isomerization of **6**, since the conversion of **6** to **7** occurs on treatment of a mixture of these compounds with 10 mol % potassium *tert*-butoxide in *tert*-butyl alcohol. However, attempts to increase the yield of **6** and **7** or to alter their ratio by reaction with a twofold excess of LiTMP followed by quenching 20 min after mixing or by inverse addition of LiTMP to **5** produced no significant change in the yield or the ratio. The formation of **4** from **3** can also be observed in 50% yield at −78° if lithium diisopropylamide is the base.



3, R = C_6H_5 **4**, R = C_6H_5 **7**
5, R = CH=CH_2 **6**, R = CH=CH_2

The reactions of benzyl methyl phthalate, dibenzyl phthalate, benzyl acrylate, and benzyl β,β-diphenylacrylate (**8**) with LiTMP were investigated in an effort to achieve an intramolecular cyclization.[4] However, only in the case of **8** was a characterizable product obtained and it proved to be **9**, formed in 25% yield at both −78 and 25°. Clearly, **9** results from an intermolecular sequence which is probably initiated by removal of the vinyl proton from **8**.[5] The structure of **9** is based on its analytical and spectral properties, as well as its conversion to dibenzhydrylacetone after cata-



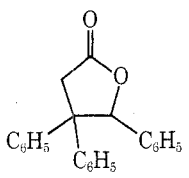
8 **9**

Table I
Formation of *o*-Benzoylbenzoates from Alkyl Benzoates and LiTMP at −78° in Tetrahydrofuran

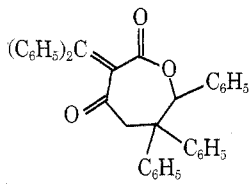
R	Reactant $C_6H_5CO_2R$	Product o-$C_6H_4(COC_6H_5)CO_2R$	Product,[a] %	Recovered reactant, %
Me	15	16	3.5[b]	72[b]
C_2H_5	17	23	44 (27)	27
C_2H_5	17	23	10[b]	79[b]
n-C_3H_7	18	24	46 (38)	27
i-C_3H_7	19	25	10 (6)	69
	19	25	18 (11)[c]	51[c]
n-C_4H_9	20	26	50 (38)	29
i-C_4H_9	21	27	52 (44)	30
t-C_4H_9	22	28	1.5[d]	86[d]

[a] Value in parentheses represents the yield of analytically pure material. [b] At −117°. [c] Reaction time is 90 min and an 8% yield of isopropyl 2,6-dibenzoylbenzoate is also obtained. [d] Reaction time is 30 min.

lytic hydrogenation and decarboxylation. The ^{13}C NMR and the latter conversion rule out the alternative structures **10** and **11.** Substitution for a vinyl proton is also observed

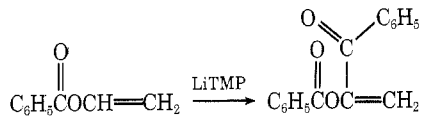


10



11

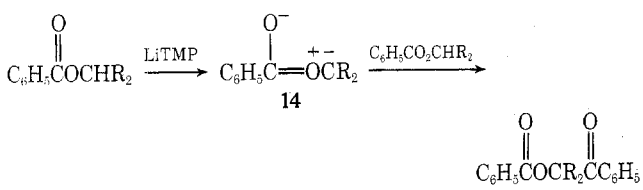
in the reaction of vinyl benzoate (**12**) with LiTMP to give in 3.5% yield α-benzoyl vinyl benzoate (**13**), which was characterized by spectral criteria.



12 **13**

The reactions of the esters **3, 5,** and **12** to give products of benzoylation α to oxygen may be rationalized by the intermediacy of the formally dipole stabilized carbanion **14** as shown in Scheme I.[6] The fact that activation by the inductive, hybridization, and/or delocalization effects of unsaturation contributes to the acidity of the proton removed and that other alkyl benzoates do not form such anions (vide infra) suggests that dipole stabilization by the ester is not sufficient by itself to favor the formation of **14,** at least under the present conditions. The possibility that reaction proceeds via a homoenolate species[1,7] which undergoes ring opening to an oxyanion which is subsequently benzoylated is discounted only by analogy to the reaction of *N,N*-dimethylbenzamide, which has been shown not to involve a homoenolate,[8] although the need for unsaturative stabilization also implies a transition state for proton removal which has significant carbanionic character.

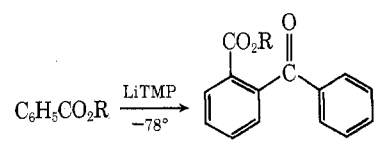
Scheme I



14

The potential use of dipole-stabilized carbanions as anionic synthetic equivalents[2] prompted a number of attempts to trap these species from **4** and **12** at −78 and −117° with electrophiles. All efforts were without success, suggesting that under the present conditions **14** is probably formed in low concentration and reacts rapidly with starting ester to give the observed products. It is also interesting to note that **14** does not undergo the Wittig rearrangement[9] under these conditions.

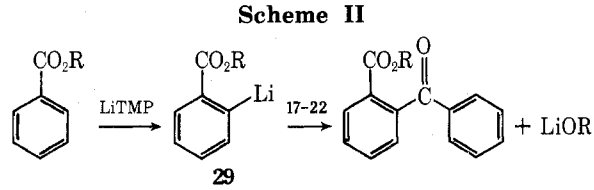
Alkyl Benzoates. Although reaction of methyl benzoate (**15**) at −78° gives uncharacterizable products, when the reaction is carried out at −117° a 3.5% yield of methyl 2-benzoylbenzoate can be detected along with 72% recovered reactant. The generality of this reaction is demonstrated by the fact that ethyl, propyl, and butyl benzoates, **17–22,** react with equimolar LiTMP at −78° in tetrahydrofuran for 10 min to produce the corresponding *o*-benzoylbenzoates, **23–28,** in yields of 1.5–52% and conversions of 10–74% (Table I). The yield of ethyl 2-benzoylbenzoate from **17** is reduced to less than 3% if lithium diisopropylamide is used as the base.



15 **16**
17-22 **23-28**

A mechanism for this reaction is given in Scheme II. There is considerable precedent for ortho lithiation[10] and the intermediate **29** is analogous to species produced by Parham and Sayed on lithiation of *o*-bromobenzoates.[11,12]

Scheme II



29

The convenience of the present procedure suggests that even though the yields may not have yet been optimized, it should be a synthetically useful alternative for the preparation of *o*-benzoylbenzoates which, in turn, can be useful precursors to anthraquinones.[11]

The possibility that ethyl benzoate reacts via initial proton removal from the carbon adjacent to oxygen, as for **3, 5,** and **12,** followed by rearrangement to **29**[13] is discounted by conversion of ethyl-d_5 benzoate to ethyl-d_5 2-benzoylbenzoate. If the possible rearrangement had occurred the product would contain an ethyl-d_4 group, and less than 2% ethyl-d_4 2-benzoylbenzoate was found.

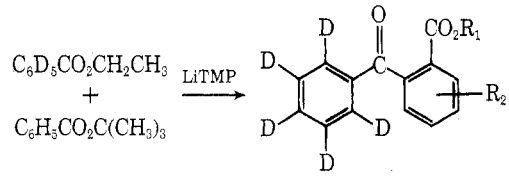
The fact that isopropyl and *tert*-butyl benzoates give the lowest yields of products (Table I) could be due either to unfavorable proton removal to form **29** or to a diminished

Table II
Deuterium Content of the Products from the Reaction of Equimolar Ethyl Benzoate and Ethyl Benzoate-d_5 with LiTMP at −78°

Product	m/e	Relative peak intensity[a]
23	254	1.00
33	259	1.12
34	258	0.11
35	263	0.09

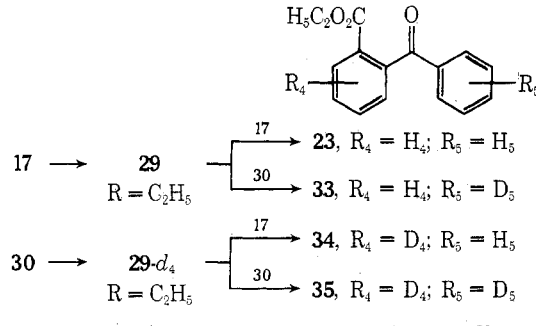
[a] From an average of four spectra at 10 eV ionizing voltage. The estimated error is 2%.

rate of nucleophilic addition of **29** to the ester. To distinguish between these possibilities, an equimolar mixture of ethyl benzoate-d_5 (**30**) and *tert*-butyl benzoate (**22**) was allowed to react with LiTMP at −78°. The products of the reaction were found to be *tert*-butyl 2-benzoyl-d_5-benzoate (**31**) in 25% yield and ethyl 2-benzoylbenzoate-d_9 (**32**) in 5% yield. It is estimated that less than 2% of other deuterated



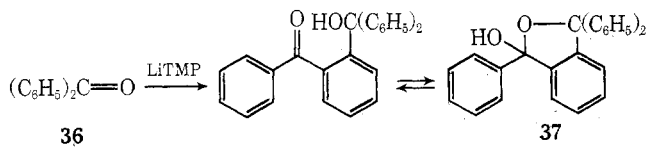
31, $R_1 = C(CH_3)_3$; $R_2 = H_4$
32, $R_1 = CH_2CH_3$; $R_2 = D_4$

isomers of *o*-benzoylbenzoates were formed and the recovered reactants (65%) showed that no detectable transesterification had occurred. Since **31** results from removal of the ortho proton of *tert*-butyl benzoate and products resulting from nucleophilic addition to *tert*-butyl benzoate by **29** (R = C_2H_5 or C_4H_9) are not observed, it appears that the low yields from *tert*-butyl benzoate are due primarily to inhibition of attack at the carbonyl carbon of the *tert*-butyl ester. The ratio of **31**:**32** also reflects a primary isotope effect toward removal of hydrogen. To assess this effect, equimolar amounts of ethyl benzoate (**17**) and ethyl benzoate-d_5 (**30**) were allowed to compete for a deficiency of LiTMP and the isotopic content of the product was determined by mass spectrometry. The analysis for d_0 (**23**), d_5 (**33**), d_4



(**34**), and d_9 (**35**) is summarized in Table II. The ratio of the products produced by proton abstraction from **17** to those produced by deuterium abstraction from **30**, **23** + **33**:**34** + **35**, is 10.6 ± 0.6 in support of the proposed mechanism with removal of the proton to give **29** effectively rate determining.[14]

It was also observed that benzophenone (**36**) reacts with LiTMP at −78° to give 42% 1,3,3-triphenyl-1-hydroxyphthalan (**37**). At 25° the yield is increased to 80%. Attempts to characterize the products from similar reactions of methoxymethyl benzoate, phenyl benzoate, and benzaldehyde were not successful.



36 **37**

Experimental Section

Melting points were taken on a Nalge hot stage and are uncorrected. Boiling points, taken from distillations, are also uncorrected. Infrared spectra calibrated with the 1601-cm^{-1} band of polystyrene were obtained with neat samples or in KBr pellets. Proton magnetic resonance spectra and ^{13}C Fourier transform nuclear magnetic resonance spectra were obtained in deuteriochloroform and peak positions are reported in δ (parts per million) from internal tetramethylsilane. Mass spectra were obtained on a Varian MAT CH5 spectrometer. Elemental analyses were performed by Mr. J. Nemeth and associates.

Materials. Commercially available solvents and starting materials were used as received. Tetrahydrofuran was distilled from sodium benzophenone ketyl in a nitrogen atmosphere and stored under nitrogen. Standardization of *n*-butyllithium (Ventron) was accomplished with *sec*-butyl alcohol in xylene with 1,10-phenanthroline indicator.[15] 2,2,6,6-Tetramethylpiperidine (Aldrich) was dried over molecular sieves before use.

Commercially available esters were purified by distillation or recrystallization. Those esters not available were synthesized from the corresponding acid chloride, alcohol, and pyridine in ether except for benzyl acylate, which was prepared by transesterification of methyl acrylate with benzyl alcohol and hydroquinone following the procedure of Rehberg and Fisher.[16] Vinyl benzoate (**12**) was prepared from vinyl acetate, benzoic acid, and mercury(II) sulfate according to the procedure of Aldelman.[17]

Methoxymethyl benzoate was prepared in 62% yield from sodium benzoates and excess chloromethyl methyl ether following a procedure similar to that of Clark, Cox, and Mack:[18] bp 94° (2 mm); ^1H NMR δ 3.50 (s, 3), 5.45 (s, 2), 7.60 (m, 3), and 8.07 (m, 2); ir (neat) 1740 (C=O), 1270, 1160, 1060, 1025, 925, and 710 cm^{-1}; mass spectrum (10 eV) *m/e* (rel intensity) 45 (21.1), 61 (72.9), 105 (16.6), 106 (100), 166 (13.4).

Anal. Calcd for $C_9H_{10}O_3$: C, 65.05; H, 6.02. Found: C, 65.03; H, 6.20.

Benzyl β,β-diphenylacrylate (**8**) was prepared from the acid chloride[19] and benzyl alcohol with pyridine in ether and purified by chromatography on silica gel followed by recrystallization from hexane: mp 74–75°; ^1H NMR δ 5.00 (s, 2), 6.37 (s, 1), and 7.20 ppm (m, 15); ir 1730 (C=O), 1145, 978, 875, 751, and 692 cm^{-1}.

Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: C, 83.88; H, 5.70.

Benzyl methyl phthalate was prepared by the reaction of phthalic anhydride, benzyl chloride, triethylamine, and methanol following a published procedure.[20] Dibenzyl phthalate was prepared from phthaloyl chloride and benzyl alcohol and pyridine in ether. Both esters were purified by column chromatography.

General Procedure for the Reactions of Esters with Lithium 2,2,6,6-Tetramethylpiperidide (LiTMP). All reactions involving LiTMP were carried out in a dry nitrogen atmosphere. The following general procedure was followed in all cases unless noted. A weighed sample of the ester (3–4 mmol) was dissolved in 10–15 ml of THF and added dropwise to an equimolar amount of LiTMP in 10 ml of THF at −78° over 10 min. The LiTMP was generated by reaction of TMP and equimolar *n*-butyllithium at room temperature followed by cooling to −78°. The reaction was quenched at −78° immediately after addition was complete with 10% HCl and allowed to warm to room temperature. Extractive work up with ether with washes of 10% HCl, 5% HCl, and water (twice) and an ether backwash gave material for chromatography. Yields are calculated on the basis of 2 mol of ester required for 1 mol of product.

"Inverse" addition used with several esters refers to the addition of LiTMP solution to the ester at −78° with work-up identical to that described.

Chromatography was carried out on Brinkmann 0.05–0.2 mm silica gel. Starting esters were eluted with either hexane or 2% (v/v) ethyl acetate–hexane. Reaction products were eluted with 5–10% ethyl acetate–hexane unless otherwise noted. Reactions of selected esters with LiTMP are described in detail below.

Benzyl benzoate (3), 3.08 mmol, was allowed to react with 3.18 mmol of LiTMP. Chromatography gave 0.5 mmol (16%) of recovered **3**, identified by its NMR and ir spectrum, and 1.00 mmol (65%) of benzoin benzoate **4**, identified by its melting point, 124–

125° (lit.[21] mp 124–125°), ^{1}H NMR,[22] and ir spectrum,[22,23] which all were identical with those of authentic material prepared from benzoyl chloride and benzoin.[21]

Allyl Benzoate (5). Analysis by TLC of the reaction mixture from 3.94 mmol of **5** with LiTMP indicated two products with nearly identical R_f values, in addition to unreacted **5**. Chromatography gave 1.14 mmol (29%) of recovered **5**, and 1.04 mmol (53%) of a mixture of **6** (80% by ^{1}H NMR) and **7** (20%).

A sample of pure **6** could be obtained by careful chromatography in which pure **6** eluted just ahead of the mixture of **6** and **7**. Recrystallization from hexane afforded an analytical sample of **6**: mp 85–86°; ^{1}H NMR 5.30–5.75 (m, 2), 5.87–6.47 (m, 1), 6.53 (d, 1, J = 6 Hz), 7.18–7.67 (m, 6), and 7.90–8.17 ppm (m, 4); ir (KBr) 1726, 1696 (C=O), 1598, 1450, 1275, 1121, 947, 713, and 703 cm^{-1}, mass spectrum (10 eV) *m/e* (rel intensity) 105 (100), 106 (8.6), 144 (12.5).

Anal. Calcd for $C_{17}H_{14}O_3$: C, 76.68; H, 5.30. Found: C, 76.66; H, 5.35.

Isomerization of 6 to 7 Catalyzed by *tert*-Butoxide. A mixture of **6** and **7** (0.41 mmol) in dry *tert*-butyl alcohol was added to a solution of 0.042 mmol of potassium *tert*-butoxide in *tert*-butyl alcohol. The reaction mixture turned deep red immediately, and after 20 min, TLC indicated only **7** in the reaction mixture. The reaction was quenched by the addition of 10% HCl and extractive work-up with ether provided a colorless oil which was chromatographed on 25% silica gel with 5% ethyl acetate–hexane to yield 0.30 mmol of **7** (73%). Recrystallization from hexane gave an analytical sample: mp 65–66°; ^{1}H NMR δ 1.71 (d, 3, J = 7 Hz), 6.28 (q, 1, J = 7 Hz), 7.18–7.61 (m, 6), 7.68–7.90 (m, 2), and 8.01–8.21 ppm (m, 2); ir (KBr) 1740, 1648 (C=O), 1252, 1262, 1170, 1100, 1063, and 710 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 51 (5.7), 77 (27.9), 105 (100), 266 (2.4).

Anal. Calcd for $C_{17}H_{14}O_3$, C, 76.68; H, 5.30. Found: C, 76.90; H, 5.32.

Benzyl β,β-diphenylacrylate (8), 2.74 mmol, was allowed to react with 2.70 mmol of LiTMP at −78°. Chromatography gave 1.45 mmol (53%) of recovered **8** and 0.35 mmol (26%) of **9**. Inverse addition, a reaction temperature of 25°, or use of excess LiTMP failed to significantly affect the yield of **9**. The amount of recovered **8**, however, varied from less than 2% with a twofold excess of LiTMP to 29% for reactions of equimolar ester and LiTMP at room temperature.

Purification was accomplished by recrystallization from hexane or methanol–water to give **9** as pale yellow crystals: mp 126–127.5°; ^{1}H NMR δ 4.92 (s, 2), 6.05 (s, 1), 6.43–6.67 (m, 4), and 6.83–7.48 ppm (m, 21); ^{13}C NMR δ 194.1 (C=O), 167.1 (O=CO), 154.8, 152.6 [$(C_6H_5)_2$**C**=], 141.7, 140.6, 138.9, 135.4, 133.4, 130.9, 138.8, 130.0, 129.5, 129.2, 192.5, 128.5, 128.2, 127.9 (>C=), 67.0 (-CH_2-); ir 1723, 1638 (C=O), and 703 cm^{-1}; mass spectrum (10 eV) *m/e* (rel intensity) 105 (75.7), 429 (100), 430 (31.6), 520 (33.9), 521 (14.8).

Anal. Calcd for $C_{37}H_{28}O_3$: C, 85.38; H, 5.38. Found: C, 85.23; H, 5.39.

Hydrogenation and Decarboxylation of 9 to Dibenzhydrylacetone. Hydrogenation of **9** (0.11 mmol) was accomplished at atmospheric pressure over 10% Pd/C in 5 ml of ethyl acetate for 24 hr. The catalyst was removed by filtration and the solution was heated at reflux for 3 hr to effect decarboxylation. Evaporation of the ethyl acetate in vacuo left 0.106 mmol (97%) of a colorless oil with a ^{1}H NMR spectrum identical with that of dibenzhydrylacetone. Two recrystallizations from methanol gave white needles, mp 124–125°, identical in ir, ^{1}H NMR, mass spectrum, melting point, and mixture melting point with authentic dibenzhydrylacetone prepared from dibenzalacetone, benzene, and aluminum trichloride.[24]

Vinyl benzoate (12) was allowed to react with LiTMP both at −78 and 25° in either the normal or inverse modes of addition. Analysis by TLC indicated low yields of **13** in both cases. Combination of the crude mixtures from two runs at 25° gave, after chromatography, 35% recovered **12** and 3.5% of a yellow oil, the ^{1}H NMR of which indicated it to be mostly **13**. Rechromatography gave 1.4% **13** as a colorless oil which on recrystallization from hexane gave **13** as white needles: mp 91–93°; ^{1}H NMR δ 5.71 (d, 1, J = 2 Hz), 5.88 (d, 1, J = 2 Hz), 7.30–7.68 (m, 6), and 7.88–8.26 ppm (m, 4); ir (KBr) 1730, 1663 (C=O), 1450, 1270, 1186, 1169, 1088, 967, 922, 743, and 712 cm^{-1}; mass spectrum (10 eV) *m/e* (rel intensity) 105 (100), 106 (8.4), 252 (1.14).

Anal. Calcd for $C_{16}H_{12}O_3$: C, 76.18; H, 4.79. Found: C, 75.62; H, 4.87.

Reaction of Methyl Benzoate and LiTMP at −117°. This reaction was carried out as described previously except that the solution of LiTMP was cooled to −117° in liquid nitrogen–ethanol slurry. The reaction produced only slight color changes in sharp contrast to the run at −78°. Quenching with methanol and work-up and chromatography as usual gave 72.5% recovered methyl benzoate and then 3.2% of crude methyl 2-benzoylbenzoate (**16**) identified by its NMR[25] and mass spectra.

Ethyl benzoate (17) was allowed to react with LiTMP. One major product was observed by TLC. Chromatography yielded recovered **17** (27%) and ethyl 2-benzoylbenzoate (**23**, 44%). The identity of **23** was established by its melting point, 58–59° (lit.[26] mp 56–58°), ^{1}H NMR[27] and ir[27] spectra, and elemental analysis.

***n*-Propyl benzoate (18)** was allowed to react with LiTMP at −78°. After chromatography **18** (26%) and *n*-propyl 2-benzoylbenzoate (**24**, 46%) were obtained. Final purification of **24** was accomplished by microvacuum distillation to yield 38% of **24** as a clear, viscous oil (lit.[28] bp 163.5° (0.3 mm): ^{1}H NMR δ 0.78 (t, distorted 3, J = 6 Hz), 1.38 (m, 2), 3.93 (t, 2, J = 6 Hz), and 7.16–8.11 ppm (m, 9); ir (neat) 1720, 1675 (C=O), 1596, 1280, 1128, 1082, 932, 770, 713, and 702 cm^{-1}; mass spectrum (10 eV) *m/e* (rel intensity) 105 (16.4), 149 (57.1), 182 (31.7), 191 (26.1), 209 (77.4), 210 (28.4), 266 (33.9), 227 (39.5), 268 (100), 269 (19.9).

Anal. Calcd for $C_{17}H_{16}O_3$: C, 76.12; H, 5.97. Found: C, 76.08; H, 6.15.

Isopropyl benzoate (19) gave a 9.6% yield of isopropyl 2-benzoylbenzoate (**25**) and 69% recovered **19** after being allowed to react with LiTMP for 10 min at −78°. Extension of the reaction time to 90 min gave 51% **19**, 17% **25**, and 8% of isopropyl 2,6-dibenzoylbenzoate. Purification of **25** was accomplished by two crystallization from 95% ethanol: mp 66–67° (lit.[29] mp 62°); ^{1}H NMR δ 1.01 (d, 6, J = 6 Hz), 4.95 (m, 1, J = 6 Hz), and 7.21–8.11 ppm (m, 9); ir (KBr) 1720, 1670 (C=O), 1290, 1132, 1110, 1090, 786, and 710 cm^{-1}; mass spectrum (10 eV) *m/e* (rel intensity) 105 (18.1), 149 (100), 150 (19.2), 182 (26.6), 191 (46.7), 209 (67.0), 210 (98.2), 211 (28.6), 266 (30.2), 227 (27.8), 268 (72.5), 269 (21.05).

Purification of isopropyl 2,6-dibenzoylbenzoate was achieved by two recrystallization from 95% ethanol: mp 88–90°; ^{1}H NMR δ 0.78 and 1.00 (each a doublet, total integral 6, J = 6 Hz), 4.68 (m, 1), and 7.16–7.93 ppm (m, 13); ir (KBr) 1722, 1668 (C=O), 1274, 708, and 644 cm^{-1}; mass spectrum (10 eV) *m/e* (rel intensity) 105 (29.1), 253 (53.2), 313 (51.2), 314 (100), 315 (27.6), 330 (29.2), 331 (43.2), 372 (17.7).

Anal. Calcd for $C_{24}H_{20}O_4$: C, 77.40; H, 5.41. Found: C, 77.40; H, 5.54.

***n*-Butyl benzoate (20)** was allowed to react with LiTMP. Chromatography gave 29% recovered **20** and 50% *n*-butyl 2-benzoylbenzoate (**26**) as a pale yellow oil. Purification by a micro vacuum distillation gave pure **26** (38%) as a colorless, very viscous liquid [lit.[30] bp 241–244° (20 mm)]: ^{1}H NMR δ 0.80 (t, distorted, 3), 1.30 (m, 4), 3.99 (t, 2), and 7.16–8.08 ppm (m, 9); ir (neat) 1723, 1678 (C=O), 1285, 718, and 704 cm^{-1}.

Anal. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.30; H, 6.27.

Isobutyl benzoate (21) was allowed to react with LiTMP. Chromatography gave 29% recovered **21** and 52% crude isobutyl 2-benzoylbenzoate (**27**). Purification by vacuum distillation gave 44% **27** as a clear, viscous liquid: ^{1}H NMR δ 0.79 (d, 6, J = 7 Hz), 1.71 (m, 1), 3.78 (d, 2, J = 6 Hz), and 7.16–8.13 ppm (m, 9); ir (neat) 1724, 1678 (C=O), 1598, 1678 (C=O), 1598, 1282, 1128, 1083, 933, 717, and 703 cm^{-1}.

Anal. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.51; H, 6.52.

Reaction of *tert*-butyl benzoate (**22**) at −78° required 30 min for appearance of product (TLC). Chromatography gave 86.5% recovered **22** and 1.5% *tert*-butyl 2-benzoylbenzoate (**28**). Recrystallization from hexane gave white crystals: mp 67–68° (lit.[26] mp 68–69°); ^{1}H NMR δ 1.25 (s, 9) and 7.28–8.08 ppm (m, 9).

Ethyl-d_5 benzoate was prepared by reaction of benzoyl chloride, ethanol-d_6 (Stohler Isotope Chemicals), and pyridine (0.045 mol) in ether: bp 45° (0.8 mm); NMR δ 7.16–7.60 (m, 3) and 7.83–8.11 ppm (m, 2), less than 2% CH present; ir (neat) 2240 (m), 2160 (w), 2130 (w) (C–D), 1725 (C=O), 1458, 1233, 1305, 1201, 1182, 1130, 1103, 1065, 1031, and 713 cm^{-1}; mass spectrum (10 eV) *m/e* (rel intensity) 105 (80.4), 123 (100), 154 (8.4), 155 (97.1)

Anal. Calcd for $C_9H_5D_5O_2$: C, 69.68; total H, 6.45. Found: C, 69.63; total H, 6.43.

Preparation of Ethyl Benzoate-d_5 (30). Benzoyl chloride-d_5, prepared via the sequence benzene-d_6, bromobenzene-d_5, benzoic acid-d_5, benzoyl chloride-d_5, was allowed to react with ethanol to give **30**: bp 52° (1.0 mm); ^{1}H NMR δ 1.36 (t, 3, J = 7 Hz) and 4.33 ppm (q, 2, J = 7 Hz), estimate less than 2% ArH; ir (neat) 2305

(w), 2280 (w) (C–D), 1726 (C=O), 1398, 1383, 1332, 1245, and 1085 cm^{-1}; mass spectrum (10 eV) *m/e* (rel intensity) 110 (24.8), 127 (78.3), 155 (100), 156 (9.8).

Anal. Calcd for $C_9H_5D_5O_2$: C, 69.68; total H, 6.45. Found: C, 69.54; total H, 6.65.

Reaction of Ethyl Benzoate-d_5 (30) and *tert*-Butyl Benzoate (22) with LiTMP. The reaction of **22** and **30** with LiTMP was carried out by addition of a THF solution of 2.07 mmol of **22** and 2.04 mmol of **30** to 4.10 mmol of LiTMP at −78°. After quenching and the usual work-up, the presence of both starting esters as well as both *tert*-butyl 2-benzoylbenzoate and ethyl 2-benzoylbenzoate were indicated as the major and minor products, respectively, by TLC. Chromatography on silica gel with 2% ethyl acetate eluted a mixture of **22** and **30** (65% by weight of the original esters) shown by ^1H NMR to be 45% **30** and 55% **22.** Continued elution gave 25% *tert*-butyl benzoyl-d_5-benzoate (**31**) and 5% ethyl 2-benzoylbenzoate-d_9 (**32**), which were purified as described previously.

Reaction between Ethyl Benzoate (17) and Ethyl Benzoate-d_5 (30) with LiTMP. A solution of 2.0 mmol of LiTMP in 15 ml of THF was added at −78° to a THF solution of 2.07 mmol of **17** and 2.18 mmol of **30** over a period of 10 min. The reaction was quenched wand worked up in the usual manner. The recovered ester mixture and ethyl 2-benzoylbenzoate products as a mixture of deuterated and undeuterated isomers were analyzed by mass spectrometry.

Reaction of Benzophenone with LiTMP. Reaction of equimolar quantities of benzophenone (**36**) and LiTMP at 25° for 10 min gave, after work-up and chromatography with 5% ethyl acetate, 6.5% recovered **36** and 80.5% **37**.[31] Crude **37** was washed with cold hexane, yielding white needles, mp 119–120° (lit.[31] mp 121°). The ^1H NMR, ir, NMR, mass spectrum, and analysis were consistent with the established structure.

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Registry No.—**3,** 120-51-4; **5,** 583-04-0; **6,** 54353-96-7; **7,** 54353-97-8; **8,** 54353-98-9; **9,** 54353-99-0; **12,** 769-78-8; **13,** 54354-00-6; **17,** 93-89-0; **18,** 2315-68-6; **19,** 939-48-0; **20,** 136-60-7; **21,** 120-50-3; **22,** 774-65-2; **24,** 604-62-6; **25,** 32017-66-6; **26,** 571-98-2; **27,** 54354-01-7; **28,** 54354-02-8; **30,** 54354-03-9; **36,** 119-61-9; LiTMP, 38227-87-1; methoxymethyl benzoate, 54354-04-0; sodium benzoate, 532-32-1; chloromethyl methyl ether, 107-30-2; β,β-diphenylacryloyl chloride, 4456-79-5; benzyl alcohol, 100-51-6; methyl benzoate, 93-58-3; isopropyl 2,6-dibenzoylbenzoate, 54354-05-1; ethyl-d_5 benzoate, 30684-04-9; benzoyl chloride, 98-88-4; ethanol-d_6, 1516-08-1; benzene-d_6, 1076-43-3.

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