

carbons in a ratio of 3:1 (by GLC on column B). On the basis of the mass spectra of the samples separated by GLC (major, m/e 256, and minor, m/e 258), it was suggested that the major product was the diene derived by the Bamford-Stevens reaction and that the minor one was the desired olefin 4. Therefore, the mixture of the above olefins (161 mg), 2 mL of 90% hydrazine hydrate, and 100 mg of cupric sulfate in 20 mL of ethanol was stirred at room temperature for 12 h (monitored by GLC) while air was bubbled through a syringe. The mixture was diluted with water and extracted with ether. The extracts were washed with 1 N hydrochloric acid and water, and then dried (Na_2SO_4). After evaporation of the solvent, the residue was chromatographed on silica gel to afford 124 mg of 4: IR 2900, 1450 cm^{-1} ; mass spectrum, m/e 258 (M^+); ^1H NMR (CDCl_3) δ 0.9–2.1 (m); ^{13}C NMR (CDCl_3) δ 141.4 (s, 2 C), 55.9 (s, 2 C), 28.5 (t, 2 C), 27.1 (t, 2 C), 26.2 (t, 2 C), 26.0 (t, 2 C), 25.3 (t, 2 C), 24.9 (t, 2 C), 23.4 (t, 2 C), 23.1 (t). Anal. Calcd for $\text{C}_{19}\text{H}_{30}$: C, 88.30; H, 11.70. Found: C, 88.14; H, 11.91.

Photocycloaddition of 1 with Cyclooctene. Compound 1 (492 mg, 3.0 mmol) and 3.3 g (30 mmol) of cyclooctene were irradiated in a Pyrex tube for 7 h. The excess cyclooctene was evaporated and the residue distilled under reduced pressure [180 °C, bath temperature (1 mmHg)] to afford 760 mg of products which solidified on standing. The products were analyzed by GLC [the retention times of 6a–d (column A, 200 °C) are given below] and separated by preparative GLC. All of 6a–d showed the carbonyl absorptions at 1710 cm^{-1} in the IR spectra, a weak parent peak at m/e 274 with a base peak at m/e 165 in the mass spectra, and only aliphatic proton multiplets at δ 0.8–2.8 in the ^1H NMR spectra. Retention times and yields are as follows: 6a, 10.3 min, 1%; 6b, 11.5 min, 6%; 6c, 12.6 min, 84% (mp 76–78 °C); 6d, 14.6 min, 2%. Anal. Calcd for $\text{C}_{19}\text{H}_{30}\text{O}$: C, 83.15; H, 11.02. Found: C, 83.21; H, 10.88.

Hydrogenation of 2. Compound 2 (95 mg) and a catalytic amount of 5% palladium carbon in 20 mL of ethyl acetate was heated at 65 °C under a 5-atm pressure of hydrogen in a stainless-steel pressure bottle for 4 days. The catalyst was filtered and the solvent evaporated to give 91 mg of products which were composed of three isomers: 6a (65%), 6b (28%), and 6c (7%). The GLC retention times and the mass spectra of these products, which were separated by preparative GLC, were identical with those of 6a–c obtained as described above.

Hydrogenation of 3. Compound 3 (95 mg) was hydrogenated as above to give 85 mg of 7: GLC retention time (column A, 200 °C) 15.2 min; IR 1710 cm^{-1} ; mass spectrum, m/e 274 (M^+); ^1H NMR (CCl_4) δ 1.0–2.4 (m). Anal. Calcd for $\text{C}_{19}\text{H}_{30}\text{O}$: C, 83.15; H, 11.02. Found: C, 83.12; H, 10.98.

Acid-Catalyzed Rearrangement of 3. Compound 3 (63 mg, 0.23 mmol) and 40 mg (0.23 mmol) of *p*-toluenesulfonic acid in 15 mL of benzene were heated at 60 °C for 18 h. The solution was washed with sodium bicarbonate solution and saturated sodium chloride solution and then dried (Na_2SO_4). After evaporation of the solvent, the residue was chromatographed on silica gel. Elution with 2% ether–petroleum ether afforded 45 mg (71%) of 8 and with 3% ether–petroleum ether afforded 2 mg (3%) of 2.

For 8: mp 70–72 °C; IR 1760 cm^{-1} ; mass spectrum, m/e 272 (M^+); ^1H NMR (CDCl_3) δ 1.0–2.6 (m); ^{13}C NMR (CDCl_3) δ 212.4 (s), 140.6 (s, 2 C), 54.1 (s, 2 C), 31.3 (t, 2 C), 30.9 (t, 2 C), 26.8 (t, 2 C), 25.7 (t, 2 C), 25.6 (t, 4 C), 23.8 (t, 2 C). Anal. Calcd for $\text{C}_{19}\text{H}_{28}\text{O}$: C, 83.77; H, 10.36. Found: C, 83.71; H, 10.45.

Acid-Catalyzed Rearrangement of 2. Compound 2 (81 mg, 0.30 mmol) and 50 mg (0.29 mmol) of *p*-toluenesulfonic acid in 20 mL of benzene were heated at 60 °C for 42 h. A workup as above gave 51% of 8 as well as some minor products which were not determined.

Decarbonylation of 8. By preparative GLC of 67 mg of 8 on column A at 200 °C there was obtained 22 mg (36%) of 9: mp 29–31 °C; IR 2900, 1460 cm^{-1} ; mass spectrum, m/e 244 (M^+); ^1H NMR (CDCl_3) δ 1.04–1.96 (m, 16 H), 1.98 (s, 4 H), 2.04–2.48 (m, 8 H). Anal. Calcd for $\text{C}_{18}\text{H}_{28}$: C, 88.45; H, 11.55. Found: C, 88.07; H, 11.54.

Registry No. 1, 38262-50-9; 2, 79172-23-9; 2 semicarbazone, 79172-24-0; 2 tosylhydrazone, 79172-25-1; 3, 79172-26-2; 3 semicarbazone, 79172-27-3; 3 epoxide, 79172-28-4; 4, 79172-29-5; 5,

79172-30-8; 5 epoxide, 79190-79-7; 6 (isomer 1), 79172-31-9; 6 (isomer 2), 79200-21-8; 6 (isomer 3), 79200-22-9; 6 (isomer 4), 79200-23-0; 7, 79172-32-0; 8, 79172-33-1; 9, 79172-34-2; cyclooctyne, 1781-78-8; cyclooctene, 931-88-4.

Benzaldehyde plus Potassium Hydride—Benzoyl Anion?¹

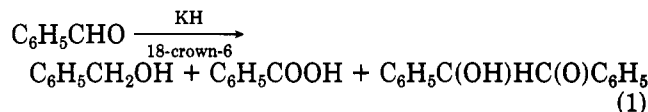
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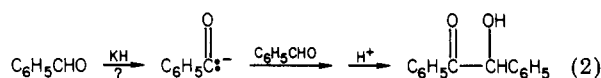
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Removal of the CHO proton of an aldehyde would lead to an acyl anion which would allow the addition of electrophiles directly to the carbonyl. Unfortunately, this deprotonation reaction does not occur,² so a vast effort has resulted in the development of indirect methods for accomplishing this by using so-called acyl anion equivalents.³ This “umpolung”⁴ has allowed many useful synthetic conversions.

In connection with another project involving the anion of substituted cyclopropanes,⁵ benzaldehyde was allowed to react with potassium hydride in the presence of 18-crown-6. After 48 h at room temperature, three products were isolated, benzyl alcohol (14%), benzoic acid (10%), and benzoin (47%) (eq 1). This last product attracted our



attention as possibly arising via benzoyl anion (eq 2).



Potassium hydride has been used to effect nearly miraculous alkylations,⁶ and so, in the absence of any complications from aldol condensations, this is not as strange as one might initially imagine.

Several attempts were made to trap the proposed benzoyl anion. The reaction of eq 1 was allowed to proceed in the presence of methyl iodide; however, only benzyl methyl ether (53%) and benzyl alcohol (33%) were formed.⁷ No evidence for the formation of acetophenone was obtained. Similarly, no benzil was isolated from the benzaldehyde/potassium hydride/crown ether reaction when run in the presence of methyl benzoate. This latter reaction gave benzoin, benzyl benzoate, and benzoic acid. These negative trapping attempts argue against the intermediacy of benzoyl anion in the reaction of eq 1.

An examination of the product distribution from this reaction as a function of time is very revealing. It is most striking that benzyl benzoate is observed as a product when shorter reaction times are used (see Table I). The amount of benzoin appears to increase with increasing reaction time at the expense of benzyl benzoate. In addition, the product distribution is affected by the amount of crown ether at low levels (see Table II), and no benzoin is produced when the weaker base sodium hydride is used. For example, after 10 h only 9% benzoin is obtained when 50 mg (1.0 mol %) of 18-crown-6 is used. In the presence of

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Table I. Reaction of Benzaldehyde with Potassium Hydride^a

time, h	% yield			
	C ₆ H ₅ CH ₂ OH ^{b,c}	C ₆ H ₅ COOH ^{b,d}	C ₆ H ₅ C(O)C(OH)HC ₆ H ₅ ^{d,e}	C ₆ H ₅ CO ₂ CH ₂ C ₆ H ₅ ^{c,e}
2	17		7	60
5	20	14	20	40
10	29	10	31	27
24	36	16	38	8
48	14	10	47	
48 ^f	58	10		26
48 ^g	12	12		62

^a All reactions use a 10% excess of potassium hydride in THF containing a catalytic amount (150 mg, 2.8 mol % based on benzaldehyde) of 18-crown-6 at room temperature unless otherwise indicated. ^b (Millimoles of product)/(millimoles of benzaldehyde) × 100%. ^c By NMR-weight data. ^d Isolated. ^e 2 (Millimoles of product)/(millimoles of benzaldehyde) × 100%. ^f No crown ether was used. ^g Using sodium hydride in THF at room temperature.

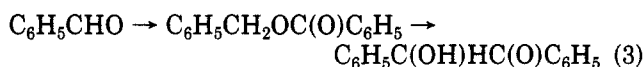
Table II. Effect of Crown Ether on the Reaction of Benzaldehyde with Potassium Hydride^a

time, h	crown ether, mg (mol %) ^b	% yield			
		C ₆ H ₅ CH ₂ OH ^{c,d}	C ₆ H ₅ COOH ^{c,e}	C ₆ H ₅ C(O)C(OH)HC ₆ H ₅ ^{e,f}	C ₆ H ₅ CO ₂ CH ₂ C ₆ H ₅ ^{d,f}
2	50 (1.0)	33	4		61
2	150 (2.8)	24		7	70
2	200 (3.8)	75	13	12	
5	50 (1.0)	33	5		59
5	150 (2.8)	28	14	20	51
5	200 (3.8)	70	8	17	
10	50 (1.0)	38	9	9	33
10	150 (2.8)	29	10	31	27
10	300 (5.7)	34	11	28	23
24	50 (1.0)	43	10	2	42
24	150 (2.8)	29	10	38	13
24	200 (3.8)	55	10	21	
48	50 (1.0)	70	22		7
48	150 (2.8)	14	10	47	
48	200 (3.8)	50	10	38	

^a All reactions were run with a 10% excess of KH in THF at room temperature. ^b Relative to benzaldehyde. ^c (Millimoles of product)/(millimoles of benzaldehyde) × 100%. ^d By NMR-weight data. ^e Isolated. ^f 2 (millimoles of product)/(millimoles of benzaldehyde) × 100%.

150 mg (2.8 mol %) of the crown ether, 31% benzoin is isolated after 10 h while 28% is produced when 300 mg of the crown is used. Apparently, larger amounts of 18-crown-6 have no extra effect on the product distribution.

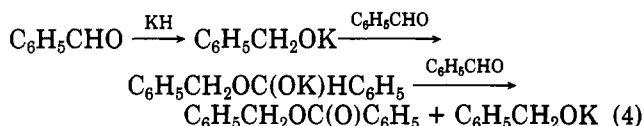
These results lead to an explanation for benzoin formation which is different than that in eq 2. This new hypothesis must involve benzyl benzoate as a primary product which then gives benzoin in a secondary reaction process (eq 3). This latter conversion apparently does not



occur with potassium hydride in the absence of crown ether or when sodium hydride is used as the base. In other words, base strength is crucial.

Support for the first part of eq 3 has been obtained in the reaction of benzaldehyde with potassium hydride in

the presence of methyl iodide. Benzyl methyl ether and benzyl alcohol are formed. Clearly, this shows that potassium hydride can add to the benzaldehyde carbonyl.^{7a} The resulting benzyl oxide then presumably converts benzaldehyde into benzyl benzoate (eq 4).⁸ In fact, sodium benzyl oxide (0.5 equiv) converts benzaldehyde into benzyl benzoate (70%) and benzoic acid (19%).



In order to test the feasibility of the second portion of eq 3, benzyl benzoate was allowed to react with potassium hydride in the presence of crown ether. After 48 h, a 10% excess of potassium hydride leads to a 15% yield of benzoin, benzyl alcohol, and benzoic acid as well as a 50% recovery of starting material. Repeating this reaction with a 2:1 ratio of potassium hydride and benzyl benzoate gives a 23% yield of benzoin in addition to benzyl alcohol, benzoic acid, and starting ester (21%).⁹

The conversion of benzyl benzoate into benzoin is not unique to this study.¹⁰ Beak¹¹ has shown that various

(1) Presented at the 181st Meeting of the American Chemical Society, Mar 29–Apr 3, 1981, Atlanta, Ga.

(2) Recent work has shown that these species can be formed in certain systems. For example, see: Rautenstrauch, V.; Delay, F. *Angew. Chem. Int. Ed. Engl.* 1980, 19, 726.

(3) For example, see: Lever, O. W., Jr. *Tetrahedron* 1976, 32, 1943.

(4) Seebach, D. *Angew. Chem., Int. Ed. Engl.* 1979, 18, 239. Grobel, B.-T.; Seebach, D. *Synthesis* 1977, 357.

(5) Pinnick, H. W.; Chang, Y.-H.; Foster, S. C.; Govindan, M. *J. Org. Chem.* 1980, 45, 4505.

(6) Groenewegen, P.; Kallenberg, H.; van der Gen, A. *Tetrahedron Lett.* 1978, 491; 1979, 2817.

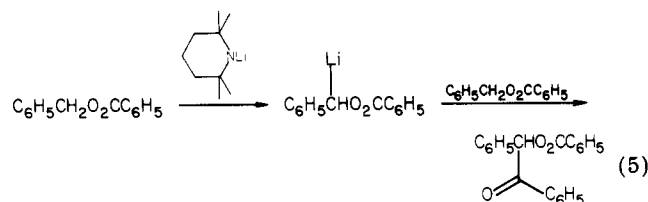
(7) (a) Potassium hydride reacts with cyclopropyl phenyl ketone to give the corresponding alcohol in 82% yield: Handel, H.; Pasquini, M.-A.; Pierre, J.-L. *Bull. Soc. Chim. Fr.* 1980, 351. (b) The ether formation is analogous to results obtained from reacting substituted adamantanones with sodium hydride and methyl iodide: Duddeck, H.; Feuerhelm, H.-T.; Snatzke, G. *Tetrahedron Lett.* 1979, 829.

(8) This is similar to the Cannizzaro and Tishchenko reactions. For example, see: Geissman, T. A. *Org. React.* 1944, 2, 94. March, J. "Advanced Organic Chemistry: Reactions, Mechanisms and Structure", 2nd ed.; McGraw-Hill: New York, 1977; pp 1139–1140.

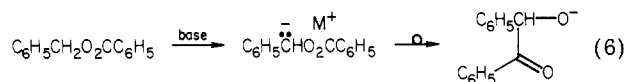
(9) The yield of benzoin apparently did not double because of other complications. For example, potassium benzylalkoxide (1.0 equiv) converts benzyl benzoate into benzoic acid (82%).

(10) This rearrangement has been observed by earlier workers also: Crooks, P. A.; Galt, R. H. B.; Matusiak, S. *Chem. Ind. (London)* 1976, 693.

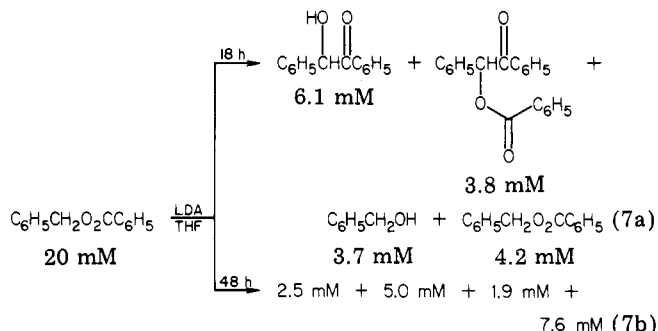
esters of aromatic acids can be deprotonated to give so-called "dipole-stabilized anions" which undergo intermolecular acylation (for example, eq 5).^{11b} Alternatively, the



intermediate carbanion could rearrange in an intramolecular fashion as in eq 6 to give benzoin. This latter pathway is analogous to the well-known Wittig rearrangement of ether anions.¹²

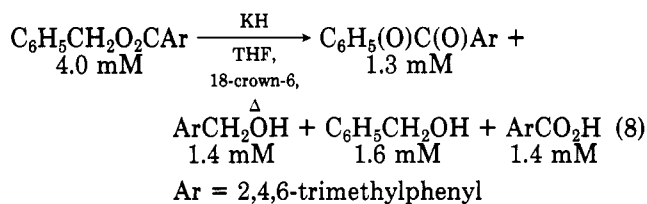


The intermolecular acylation pathway of eq 5 seems unlikely in the present study since no benzoin benzoate¹³ has been observed as a product even though it is stable to the workup conditions;¹⁴ however, the use of lithium diisopropylamide (LDA) as a base gives rise to benzoin as well as benzoin benzoate. Furthermore, the product distribution from this latter reaction changes with time (eq 7). The combined yield of benzoin and benzoin benzoate

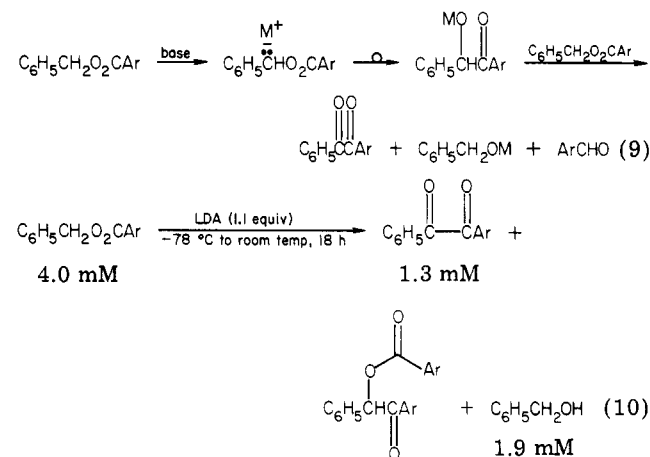


is constant (9.9 mmol after 18 h and 10.1 mmol after 48 h), but the reaction which was allowed to stir for the longer time contained more of the ester. This implies that benzoin is formed first and then undergoes acylation to give benzoin benzoate, thus supporting the intramolecular rearrangement hypothesis (eq 6).

A final set of experiments also supports the "acyl Wittig" rearrangement pathway of eq 6. Benzyl mesitoate was allowed to stir at room temperature with potassium hydride (3 equiv) in THF containing 3 mol % of 18-crown-6, but the workup gave only unreacted ester. More forcing conditions, the use of 50 mol % of crown ether at 60 °C for 2 days, led to several products (eq 8). The α -diketone



is the important product and presumably is formed via rearrangement of the dipole-stabilized anion followed by a hydride-transfer reaction as in the Cannizzaro and Tishchenko reactions⁸ (eq 9). Less vigorous reaction



conditions are possible by using LDA as the base (eq 10). Any rearrangement at all in this benzyl mesitoate system strongly suggests an intramolecular pathway for this reaction because of the hindrance of the mesitoate carbonyl to intermolecular nucleophilic attack.^{15,16}

In conclusion, while the elusive benzoyl anion is not formed from the title reaction, many other interesting phenomena, including an acyl Wittig rearrangement, are taking place.

Experimental Section

All reactions were run under nitrogen in flamed-out, three-necked flasks equipped with addition funnels. Tetrahydrofuran was freshly distilled from potassium. Proton NMR spectra were recorded with a Varian EM-390 spectrometer and IR spectra were obtained on Perkin-Elmer Model 257 and 297 spectrophotometers. Melting points were determined on a Thomas-Hoover apparatus and are uncorrected.

All products are known compounds and were identified by comparison of melting points (for solids), proton NMR, IR, and TLC with those of authentic samples.

Reaction of Benzaldehyde with Potassium Hydride. General Procedure. The potassium hydride (dispersion in mineral oil) was placed in a three-necked flask under nitrogen and washed three times with dry THF. The required amount of THF was then added followed by approximately 150 mg of 18-crown-6 if applicable. Freshly distilled benzaldehyde was then added dropwise as a solution in 10 mL of THF, and the reaction mixture was allowed to stir at the specified temperature under nitrogen for the required length of time. The reaction mixture was then poured into ice-water, and the aqueous layer was saturated with sodium chloride and extracted three times with ether. The combined ether extracts were dried over anhydrous magnesium sulfate and evaporated to give the crude product as an

(11) (a) Beak, P.; Reltz, D.B. *Chem. Rev.* 1978, 78, 275 and references cited therein. (b) Upton, C. J.; Beak, P. *J. Org. Chem.* 1975, 40, 1094.

(12) For example, see: (a) Garst, J. F.; Smith, C. D. *J. Am. Chem. Soc.* 1976, 98, 1526 and references cited therein. (b) Herbert, E.; Welvert, Z. *J. Chem. Soc., Chem. Commun.* 1980, 1035. (c) For other carbanion-mediated rearrangements closely related to the Wittig rearrangement, see: Katritzky, A. R.; Ponskhe, N. K. *Tetrahedron Lett.* 1981, 1215.

(13) This was prepared in 80% yield from benzoin and benzoyl chloride in THF in the presence of triethylamine: mp 123–124 °C; ¹H NMR (CDCl₃, 60 MHz) δ 7.2 (s, 1 H), 7.2–7.7 (m, 11 H), 7.8–8.3 (m, 4 H).

(14) Benzoin benzoate is converted into benzoic acid (66%), benzyl phenyl ketone (37%), and benzoin (13%) when allowed to react with potassium hydride (1.1 equiv) in THF for 24 h at room temperature (32% of the starting material is recovered). This is an interesting reaction which deserves additional study. The benzoic acid and benzyl phenyl ketone apparently arise by alkyl oxygen cleavage of benzoin benzoate possibly initiated by electron transfer from potassium hydride.

(15) March, J. "Advanced Organic Chemistry", 2nd ed.; McGraw-Hill: New York, 1977; p 352.

(16) Professor P. Beak recently has obtained evidence with a thiol ester which supports an intramolecular reaction pathway: personal communication.

oil from which benzoin precipitates upon standing. The last traces of benzoin were obtained by dissolving the oil in a minimum of ether and adding petroleum ether. The mother liquor was concentrated to give a mixture of benzyl alcohol and benzyl benzoate which were analyzed by NMR. The original aqueous layer was acidified with HCl to precipitate the benzoic acid which was filtered, dried, and weighed.

Benzaldehyde plus Potassium Hydride in the Presence of Methyl Iodide. Methyl iodide (8.5 g, 60 mmol) and crown ether (50 mg) were added to washed potassium hydride (4.41 g of dispersion, 33 mmol) in 50 mL of THF. Benzaldehyde (3.2 g, 30 mmol) in 10 mL of THF was added dropwise, and the reaction mixture was allowed to stir at room temperature for 48 h. Workup as usual gave 3.10 g of an oil which analyzed for benzyl alcohol (33%, 10 mmol) and benzyl methyl ether (53%, 16 mmol).

Benzaldehyde plus Potassium Hydride in the Presence of Methyl Benzoate. Methyl benzoate (3.0 g, 22 mmol) and crown ether (50 mg) were added to washed potassium hydride (3.8 g of dispersion, 22 mmol) in 50 mL of THF. Benzaldehyde (2.1 g, 20 mmol) in 10 mL of THF was added dropwise, and the reaction mixture was allowed to stir for 24 h. The usual workup gave benzoin (0.3 g, 1.4 mmol, 14%), benzyl benzoate and methyl benzoate [3.8 g, which analyzed to give 31% (6.1 mmol) and 82% (18 mmol), respectively], and benzoic acid (0.50 g, 4.1 mmol, 21%).

Benzaldehyde plus Sodium Benzyl Oxide. Benzyl alcohol (3.2 g, 30 mmol) was added to washed sodium hydride (1.4 g of dispersion, 33 mmol) in 50 mL of THF. After the sodium hydride had reacted, benzaldehyde (6.6 g, 60 mmol) in 10 mL of THF was added dropwise, and the reaction mixture was allowed to stir for 48 h. Workup as before gave 8.2 g of oil which analyzed for 53% (32 mmol) benzyl alcohol, 33% (21 mmol) benzyl benzoate, and 5% (3 mmol) benzaldehyde. In addition, 1.4 g (12 mmol, 20%) of benzoic acid was isolated.

Benzyl Benzoate plus Potassium Hydride and Crown Ether. Benzyl benzoate (4.3 g, 20 mmol) and crown ether (150 mg) were added to washed potassium hydride (3.8 g of dispersion, 22 mmol) in 50 mL of THF. After 48 h, the reaction mixture was worked up as usual to give 0.64 g (3.0 mmol, 15%) of benzoin, 3.2 g of benzyl benzoate and benzyl alcohol [which analyzed for 50% (10 mmol) and 50% (10 mmol); respectively], and 0.1 g (0.8 mmol, 4%) of benzoic acid.

This procedure was repeated with a larger amount of potassium hydride (7.0 g of dispersion, 40 mmol) to give benzoin (0.95 g, 4.5 mmol, 23%), benzyl benzoate and benzyl alcohol [2.0 g, which analyzed to give 21% (4.1 mmol) and 50% (10 mmol), respectively], and benzoic acid (0.50 g, 4.1 mmol, 21%).

Benzoin Benzoate plus Potassium Hydride and Crown Ether. Benzoin benzoate (3.2 g, 10 mmol)¹³ and crown ether (50 mg) were added to washed potassium hydride (1.9 g of dispersion, 11 mmol) in 50 mL of THF. The workup after 24 h at room temperature gave a wet solid from which 1.0 g (3.2 mmol, 32%) of benzoin benzoate was obtained by successive recrystallization with ether/hexane. The mother liquor consisted of benzoin (1.3 mmol, 13%) and deoxybenzoin (3.7 mmol, 37%) plus benzoic acid (0.80 g, 6.6 mmol, 66%).

Benzyl Benzoate plus Potassium Benzyl Oxide and Crown Ether. Potassium (0.86 g, 22 mol) was dissolved in benzyl alcohol (2.2 g, 20 mmol) in 50 mL of THF. The crown ether (100 mg) was added followed by benzyl benzoate (4.3 g, 20 mmol), and the reaction mixture was allowed to stir for 96 h at room temperature. The usual workup gave a mixture of benzyl benzoate and benzyl alcohol (3.5 g, which analyzed for 3.3 mmol (17%) and 2.6 mmol (13%), respectively) plus 2.0 g (16 mmol, 80%) of benzoic acid.

Preparation of Benzyl Mesitoate. Mesitoyl chloride¹⁷ (4.0 g, 22 mmol) was added slowly to a mixture of benzyl alcohol (2.2 g, 20 mmol) and triethylamine (4.0 g, 40 mmol) in 50 mL of toluene, and the reaction mixture was heated to reflux for 12 h. This was cooled, poured into 100 mL of cold water, and extracted with three 50-mL portions of toluene. The combined organic layers were washed twice with 50 mL of saturated, aqueous NaHCO₃, dried over anhydrous MgSO₄, and concentrated to give a crude solid which was recrystallized from ether/hexane to yield

4.5 g (89%) of the desired ester as white crystals: mp 37–38 °C; NMR (CDCl₃, 90 MHz) δ 2.20 (s, 6 H), 2.25 (s, 3 H), 5.20 (s, 2 H), 6.67 (s, 2 H), 7.25 (m, 5 H).

Reaction of Benzyl Mesitoate with Potassium Hydride. A solution of benzyl mesitoate (1.0 g, 4.0 mmol) in 10 mL of THF was added to prewashed potassium hydride (2.0 g of dispersion, 12 mmol) in 25 mL of THF containing 0.52 g (2.0 mmol) of 18-crown-6. The reaction mixture was stirred for 30 min at room temperature and 48 h at 50–60 °C. This was cooled and poured into 50 mL of ice cold 2% HCl and then extracted with three 50-mL portions of ether. The combined organic layers were washed with three 50-mL portions of saturated, aqueous NaHCO₃, dried over anhydrous MgSO₄, and concentrated to give 0.70 g of a wet solid which was analyzed by NMR integration and comparison with known samples: benzyl alcohol (0.17 g, 1.6 mmol, 40%), 2,4,6-trimethylbenzyl alcohol (0.21 g, 1.4 mmol, 35%), and the mixed α -diketone¹⁸ (0.32 g, 1.3 mmol, 33%). The combined NaHCO₃ layers were acidified with dilute HCl to precipitate mesitoic acid which was collected by filtration and allowed to dry to give 0.23 g of product (1.4 mmol, 35%).

Reaction of Benzyl Mesitoate with LDA. LDA (6.0 mmol) was prepared in the usual manner from *n*-BuLi in THF and cooled to -78 °C. A solution of 1.0 g (4.0 mmol) of benzyl mesitoate in 10 mL of THF was added over a 10-min period, and the reaction mixture was allowed to warm to room temperature and stir for a total of 18 h. The same workup as before in potassium hydride reactions gave 1.0 g of a wet solid which was analyzed by NMR integration: benzyl alcohol (0.21 g, 1.9 mmol, 48%), the mixed α -diketone¹⁸ (0.33 g, 1.3 mmol, 33%), and the α -mesitoxy ketone¹⁸ (0.47 g, 1.2 mmol, 30%).

Reaction of Benzyl Benzoate with LDA. LDA (22.0 mmol) was prepared in the usual manner in THF and cooled to -78 °C, and a solution of benzyl benzoate (4.3 g, 20 mmol) in 10 mL of THF was added over a 10-min period. The reaction mixture was allowed to warm to room temperature and, after 18 h of stirring, was worked up as usual to give 4.0 g of crude solid which was analyzed by NMR as benzoin¹⁸ (1.3 g, 6.1 mmol, 31%), benzoin benzoate¹⁸ (1.2 g, 3.8 mmol, 38%), benzyl benzoate (0.9 g, 4.2 mmol, 21%), and benzyl alcohol (0.4 g, 3.7 mmol, 19%).

Another reaction was run in the same way for a total of 48 h at room temperature to give 4.2 g of crude product which analyzed as benzoin¹⁸ (0.53 g, 2.5 mmol, 13%), benzoin benzoate¹⁸ (2.4 g, 7.6 mmol, 76%), benzyl benzoate (1.1 g, 5.0 mmol, 25%), and benzyl alcohol (0.2 g, 1.9 mmol, 10%).

Registry No. Benzaldehyde, 100-52-7; potassium hydride, 7693-26-7; methyl iodide, 74-88-4; methyl benzoate, 93-58-3; sodium benzyl oxide, 20194-18-7; benzyl benzoate, 120-51-4; benzoin benzoate, 1459-20-7; potassium benzyl oxide, 22379-62-0; benzyl mesitoate, 4909-77-7.

(18) This compound was later isolated as a crystalline solid for unambiguous identification and confirmation of yield.

Selective Nitration of Benzophenone

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We report the first selective nitration of benzophenone to give *m,m'*-dinitrobenzophenone (93%), a precursor for the corresponding diamino benzophenone which is of interest in polyimide resins.¹ Most important syntheses of

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