α-Heterosubstituted Phosphonate Carbanions. 11.[1] Benzoins[2] via an Acyl Anion Equivalent. Novel One-Pot Preparation of Benzo[*b*]furans via Benzoins Using Hydriodic Acid

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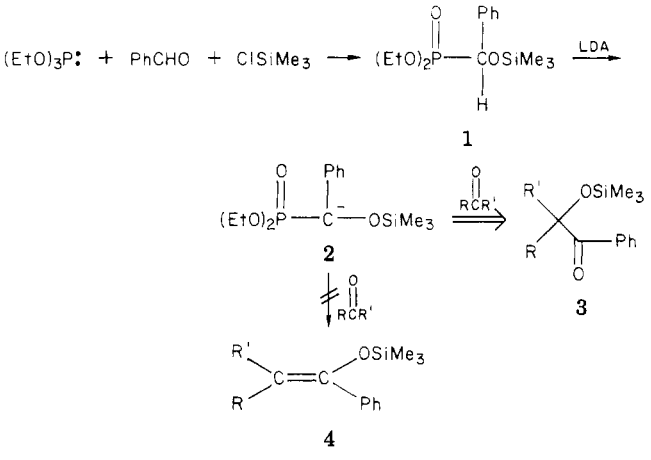
Diethyl 1-(trimethylsiloxy)-1-phenylmethanephosphonate carbanion **2** is introduced as a novel acyl anion equivalent. When **2** reacts with aldehydes or ketones, a 1,4 oxygen–oxygen silicon migration with subsequent loss of diethyl lithium phosphite is observed. An efficient method utilizing **2** for the preparation of otherwise difficultly obtainable substituted benzoins is presented. Also a novel one-pot method which offers a facile entry into the 2-phenylbenzo[*b*]furan ring system from **2** via benzoin intermediates using hydriodic acid was developed.

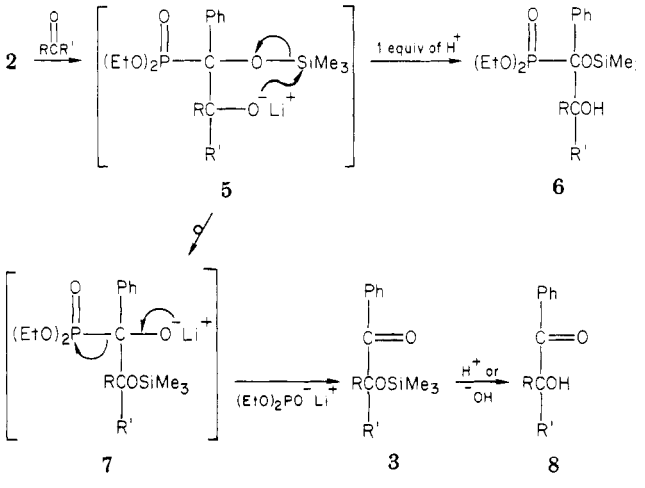
Over the past two decades the arsenal of the synthetic organic chemist has grown steadily in the area of masked acyl anions. Among the most popular acyl anion equivalents are the dithioacetals,[4] α-(dialkylamino)acetonitriles,[5] and the O-protected cyanohydrins.[6] Their usefulness as synthetic tools in organic synthesis has been described in several reviews[7] dealing with the concept of charge affinity inversion[8] or "umpolung".[9] In a recent paper,[10i] we described the utility of diethyl 1-(trimethylsiloxy)-1-phenylmethanephosphonate carbanion **2** as a general acyl anion equivalent in the preparation of α-hydroxy ketones.

During the course of that work, it was observed that strategically substituted α-hydroxy ketones, namely, 2′-methoxybenzoins,[11] could be converted efficiently into 2-phenylbenzo[*b*]furans by using hydriodic acid. Although several different methods[12] exist for preparing these compounds, only one reference[13] deals with the use of benzoins as precursors. In the past, 2-phenylbenzo[*b*]furans have been prepared in moderate overall yields by (a) the reaction of diazoacetophenones with phenols,[14] (b) the reaction of esters of α-bromophenylacetic acid with salicyl-

Scheme I



Scheme II



(1) Paper X of this series: H. Zimmer, R. E. Koenigkramer, R. L. Cepulis, and D. M. Nene, *J. Org. Chem.*, **45**, 2018 (1980).

(2) For brevity and convenience in the body of the paper, the common names benzoin and deoxybenzoin for 2-hydroxy-1,2-diphenylethanone and 1,2-diphenylethanone, respectively, are used. The IUPAC nomenclature, however, is applied in the Experimental Section.

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(8) D. A. Evans and G. C. Andrews, *Acc. Chem. Res.*, **7**, 147 (1974).

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(11) For a review on "The Synthesis of Benzoins" see W. S. Ide and J. S. Buck, *Org. React.*, **4**, 269 (1948).

(12) For reviews on benzo[*b*]furans in general, see: (a) P. Cagniant and D. Cagniant, *Adv. Heterocycl. Chem.*, **18**, 338 (1975); (b) A. Mustafa, "Heterocyclic Compounds", Vol. 29, Interscience, Wiley, New York, 1974.

(13) J. C. Sheehan and R. M. Wilson, *J. Am. Chem. Soc.*, **86**, 5277 (1964). In this reference 2-phenylbenzo[*b*]furan is synthesized from benzoin acetate by a photochemical reaction in 8–15% yield. Also see J. C. Sheehan, R. M. Wilson, A. W. Oxford, *ibid.*, **93**, 7222 (1971).

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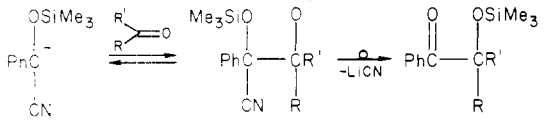
Scheme III

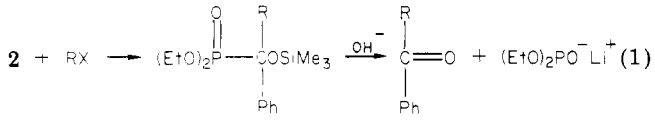


aldehydes,[15] (c) the cyclization of 2'-methoxydeoxybenzoins,[16,10g] and (d) the reaction of salicylaldehydes with benzyl halides followed by cyclization.[17]

In a series of papers,[10] we have described the utility of α-heterosubstituted phosphonate carbanions for the preparation of a wide variety of different classes of compounds. We now wish to report the synthesis of benzoins using the phosphonate carbanion **2** as an acyl anion equivalent and the one-pot preparation of 2-phenylbenzo[*b*]furans from **2** without isolation of the intermediate benzoins using hydriodic acid as a reducing, ether cleaving, and cyclization agent.

Discussion

(A) Benzoins. For the present studies (Scheme I) diethyl 1-(trimethylsiloxy)-1-phenylmethanephosphonate (**1**) was prepared[10i,18] in excellent yield (94%) in an Arbuzov-type reaction by refluxing a mixture of triethyl phosphite, chlorotrimethylsilane, and benzaldehyde evolving ethyl chloride as byproduct. At −60 °C, the treatment of **1** with lithium diisopropylamide (LDA) in tetrahydrofuran (THF) yields a yellow suspension of **2**. With aldehydes and ketones as the electrophiles, **2** produces α-siloxy ketones (**3**) instead of vinyl silyl ethers (**4**), the expected Horner–Emmons[19] products. This is in marked contrast to the reported use of diethyl 1-ethoxy-1-phenylmethanephosphonate carbanion[20] to give ethyl enol ethers by a typical Horner–Emmons reaction. In a different vein, Hata[21] et al. very recently used **2** to synthesize ketones. In their reaction sequence **2** was alkylated with alkyl halides. The resulting phosphonate fragments with aqueous hydroxide to yield unsymmetrical ketones as shown in eq 1.



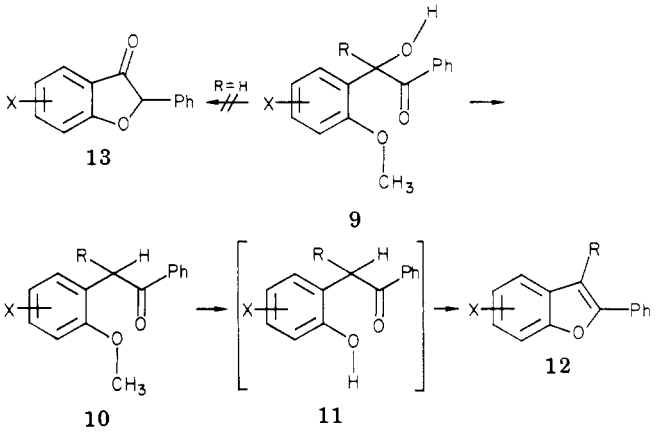
In our studies, as is illustrated in Scheme II, an aldehyde or ketone reacts with **2** to give the expected 1,2-adduct **5** which in some cases was isolated as the alcohol **6**. For further characterization of **6**, **6a** was transformed into the corresponding 1,2-glycol by refluxing an ethanolic solution of it with a trace of *p*-toluenesulfonic acid. With the reaction mixture kept at −60 °C, the formation of **3** was usually complete within 1 h. Formation of **3** from **5** is rationalized by a 1,4 oxygen–oxygen silicon migration proceeding through the unstable intermediate **7** followed by elimination of diethyl lithium phosphite. Compounds of type **7** (alkoxides of α-hydroxyphosphonates) are well-known to fragment easily.[22] Observations of 1,4 and 1,5 oxygen–oxygen silicon migrations of this type have been reported.[23] A 1,4-migration followed by the elimination of lithium cyanide was recently observed and is outlined in Scheme III.[6d] In the reaction studied by us diethyl

Table I

compd	electrophile	overall[a] % yield: benzoin (8)	benzo[*b*]furan (12)
a	benzaldehyde	91[b]	
b	benzophenone	92[c]	
c	5-methylthiophenecarboxaldehyde	92[b]	
d	acetophenone	91[c]	
e	4-cyanobenzaldehyde	81[b,d]	
f	2-methoxybenzaldehyde	90[b]	91
g	2-methoxynaphthaldehyde	94[c]	92
h	2,3-dimethoxybenzaldehyde	89[c]	74[f]
i	2,4-dimethoxybenzophenone	90[c]	80[f]
j	2-methoxyacetophenone	83[c]	84
k	4,6-dimethoxyisophthalaldehyde	73[c]	67[g]
l	2-(trimethylsiloxy)benzaldehyde	76[b,e]	86[h]

[a] All yields are isolated yields based on starting electrophile. [b] Hydrolyzed with 2 equiv of 2 N NaOH for 20 min at room temperature. [c] Refluxed with 4 equiv of 2 N HCl until TLC indicated that hydrolysis was complete. [d] 15% 1-(4-cyanophenyl)-2-phenylethanedione was also isolated; see the Experimental Section. [e] The phenolic trimethylsilyl ether was hydrolyzed in the workup to give the phenol. [f] Because the second methoxy group also was cleaved, the free phenol was isolated. [g] The benzo[1,2-*b*:5,4-*b'*]difuran was isolated. [h] This compound was prepared from the crude **81** by the method given in the Experimental Section.

Scheme IV



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(16) (a) O. Dann, J. Lang, and H. Vohl, *Justus Liebigs Ann. Chem.*, **631**, 116 (1960); (b) L. Christiaens and M. Renson, *Bull. Soc. Chim. Belg.*, **79**, 235 (1970).

(17) W. Sahm, E. Schinzel, and P. Jurges, *Justus Liebigs Ann. Chem.*, 523 (1974).

(18) G. H. Birum and G. A. Richardson (Monsanto Chemical Co.), U.S. Patent 3 113 139 (1963); *Chem. Abstr.*, **60**, 5551 (1964).

(19) For a review see W. S. Wadsworth, Jr., *Org. React.*, **25**, 73 (1977).

(20) E. Schaumann and F.-F. Grabley, *Justus Liebigs Ann. Chem.*, 88 (1977).

(21) T. Hata, A. Hashizume, M. Nakajima, and M. Sekine, *Tetrahedron Lett.*, 363 (1978). The method used to prepare **1** in ref 18 is far superior to the method referred to in ref 21 because not only is a better yield obtained but also readily available starting materials are used instead of the costly diethyl trimethylsilyl phosphite.

(22) (a) G. M. Kosolapoff and L. Maier, "Organic Phosphorus Compounds", Vol. 7, Wiley, New York, 1976, p 30; (b) L. Horner and H. Roder, *Ber. Dtsch. Chem. Ges.*, **103**, 2984 (1970).

(23) (a) T. J. Pinnavaia and J. A. McClarin, *J. Am. Chem. Soc.*, **96**, 3012 (1974); (b) A. G. Brook and D. M. Macrae, *J. Organomet. Chem.*, **77**, C19 (1974); (c) G. M. Rubottom, M. A. Vazquez, and D. R. Pelegrina, *Tetrahedron Lett.*, 4319 (1974).

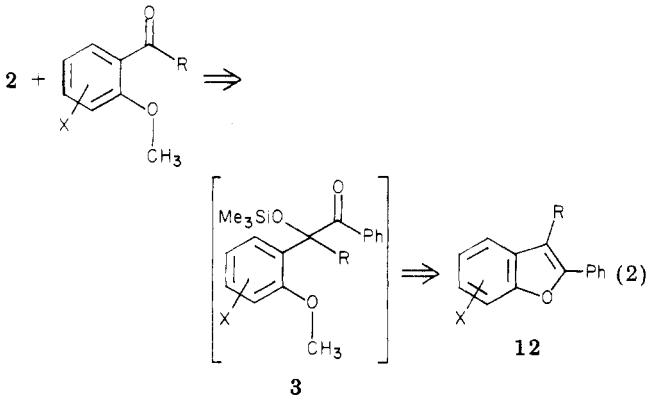
lithium phosphite is eliminated (Scheme II).

In agreement with newly reported results[10i,24] we have also found that lowering the initial reaction temperature from −60 to −100 °C led[25] to dramatically increased yields in this reaction when enolizable ketones were the electrophiles. Thus, with acetophenone as electrophile, a 51% yield of the corresponding α-hydroxy ketone (**8d**) was obtained at −60 °C; at −100 °C the yield increased to 91%. The silyl ether could be isolated as shown for **3b** in 95% yield or **3g** in 94% yield. However, these ethers were usually hydrolyzed in the same reaction flask without prior workup (Table I). The total reaction time for the described high-yielding transformation averaged 3 h when base hydrolysis was employed. In some cases it was noted that base hydrolysis promotes air oxidation of the benzoin to the corresponding benzil; therefore, acid hydrolysis was usually preferred. The nucleophilicity of **2** was tested by attempted reactions with salicylaldehyde and with 2-(trimethylsiloxy)benzaldehyde. The former gave the expected, though undesired, proton transfer; after workup the latter gave the previously unknown 2′-hydroxybenzoin in 76% yield.

(B) Benzo[*b*]furans. In addition, we have found (Scheme IV) that 2-phenylbenzo[*b*]furans (**12**) can be conveniently and cleanly prepared by refluxing 2′-methoxybenzoins (**9**) with excess 47% hydriodic acid (HI) in glacial acetic acid (HOAc). In contrast, preliminary attempts to convert **9** to 2-phenyl-3(2*H*)-benzo[*b*]furanone **13** with 48% hydrobromic acid in HOAc gave a multitude of compounds as shown by TLC. The ease by which **12** is prepared can be rationalized by first reducing **9** to a deoxybenzoin (**10**) with 2 equiv of HI followed by methyl ether cleavage to the phenol **11**.[10g] The deoxybenzoin **11** would be expected to cyclize spontaneously and dehydrate to give **12**.[10g,16] Evidence for the initial reduction is based upon the fact that HI is well-known as a reducing agent. Indeed, α-diketones,[26,27] aliphatic α-ketols,[27] and polyarene quinones[28] are all effectively reduced with HI. In addition, when **9g** (where R = H and X = −(CH)$_4$−) was stirred with 2.5 equiv of HI in HOAc at room temperature for 30 h, the corresponding deoxybenzoin (**10g**) was obtained in 91% yield. In all the above reaction mixtures, a dark red-black iodine color was observed, indicating that a redox reaction had occurred.

For maximization of the efficiency of the overall sequence, the following one-pot procedure was developed for the preparation of **12**. At −60 °C (or −100 °C) the electrophile was added to a THF solution of **2** and stirred for 15 min after which the solution was allowed to warm to room temperature (ca. 30 min). Then, upon removal of the volatiles in vacuo, the residue was refluxed with excess HI and HOAc for 4 h to give a yellowish solution. Upon workup (including chromatography if needed), **12** is obtained (Table I) as summarized in eq 2.

It is noteworthy that this one-pot procedure gives a yellowish solution instead of the dark red-black iodine-colored solution obtained in the two-step procedure. We find this is due to the phosphorus moiety generated in the rearrangement–elimination step. Although diethyl phosphite gives an equilibrium mixture of diethyl phosphite and diethyl iodophosphate with iodine in methylene



chloride[29a] or diethyl ether,[29b] we have found that diethyl lithium phosphite reduced iodine in refluxing HOAc in just a few minutes.[30]

Almost all of the 2-phenylbenzo[*b*]furans reported in Table I are known compounds (see Experimental Section). However, the one-pot method presented here for the preparation of 2-phenylbenzo[*b*]furans has two advantages over the methods in the literature. First, readily available starting materials are employed. Second, the overall yields are superior to the reported overall yields obtained in the past. The following examples were randomly selected for comparison. Thus, the use of ethyl bromophenylacetate with *o*-vanillin[15a] followed by methyl ether cleavage[31] to prepare **12h** yields only 14.4% while we obtained 74%. Also our method gave a 91% yield of **12f** whereas the reduction of diazoacetophenone with phenol yields 29%,[14a] the reaction of salicylaldehyde with benzyl bromide followed by cyclization yields only 22%,[17] and the reaction of (2-methoxyphenyl)acetonitrile with phenylmagnesium bromide followed by ether cleavage and cyclization yields 30%[16b] **12f**.

Conclusion

We believe the phosphonate reagent presented here could find general application as a useful synthon in organic chemistry. We are pursuing the study of these types of reagents with the goal set toward the further expansion of their synthetic utility. Additionally, we are investigating the synthesis of other biologically active molecules as well as other classes of compounds via this novel acyl anion equivalent.

Experimental Section

General Methods. Melting points were determined with a Mel-Temp melting point apparatus and are uncorrected as are boiling points. Infrared spectra (IR) were recorded by using a Perkin-Elmer Model 599 spectrometer calibrated against the 1601-cm^{-1} band of polystyrene. Proton nuclear magnetic resonance (NMR) spectra were recorded on a Varian T-60 spectrometer. Chemical shifts are expressed in δ units relative to 1% tetramethylsilane as internal standard, and coupling constants (*J* values) are given in hertz. Mass spectral data were obtained on a Perkin-Elmer RMU-7 mass spectrometer. Elemental analyses were performed at Integral Microanalytical Laboratories or at Galbraith Laboratories.

The THF was purified by continuous distillation under argon from sodium metal and benzophenone. The diisopropylamine was distilled from CaH_2 and stored under argon. Standardized solutions of *n*-butyllithium in hexane were obtained from Lithium

(24) (a) A. F. Kluge, *Tetrahedron Lett.*, 3629 (1978); (b) A. F. Kluge and I. S. Cloudsdale, *J. Org. Chem.*, **44**, 4847 (1979).
(25) A −100 °C temperature was conveniently obtained by adding liquid N_2 to a methanol/dry ice bath already at −60 °C. After addition of the electrophile, the solution was allowed to warm up to −60 °C.
(26) R. C. Fuson and P. E. Hoch, *J. Am. Chem. Soc.*, **71**, 1585 (1949).
(27) W. Reusch and R. LeMahieu, *J. Am. Chem. Soc.*, **86**, 3068 (1964).
(28) M. Konieczny and R. G. Harvey, *J. Org. Chem.*, **44**, 4813 (1979).
(29) (a) A. Skowronska, M. Pakulski, J. Michalski, D. Cooper, and S. Trippett, *Tetrahedron Lett.*, 321 (1980); (b) H. McCombie, B. C. Saunders, and G. J. Stacey, *J. Chem. Soc.*, 921 (1945).
(30) R. E. Koenigkramer and H. Zimmer, unpublished results.
(31) G. Bondesson, T. Hogberg, A. Misiorny, and N. E. Stjernstrom, *Acta Pharm. Suec.*, **13**, 97 (1976).

Corp. of America. 4,6-Dimethoxyisophthalaldehyde[32] and 2-(trimethylsiloxy)benzaldehyde[33] were prepared by literature methods. Other reagents were commercially available from Aldrich Chemical Co. and were purified before use by distillation or recrystallization. All reactions were run under argon and all glassware was oven-dried before use.

Preparation of Diethyl 1-(Trimethylsiloxy)-1-phenylmethanephosphonate (1). This was prepared[10i,18] in 94% yield by refluxing for 4 h 1.1 equiv of chlorotrimethylsilane, 1.1 equiv of benzaldehyde, and 1.0 equiv of triethyl phosphite: bp 95–96 °C (0.05 mm) [lit.[34] bp 124–125 °C (1.0 mm)]; IR (neat) 1250 cm^{-1}; NMR (CCl_4) δ 0.03 (s, 9 H), 0.9–1.4 (m, 6 H), 3.6–4.1 (m, 4 H), 4.85 (d, 1 H, J = 14 Hz), 7.0–7.5 (m, 5 H); mass spectrum (20 eV), m/e (relative intensity) 316 (M^+, 1), 301 (M^+ – 15, 2), 211 (9), 210 (61), 195 (6), 183 (6), 180 (17), 179 (100), 106 (6), 105 (9), 77 (6), 73 (14). Anal. Calcd for $C_{14}H_{25}O_4PSi$: C, 53.14; H, 7.96; Si, 8.88. Found: C, 53.25; H, 7.69; Si, 8.59.

General Procedure for the Preparation of 1,2-Adducts (6). To a solution of freshly distilled THF (15 mL/g of 1) and 1.0 equiv of diisopropylamine was added at –60 °C 1.0 equiv of n-BuLi. After 30 min, 1.0 equiv of 1 was added via syringe to give after 20 min a yellowish suspension. Next, at –60 °C (or –100 °C[25]) 0.9 equiv of the appropriate electrophile was added via syringe. After being stirred for 5–10 min, the solution was neutralized with 2 equiv of 1 N HCl and allowed to warm to 10–20 °C. After extraction with Et_2O, the organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo to give crude 6 which was recrystallized from Et_2O.

Diethyl 2-hydroxy-1-(trimethylsiloxy)-1,2-diphenylethanephosphonate (6a): yield 86%; mp 115–117 °C; IR (KBr) 3250 cm^{-1}; NMR (CCl_4) δ –0.07 (s, 9 H), 1.1–1.5 (m, 6 H), 3.7–4.5 (m, 4 H), 4.82 (d, 1 H, J = 8 Hz, D_2O exchangeable), 3.71 (d, 1 H, J = 5 Hz), 7.0–7.85 (m, 10 H); mass spectrum (20 eV), m/e (relative intensity) 422 (M^+, absent),[35] 407 (M^+ – 15, 1), 318 (5), 316 (63), 270 (11), 269 (42), 244 (9), 243 (5), 179 (100), 111 (26), 105 (19), 83 (9), 73 (35). Anal. Calcd for $C_{21}H_{31}O_5PSi$: C, 59.69; H, 7.40; P, 7.33; Si, 6.65. Found: C, 59.74; H, 7.35; P, 7.02; Si, 6.42.

Diethyl 2-hydroxy-1-(trimethylsiloxy)-2-(5-methylthien-2-yl)-1-phenylethanephosphonate (6c): yield 87%; mp 114.0–115.5 °C; IR (KBr) 3260 cm^{-1}; NMR ($CDCl_3$) δ –0.20 (s, 9 H), 0.8–1.4 (m, 6 H), 2.48 (s, 3 H), 3.1–4.3 (m, 5 H, 1 H is D_2O exchangeable), 5.62 (d, 1 H, J = 2 Hz), 6.6–8.0 (m, 7 H). Anal. Calcd for $C_{20}H_{31}O_5PSSi$: C, 54.15; H, 7.27; S, 7.23. Found: C, 54.51; H, 7.30; S, 7.43.

Diethyl 2-(4-cyanophenyl)-2-hydroxy-1-(trimethylsiloxy)-1-phenylethanephosphonate (6e): yield 82%; mp 173.0–174.5; IR (KBr) 3260, 2220 cm^{-1}; NMR ($CDCl_3$) δ –0.15 (s, 9 H), 0.9–1.4 (m, 6 H), 3.2–4.25 (m, 5 H, 1 H is D_2O exchangeable), 5.38 (d, 1 H, J = 4 Hz), 7.2–7.9 (m, 9 H). Anal. Calcd for $C_{22}H_{30}NO_5PSi$: C, 59.04; H, 6.76; N, 3.13. Found: C, 59.39; H, 6.65; N, 2.95.

Diethyl 2-hydroxy-2-(2-methoxyphenyl)-1-(trimethylsiloxy)-1-phenylethanephosphonate (6f): yield 84%; mp 137.0–138.5 °C; IR (KBr) 3250 cm^{-1}; NMR ($CDCl_3$) δ –0.12 (s, 9 H), 0.9–1.4 (m, 6 H), 3.4–4.4 (m, 8 H, 1 H is D_2O exchangeable), 5.81 (d, 1 H, J = 6 Hz), 6.6–8.0 (m, 9 H); mass spectrum (20 eV), m/e (relative intensity) 452 (M^+, absent),[35] 437 (M^+ – 15, 1), 318 (6), 316 (73), 300 (6), 299 (21), 284 (15), 210 (100), 179 (19), 135 (22), 111 (100), 105 (11), 83 (74), 73 (98). Anal. Calcd for $C_{22}H_{33}O_6PSi$: C, 58.38; H, 7.35. Found: C, 58.36; H, 7.34.

General Procedure for the Preparation of α-Siloxy Ketones (3). The general procedure is the same as that for the preparation of 1,2-adducts 6 above except that after addition of the electrophile and stirring of the mixture for 15–20 min at –60 °C, the solution was allowed to warm to room temperature (ca. 30 min). Next H_2O was added and the product extracted with Et_2O. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo to give the crude 3 which was purified by chromatography.

2-(Trimethylsiloxy)-1,2,2-triphenylethanone (3b): yield 95%; mp 54.5–56.0 °C (hexane); IR (KBr) 1680 cm^{-1}; NMR (CCl_4) δ 0.08 (s, 9 H), 7.4–7.9 (m, 13 H), 8.1–8.3 (m, 2 H). Anal. Calcd for $C_{23}H_{24}O_2Si$: C, 76.62; H, 6.71; Si, 7.79. Found: C, 77.02; H, 7.01; Si, 7.83.

2-(2-Methoxynaphthyl)-2-(trimethylsiloxy)-1-phenylethanone (3g): yield 94%; mp 136.5–138.5 °C (Et_2O); IR (KBr) 1675 cm^{-1}; NMR ($CDCl_3$) δ 0.08 (s, 9 H), 3.98 (s, 3 H), 7.0–8.5 (m, 12 H). Anal. Calcd for $C_{22}H_{24}O_3Si$: C, 72.49; H, 6.64; Si, 7.71. Found: C, 72.20; H, 6.43; Si, 8.11.

General Procedure for the Preparation of Benzoins (8). The general procedure is the same as that for the preparation of α-siloxy ketones 3 above except that after warming to room temperature, the solution was hydrolyzed as indicated in Table I. After hydrolysis was complete, the product was extracted with Et_2O. The combined organic layers were then washed with 5% $NaHCO_3$ (or 0.5 N HCl, depending on hydrolyzing solution), dried over $MgSO_4$, filtered, and concentrated in vacuo to give crude 8 which was recrystallized from diethyl ether–hexane.

2-Hydroxy-1,2-diphenylethanone (8a): yield 91%; mp 134.0–135.5 °C (lit.[36] 129 °C); IR (KBr) 3380, 1680 cm^{-1}; NMR ($CDCl_3$) δ 4.05 (s, 1 H, D_2O exchangeable), 5.93 (s, 1 H), 6.97–8.03 (m, 10 H). Anal. Calcd for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70. Found: C, 79.47; H, 6.00.

2-Hydroxy-1,2,2-triphenylethanone (8b): yield 92%; mp 82–84 °C (lit.[6d] 84 °C); IR (KBr) 3470, 1660 cm^{-1}; NMR ($CDCl_3$) δ 4.95 (br s, 1 H, D_2O exchangeable), 7.1–7.9 (m, 15 H). Anal. Calcd for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C, 83.33; H, 5.77.

2-Hydroxy-2-(5-methylthien-2-yl)-1-phenylethanone (8c): yield 92%; mp 142.0–143.5 °C; IR (KBr) 3440, 1645 cm^{-1}; NMR ($CDCl_3$) δ 2.45 (s, 3 H), 4.42 (d, 1 H, J = 5 Hz, D_2O exchangeable), 5.67 (d, 1 H, J = 5 Hz, collapses to s with D_2O addition), 6.72 (d, 1 H, J = 4 Hz), 7.1–7.6 (m, 6 H). Anal. Calcd for $C_{13}H_{12}O_2S$: C, 67.21; H, 5.21. Found: C, 67.34; H, 5.05.

2-Hydroxy-2-methyl-1,2-diphenylethanone (8d): yield 91%; mp 66–68 °C (lit.[6d] mp 66–67 °C); bp 132–134 °C (0.30 mm); IR (KBr) 3440, 1670 cm^{-1}; NMR ($CDCl_3$) δ 1.87 (s, 3 H), 4.7 (mound, 1 H, D_2O exchangeable), 7.1–7.9 (m, 10 H). Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.69; H, 6.26.

2-(4-Cyanophenyl)-2-hydroxy-1-phenylethanone (8e): yield 81%; mp 112–113 °C; IR (KBr) 3460, 2230, 1670 cm^{-1}; NMR ($CDCl_3$) δ 4.65 (d, 1 H, J = 6 Hz, D_2O exchangeable), 6.02 (d, 1 H, J = 6 Hz, collapses to s with D_2O addition), 7.2–8.0 (m, 9 H). Anal. Calcd for $C_{15}H_{11}NO_2$: C, 75.93; H, 4.67; N, 5.91. Found: C, 75.91; H, 4.44; N, 5.75.

2-Hydroxy-2-(2-methoxyphenyl)-1-phenylethanone (8f): yield 90%; mp 57.0–8.5 °C (lit.[37] mp 58 °C); IR (KBr) 3460, 1690 cm^{-1}; NMR ($CDCl_3$) δ 3.73 (s, 3 H), 4.33 (br s, 1 H, D_2O exchangeable), 6.23 (s, 1 H), 6.7–8.0 (m, 9 H). Anal. Calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82. Found: C, 74.65; H, 5.60.

2-Hydroxy-2-(2-methoxynaphthyl)-1-phenylethanone (8g): yield 94%; mp 131.5–133.0 °C; IR (KBr) 3390, 1675 cm^{-1}; NMR ($CDCl_3$) δ 3.63 (s, 3 H), 4.75 (d, 1 H, J = 4 Hz, D_2O exchangeable), 6.52 (d, 1 H, J = 4 Hz, collapses to s with D_2O addition), 6.9–8.3 (m, 11 H). Anal. Calcd for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52. Found: C, 78.18; H, 5.43.

2-Hydroxy-2-(2,3-dimethoxyphenyl)-1-phenylethanone (8h): yield 89%; mp 128–129 °C; IR (KBr) 3460, 1675 cm^{-1}; NMR ($CDCl_3$) δ 3.78 (s, 3 H), 3.92 (s, 3 H), 4.60 (d, 1 H, J = 5 Hz, D_2O exchangeable), 6.22 (d, 1 H, J = 5 Hz, collapses to s with D_2O addition), 6.6–7.6 (m, 6 H), 7.8–8.1 (m, 2 H). Anal. Calcd for $C_{16}H_{16}O_4$: C, 70.57; H, 5.92. Found: C, 70.80; H, 5.85.

2-Hydroxy-2-(2,4-dimethoxyphenyl)-1,2-diphenylethanone (8i): yield 90%; mp 88–90 °C; IR (KBr) 3510, 1675 cm^{-1}; NMR ($CDCl_3$) δ 3.67 (s, 3 H), 3.73 (s, 3 H), 4.90 (s, 1 H, D_2O exchangeable), 6.1–6.8 (m, 3 H), 7.1–8.0 (m, 10 H). Anal. Calcd

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for $C_{22}H_{20}O_4$: C, 75.84; H, 5.79. Found: C, 76.13; H, 5.97.

2-Hydroxy-2-(2-methoxyphenyl)-2-methyl-1-phenylethanone (8j): yield 83%; mp 120–121 °C; IR (KBr) 3440, 1680 cm^{-1}; NMR ($CDCl_3$) δ 1.83 (s, 3 H), 3.45 (s, 3 H), 4.80 (s, 1 H, D_2O exchangeable), 6.6–8.0 (m, 9 H). Anal. Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 75.32; H, 6.36.

2,2′-(4,6-Dimethoxy-1,3-phenylene)bis(2-hydroxy-1-phenylethanone) (8k): yield 73%; mp 171–172 °C; IR (KBr) 3430, 1680 cm^{-1}; NMR ($CDCl_3$) δ 3.77 (s, 6 H), 4.45 (d, 2 H, J = 6 Hz, D_2O exchangeable), 6.03 (d, 2 H, J = 6 Hz, collapses to s with D_2O addition), 6.37 (s, 1 H), 6.97–8.0 (m, 11 H). Anal. Calcd for $C_{24}H_{22}O_6$: C, 70.92; H, 5.46. Found: C, 69.68; H, 4.93.[38]

2-Hydroxy-2-(2-hydroxyphenyl)-1-phenylethanone (8l): yield 79%; mp 160.0–161.5 °C; IR (KBr) 3420, 3260, 1670 cm^{-1}; NMR (Me_2SO-d_6) δ 5.10 (d, 1 H, J = 6 Hz, D_2O exchangeable), 6.37 (d, 1 H, J = 6 Hz, collapses to s with D_2O addition), 6.6–8.3 (m, 9 H), 9.43 (br s, 1 H, D_2O exchangeable). Anal. Calcd for $C_{14}H_{12}O_3$: C, 73.67; H, 5.30. Found: C, 74.07; H, 5.49.

General Procedure for the One-Pot Preparation of Compounds 12. The general procedure is the same as that for α-siloxy ketones **3** above except that after the mixture was warmed to room temperature the volatiles were removed in vacuo. Next, 20 mL of HOAc/g of benzoin (**8**) and 15–25 equiv of 47% HI were added and the mixture was refluxed for 4 h. After the mixture was cooled and diluted with H_2O, the product was extracted with $CHCl_3$. The combined organic layers were washed with 5% $NaHCO_3$, dried over $MgSO_4$, and concentrated in vacuo to give the crude 2-phenylbenzo[*b*]furans. The most expedient method of purification was by column chromatography using silicon gel (25 g of 70–230 mesh ASTM/g of benzofuran) with $CHCl_3$ as eluent.

2-Phenylbenzo[*b*]furan (12f): yield 91%; mp 120–121 °C (hexane) (lit.[39] mp 120–121 °C); IR (KBr) 750 cm^{-1}; NMR ($CDCl_3$) δ 6.97 (s, 1 H), 7.1–8.0 (m, 9 H). Anal. Calcd for $C_{14}H_{10}O$: C, 86.57; H, 5.19. Found: C, 86.78; H, 4.83.

2-Phenylnaphtho[2,1-*b*]furan (12g): yield 92%; mp 146–147 °C (Et_2O) (lit.[40] mp 143–144 °C); IR (KBr) 760 cm^{-1}; NMR ($CDCl_3$) δ 7.2–8.3 (m, aromatic H only). Anal. Calcd for $C_{18}H_{12}O$: C, 88.50; H, 4.95. Found: C, 88.38; H, 4.69.

7-Hydroxy-2-phenylbenzo[*b*]furan (12h): yield 74%; mp 133.5–134.0 °C (Et_2O (lit.[31] mp 126–127 °C); IR (KBr) 3240, 735 cm^{-1}; NMR ($CDCl_3$) δ 5.35 (br s, 1 H, D_2O exchangeable), 6.7–8.0 (m, 9 H). Anal. Calcd for $C_{14}H_{10}O_2$: C, 79.98; H, 4.79. Found: C, 79.63; H, 4.46.

6-Hydroxy-2,3-diphenylbenzo[*b*]furan (12i): yield 80%; mp 118.5–119.5 °C (Et_2O) (lit.[41] mp 118–120 °C); IR (KBr) 3320, 1150 cm^{-1}; NMR ($CDCl_3$) δ 4.65 (br s, 1 H, D_2O exchangeable), 6.6–7.8 (m, 13 H). Anal. Calcd for $C_{20}H_{14}O_2$: C, 83.90; H, 4.93. Found: C, 83.91; H, 5.08.

3-Methyl-2-phenylbenzo[*b*]furan (12j): yield 84%; bp 117–118 °C (0.30 mm) [lit.[42] bp 127–128 °C (0.3 mm)]; IR (neat) 750 cm^{-1}; NMR ($CDCl_3$) δ 2.38 (s, 3 H), 7.1–8.0 (m, 9 H).

2,6-Diphenylbenzo[1,2-*b*:5,4-*b*']difuran (12k). The workup included sublimation: yield 67%; mp 279–280 °C ($CHCl_3$) (lit.[14b] mp 280–281 °C); IR (KBr) 770 cm^{-1}; the NMR spectrum was not obtained because of extreme insolubility. Anal. Calcd for $C_{22}H_{14}O_2$: C, 85.14; H, 4.55. Found: C, 85.41; H, 4.46.

Procedure for the Preparation of 3-Methoxy-2-phenylbenzo[*b*]furan (12l). This compound was prepared by dissolving at room temperature 0.84 g (3.68 mmol) of **8l** in 12 mL of MeOH and saturating the mixture wth HCl gas. Evaporation of volatiles and distillation give 0.71 g (86% yield) of **12l**: bp 117–120 °C (0.40 mm); IR (neat) 750 cm^{-1}; NMR (CCl_4) δ 3.97 (s, 3 H), 7.0–7.6 (m, 7 H), 7.8–8.1 (m, 2 H). Anal. Calcd for $C_{15}H_{12}O_2$: C, 80.33; H, 5.40. Found: C, 80.16; H, 5.33.

Procedure for the Preparation of Diethyl 1,2-Dihydroxy-1,2-diphenylethanephosphonate. A solution consisting of 0.31 g (0.734 mmol) of **6a**, 0.01 g (0.053 mmol) of *p*-toluenesulfonic acid, and 5 mL of absolute ethanol was refluxed for 20 min. After removal of the ethanol in vacuo, the residue was dissolved in 20 mL of Et_2O and was quickly washed with 10 mL of 5% $NaHCO_3$. After the ether layer was dried over $MgSO_4$ and the solvent removed in vacuo, a colorless solid was obtained. The product was recrystallized from Et_2O to give 0.25 g (96% yield) of product: mp 134–136 °C; IR (KBr) 3360 cm^{-1}; NMR ($CDCl_3$) δ 0.8–1.3 (m, 6 H), 3.2–4.2 (m, 6 H, 2 H are D_2O exchangeable), 5.32 (m, 1 H, J = 6 Hz, collapses to d with D_2O addition), 7.0–7.9 (m, 10 H); mass spectrum (40 eV), *m/e* (relative intensity) 350 (M^+, absent),[43] 246 (2), 245 (11), 244 (88), 243 (4), 216 (18), 188 (7), 151 (9), 123 (14), 111 (10), 107 (23), 106 (49), 105 (100), 79 (11), 77 (18). Anal. Calcd for $C_{18}H_{23}O_5P$: C, 61.71; H, 6.62; P, 8.84. Found: C, 61.86; H, 6.65; P, 8.76.

Procedure for the Preparation of 2-(2-Methoxynaphthyl)-1-phenylethanone (10g). This compound was prepared by stirring a solution consisting of 0.32 g (1.09 mmol) of **8g**, 0.42 mL (2.72 mmol) of 47% HI, and 5.5 mL of HOAc at room temperature for 30 h. The workup consisted of addition of 40 mL of H_2O to the iodine-colored heterogeneous reaction mixture and extraction with $CHCl_3$ (3 × 20 mL). The combined organic layers were washed with 0.5 M $Na_2S_2O_3$ and with 10% Na_2CO_3. Upon drying of the organic layer with $MgSO_4$, removal of the volatiles in vacuo, and chromatography, 0.275 g (91% yield) of the deoxybenzoin was realized: mp 150.5–151.5 °C (Et_2O); IR (KBr) 1680 cm^{-1}; NMR ($CDCl_3$) δ 3.88 (s, 3 H), 4.77 (s, 2 H), 7.1–8.3 (m, 11 H). Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.96; H, 5.81.

1-(4-Cyanophenyl)-2-phenylethanedione. This compound was isolated from the reaction mixture of **8e** by column chromatography: yield 15%; mp 111.5–113.0 °C (Et_2O) (lit.[44] mp 108–109 °C); IR (KBr) 2240, 1685, 1665 cm^{-1}; NMR ($CDCl_3$) δ 7.3–8.3 (m, aromatic H only). Anal. Calcd for $C_{15}H_9NO_2$: C, 76.58; H, 3.86; N, 5.96. Found: C, 76.99; H, 3.75; N, 5.80.

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Registry No. **1**, 31675-43-1; **3b**, 28698-05-7; **3g**, 74552-48-0; **6a**, 74552-49-1; **6c**, 74552-50-4; **6e**, 74562-17-7; **6f**, 74552-51-5; **8a**, 119-53-9; **8b**, 4237-46-1; **8c**, 74552-52-6; **8d**, 5623-26-7; **8e**, 74552-53-7; **8f**, 74552-54-8; **8g**, 74552-55-9; **8h**, 74552-56-0; **8i**, 74552-57-1; **8j**, 74552-58-2; **8k**, 74552-59-3; **8l**, 74552-60-6; **10g**, 74552-61-7; **12f**, 1839-72-1; **12g**, 14385-54-7; **12h**, 59920-57-9; **12i**, 38256-48-3; **12j**, 4521-08-8; **12k**, 24534-44-9; **12l**, 74552-62-8; chlorotrimethylsilane, 75-77-4; benzaldehyde, 100-52-7; triethyl phosphite, 122-52-1; diethyl 1,2-dihydroxy-1,2-diphenylethanephosphonate, 74552-63-9; 1-(4-cyanophenyl)-2-phenylethanedione, 36803-56-2; benzophenone, 119-61-9; 5-methylthiophenecarboxaldehyde, 13679-70-4; acetophenone, 98-86-2; 4-cyanobenzaldehyde, 105-07-7; 2-methoxybenzaldehyde, 135-02-4; 2-methoxynaphthaldehyde, 5392-12-1; 2,3-dimethoxybenzaldehyde, 86-51-1; 2,4-dimethoxybenzophenone, 613-45-6; 2-methoxyacetophenone, 4079-52-1; 4,6-dimethoxyisophthalaldehyde, 28006-83-9; 2-(trimethylsiloxy)benzaldehyde, 1078-31-5.

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