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Reactions of Bis(2,6-dimethoxyphenyl)methanol in Common Organic Solvents in the Presence of an Acid

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(Received February 4, 1998)

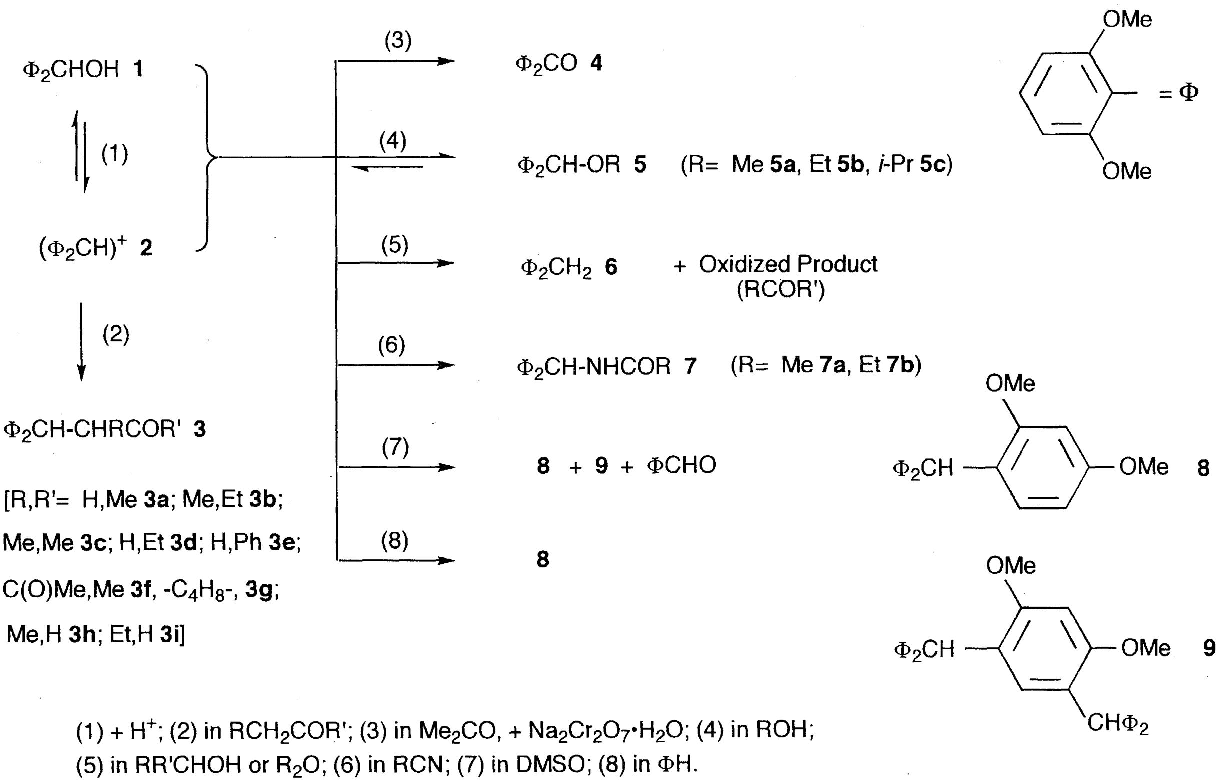
The title compound, Φ_2CHOH [$\Phi = 2,6\text{-}(MeO)_2C_6H_3$] (**1**), reacted in acetone under mild conditions in the presence of acid to give a new ketone, Φ_2CHCH_2COMe. Analogous reactions were observed in some other alkyl ketones and aldehydes, such as diethyl ketone, methyl phenyl ketone, 2,4-pentanedione, propanal, and butanal. In ethyl methyl ketone, an 80 : 20 mixture of $\Phi_2CHCHMeCOMe$ and Φ_2CHCH_2COEt was obtained in agreement with the pK_E values of two enols derived from ethyl methyl ketone. Compound **1** reacted in primary and secondary alcohols to give the reduced compound, Φ_2CH_2 (**6**), and the corresponding aldehyde and ketone derived from the alcohols, respectively. The reactivity of the alcohols was in the order, 1-propanol≈1-butanol < ethanol < 2-butanol < 2-propanol. Compound **1** also reacted in ethers, such as tetrahydrofuran and diethyl ether, to give **6**. It was either recovered unreacted from 2-methyl-2-propanol and from dimethyl sulfoxide, or it reacted under more forcing conditions to give products derived by Φ–C bond cleavage, followed by reactions of **1** with ΦH.

The chemical properties of tri- and diphenylmethanols vary drastically depending on the number and position of the methoxy substituent on the phenyl groups.[1,2] Triphenylmethanols bearing at least four *ortho*-methoxy groups, such as Φ_3COH and $Ph\Phi_2COH$ [$\Phi = 2,6\text{-}(MeO)_2C_6H_3$], were highly basic to form isolable triarylcarbenium salts, [$Ar\Phi_2C$]X, even in secondary alcohols and water; these salts were highly reactive in primary alcohols to give the reduced compound, $Ar\Phi_2CH$.[1] Bis(2,4,6-trimethoxyphenyl)methanol, Φ'_2CHOH [$\Phi' = 2,4,6\text{-}(MeO)_3C_6H_2$], also reacted with a slight excess of perchloric acid in methanol to give dark-red crystals of the diarylcarbenium salt, [Φ'_2CH]ClO_4. This salt was easily reduced both in primary and secondary alcohols to give Φ'_2CH_2, or it decomposed in some other solvents by Φ′–C bond cleavage.[2] For further understanding the effect of *ortho*-methoxy substitutions, we were also interested in the properties of bis(2,6-dimethoxyphenyl)methanol, Φ_2CHOH (**1**), in common organic solvents in the presence of an acid. We report here on its facile reaction with ketones and aldehydes catalyzed by acid to form a new C–C bond (see Scheme 1).

Results and Discussion

Preparation of Bis(2,6-dimethoxyphenyl)methanol (1). Compound **1** has long been known, which was prepared by a reaction of Grignard reagent derived from 1-iodo-2,6-dimethoxybenzene, or by a reaction of 2,6-dimethoxyphenylpotassium with ethyl formate or *N*-methylformanilide.[3,4] We prepared **1** more easily and in good yields using 2,6-dimethoxyphenyllithium derived from 1,3-dimethoxybenzene and butyllithium. It is advisable, however, that the use of acid should be avoided to neutralize the reaction mixture, since **1** is highly reactive in a variety of solvents in the presence of acid, as described below. Compound **1** is stable in alcohols in the absence of an acid, and can be recrystallized as colorless crystals. The ^{1}H NMR spectrum of **1** is very simple, showing a very sharp singlet due to 2,6-dimethoxy protons at $\delta = 3.75$, a triplet due to 4-H at $\delta = 7.12$, a doublet due to 3,5-di-H at $\delta = 6.50$, a doublet due to the central CH at $\delta = 6.67$, and a doublet due to OH at $\delta = 5.62$. Upon the addition of deuterium oxide (D_2O), the doublet at $\delta = 6.67$ changed to a singlet and the doublet at $\delta = 5.62$ disappeared. Upon the addition of trifluoroacetic acid, the chloroform-*d* solution turned purple, and the resonances shifted to lower magnetic fields, such as $\delta = 3.76$ s, 7.17 t, 6.53 d, and 6.82 s, respectively, in accordance with the formation of the carbenium ion, $[\Phi_2CH]^+$ (**2**), possibly in equilibrium. Upon standing this solution at room temperature, the resonances broadened, possibly caused by a variety of reactions, such as mentioned below.

Reactions of Bis(2,6-dimethoxyphenyl)methanol with Ketones and Aldehydes in the Presence of an Acid. The standard condition throughout our work was such a mild one as 1 mmol of **1** in 10 ml of solvent containing ca. 1 mmol of aqueous acid, otherwise mentioned. When **1** was treated in acetone under this condition for 15 h at room temperature, it gave a new ketone, Φ_2CHCH_2COMe (**3a**), in good yield. No essential difference was observed upon changing the kind of acid, such as perchloric acid, hydrochloric acid, sulfuric acid, and trifluoroacetic acid, or the amount of acid between 0.2—10 molar amounts, although the yield was poorer for 0.2 molar amount of acid. Compound **3a** was well characterized by the ^{1}H- and ^{13}C NMR spectra and elemental analyses. The formation of **3a** can be understood to have been caused by the reaction of **2** with the enol form of acetone (Eq. 1). In diethyl ketone, an analogous ketone, $\Phi_2CHCMeHCOEt$



Scheme 1.

(**3b**), was obtained. The ^{1}H- and ^{13}C NMR spectra of **3b** showed the presence of two kinds of Φ group due to the asymmetric character of the molecule. In ethyl methyl ketone, an 80 : 20 mixture of Φ_2CHCMeHCOMe (**3c**) and Φ_2CHCH$_2$COEt (**3d**) was obtained. The relative ratio of these isomers was little affected by the reaction temperature between 0 and 50 °C. By reactions with methyl phenyl ketone, 2,4-pentanedione, and cyclohexanone in methanol or in 2-methyl-2-propanol (*t*-BuOH), analogous ketones, Φ_2CHCH$_2$COPh (**3e**), Φ_2CHCH[COMe]$_2$ (**3f**), and Φ_2CHCH(CH$_2$CH$_2$CH$_2$CH$_2$)CO (**3g**), were obtained, respectively.

$$\mathrm{RCH_2COR'} \overset{K_\mathrm{E}}{\rightleftharpoons} \mathrm{RCH{=}CR'{-}OH} \qquad (1)$$

Triphenylcarbenium ion and triarylcarbenium ions of type $[\mathrm{Ar}\Phi_2\mathrm{C}]^+$ (Ar = Ph, Φ) were inert in these ketones.[1,5] Bis(4-methoxyphenyl)methanol has been known to react in acetone to give bis(4-methoxyphenyl) ketone and 2-propanol, where the diarylmethanol was oxidized by acetone.[6] On the other hand, some diarylchloromethanes have been reported to react with alkenes and alkynes in the presence of Lewis acid to give the addition products.[7]

It is worth mentioning here the oxidation of **1** with sodium dichromate in *aqueous acetone*. When **1** was treated with a slight excess of sodium dichromate in aqueous *acetone* containing 4—5 molar amounts of acid, the ketone, Φ_2CO (**4**), was obtained selectively rather than **3a**.

Of interest is the result that the bulkier enol of ethyl methyl ketone reacted more readily, which may be attributed to the relative amounts of the enol forms in equilibrium. In order to confirm this, reactions of **1** with some ketones, RCH$_2$COR′, were studied in 2-methyl-2-propanol (*t*-BuOH) under the following condition: **1** (1 mmol), ketone (20 mmol) in *t*-BuOH (10 ml) in presence of hydrochloric acid (1 mmol) at 60 °C for 6 h. Cyclohexanone ($\mathrm{p}K_\mathrm{E}$ = 6.39) was the most reactive to complete the reaction, followed by diethyl ketone ($\mathrm{p}K_\mathrm{E}$ = 7.43) to give a 41 : 57 mixture of **1** and **3b** and by acetone ($\mathrm{p}K_\mathrm{E}$ = 8.33; **1** : **3a** = 51 : 49) in agreement with the order of their keto–enol equilibrium constants ($\mathrm{p}K_\mathrm{E}$).[8]

The generation of enolates of carbonyl compounds usually requires basic conditions. On the other hand, there have been known reactions of acetone under neutral conditions to give C-substituted derivatives of some heavy elements, such as mercury,[9] bismuth,[10] rhodium,[11] gold,[12] iodine,[13] and tellurium.[14]

Reactions of **1** with some aldehydes, RCH$_2$CHO, (1 ml) in hot *t*-BuOH (10 ml) also gave analogous products, Φ_2CHCHRCHO [R = Me (**3h**), Et (**3i**)].

Reactions of Bis(2,6-dimethoxyphenyl)methanol (1) with Alcohols in the Presence of an Acid. When **1** was treated in methanol in the presence of hydrochloric acid (0.2—2.0 molar amounts), the mixtures of an ether, Φ_2CHOR [R = Me, (**5a**)], and **1** were obtained in a variety of ratios, as estimated by the ^{1}H NMR spectra. The formation of **5a** must be reversible in the presence of water. Ether **5a** formed predominantly when **1** was treated in hot methanol in the presence of anhydrous acetic acid (0.2—2.0 molar amounts). In ethanol in the presence of acid, the mixtures of the reduced compound, Φ_2CH$_2$ (**6**), **5b** (R = Et), and **1** were obtained in a variety of ratios. In hot ethanol, the formation of **6** predominated, and the formation of acetaldehyde, the byproduct, was confirmed by derivatization to the 2,4-dinitrophenylhydrazone. The ^{1}H NMR spectrum of **6** showed a resonance at $\delta = 4.01$ with a relative intensity of two protons (Φ_2CH_2) in addition to the resonances assignable to Φ-group protons. The ^{13}C NMR spectrum showed the central carbon resonance at $\delta = 17.6$ as a 1 : 2 : 1 triplet with a J_H value of 130 Hz. Reactions in primary alcohols, such as 1-butanol and 1-octanol, gave analogous results to give **6** and the corresponding aldehyde. Analogous reductions to give **6** were also observed in secondary alcohols, such as 2-propanol or 2-butanol, and the corresponding ketones were detected in the filtrates. The use of perchloric acid, sulfuric acid, or trifluoroacetic acid in place of hydrochloric acid resulted in no essential difference. In *t*-BuOH, such a reduction of **1** was not observed, or it gave polymeric materials upon prolonged heating.

In order to see the reactivity of alcohols, the reactions of **1** with several alcohols were performed in *t*-BuOH containing an alcohol and hydrochloric acid heated at 60 °C for 4 and 12 h. The amount of **6** in isolated mixtures increased in the order, MeOH (0 and 0%) < BuOH (4 and 13%) ≤ PrOH (8 and 15%) < EtOH (9 and 36%) ≤ *s*-BuOH (17 and 39%) < *i*-PrOH (26 and 60%). Thus, secondary alcohols were more reactive than primary alcohols, and methanol was inert under these conditions during 24 h. It is worth adding here that alcohols are not suitable as the solvent of **1** for measuring GC-MS spectrum, since they react with **1** at high temperatures, even in the absence of acid to give **5** and **6**.

Diphenylmethanol was inert in these alcohols under analogous conditions, or reacted with methanol to give the methyl ether, Ph_2CHOMe.[15] We confirmed that bis(2-methoxyphenyl)methanol was also inert under analogous conditions, or reacted to give the ethers, $(2\text{-}MeOC_6H_4)_2CHOR$ (R = Me, Et, *i*-Pr), while Balfe et al. reported that chlorobis(4-methoxyphenyl)methane reacted in hot ethanol or in 1-propanol to give bis(4-methoxyphenyl)methane and ethanal or propanal, respectively.[16]

Reactions of 1 in Some Other Organic Solvents. In order to measure the pK_{R^+} value of **1**, we looked for a suitable solvent; however, **1** was also too reactive in some other solvents in the presence of an acid. In tetrahydrofuran in the presence of aqueous perchloric acid (0.2—2.0 molar amounts), **1** was reduced at room temperature in less than 15 h to give **6** in good yield, and 2,3-dihydrofuran was detected based on the GC-MS spectrum. An analogous reduction was observed in diethyl ether in the presence of hydrochloric acid, although we have not yet succeeded in characterizing the oxidized products. In nitriles, RCN, in the presence of acid, **1** reacted to give the amides, $\Phi_2CHNHCOR$ [R = Me (**7a**), Et (**7b**)].

In *t*-BuOH and in dimethyl sulfoxide, **1** was inert under standard conditions, and most of **1** was recovered even upon being heated at 60 °C for 6 h. However, in the presence of a larger amount of acid, **1** reacted in complex manners. As an example, the treatment of **1** in dimethyl sulfoxide in the presence of hydrochloric acid (36 molar amounts) resulted to give a 25 : 75 mixture of triarylmethane, **8** and **9**, as shown in Scheme 1. The GC-MS spectrum of the filtrate showed the possible presence of an aldehyde, ΦCHO. The results are best understood by assuming the cleavage of a Φ–C bond in **1** by acid to give ΦCHO and 1,3-dimethoxybenzene (ΦH), which reacts with **2** to give **8** and **9**. We confirmed by separate experimentals that **1** easily reacted with ΦH in the presence of acid to give **8** and **9**. An analogous C–C bond cleavage has been observed for Φ'_2CHOH.[2)]

Under more forcing conditions in these organic solvents, complex mixtures of polymeric products were obtained, which were probably formed by reactions involving Φ–C bond cleavages and/or substitutions at the 3,5-positions of the Φ-groups.

Experimental

Physical Measurements. The NMR spectra were recorded for solutions in $CDCl_3$ using a JEOL model JNM-GX-270 spectrometer. IR spectra were recorded for Nujol® mulls using a Shimadzu FTIR-4200 spectrophotometer. GC-MS spectra were recorded using a Shimadzu QP-5000 mass spectrometer (gasified at 250 °C).

The ^{1}H- and ^{13}C NMR spectral data are summarized in Tables 1 and 2, respectively.

Preparation of Diarylmethanols. Φ_2CHOH (1). To a 15% hexane solution of butyllithium (160 ml, 250 mmol) were added 1,3-dimethoxybenzene (32.5 ml, 252 mmol) and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) (1.3 ml) at 0 °C under argon. The mixture was stirred at room temperature for 1 h to give a white suspension of ΦLi. To the suspension was added a solution of ethyl formate (8.8 ml, 110 mmol) in diethyl ether (200 ml); the mixture was stirred for 6 h at room temperature. Methanol (150 ml) was added at 0 °C, and the mixture was concentrated to give white crystals of **1** in 75—85% yield after recrystallization from 2-propanol; mp 178—179 °C (reported,[3)] 179 °C); IR 3500 cm^{-1} (OH); MS (Me_2CO solution) *m*/*z* (rel intensity) 304 (M^+; 10), 138 (ΦH^+; 100). Found: C, 66.85; H, 6.61%. Calcd for $C_{17}H_{20}O_5$: C, 67.09; H, 6.62%. This compound is very soluble in benzene, chloroform, and acetone, soluble in hot alcohols, and poorly soluble in diethyl ether, hexane, and water.

$(2\text{-}MeOC_6H_4)_2$CHOH (1′). 2-Methoxyphenyllithium was prepared in situ from *o*-bromoanisole (1.5 ml, 12 mmol) and 15% hexane solution of butyllithium (7.4 ml, 12 mmol) in dry diethyl ether (20 ml). To this solution was added ethyl formate (0.4 ml, 5 mmol). The mixture was stirred for 5 h at room temperature; it was then treated with water (10 ml), and hexane (10 ml) was added to give precipitates of **1′** in 82% yield; mp 79—80 °C after recrystallization from hexane; IR 3500 cm^{-1} (OH); MS (Me_2CO solution) *m*/*z* (rel intensity) 244 (M^+; 40), 135 ($ArCO^+$; 100). Found: C, 73.52; H, 6.59%. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60%. This compound is very soluble in benzene, chloroform, acetone, and diethyl ether, soluble in hot alcohols and hexane, but insoluble in water.

Oxidation of Φ_2CHOH (1) to Give Φ_2CO (4). A mixture of **1** (2.43 g, 8 mmol) and sodium dichromate dihydrate (2.68 g, 9 mmol) was suspended in acetone (60 ml). Water (15 ml), and then concentrated sulfuric acid (2 ml, 36 mmol), were carefully added. The mixture was stirred at room temperature for 6—10 h to give a greenish-brown suspension. After water (15 ml) was added, the resultant light yellow crystals were collected by filtration, and then

Table 1. ^{1}H NMR Spectral Data[a] for 2,6-Dimethoxyphenyl and 2-Methoxyphenyl Derivatives

Compounds	4-H[b]	3,5-H[c]	MeO[d]	Others[e]
Φ_2CHOH **1**	7.12	6.50	3.75	6.67d[10](1H), 5.62d[10](1H)
Φ_2CHCH$_2$COMe **3a**	7.06	6.46	3.65	5.36t[8](1H), 3.18d[8](2H), 2.12s(3H)
Φ_2CHCHMeCOMe **3b**	7.06 6.99	6.47 6.41	3.68 3.67	5.13d[12](1H, Φ_2C*H*), 3.98dq[12][7] (1H, C*H*Me), 2.14s(3H, C(O)*Me*), 0.94d[7](3H, CH*Me*).
Φ_2CHCH$_2$COEt **3c**	7.03	6.45	3.64	5.38t[8], 3.19d[8], 2.42q[8], 1.00t[7].
Φ_2CHCHMeCOEt **3d**	7.06 6.99	6.46 6.40	3.67	5.17d[12](1H), 3.97dq[11][7](1H), 2.50m(2H), 0.98d and 0.92t[7](6H).
Φ_2CHCH$_2$COPh **3e**	7.05	6.46	3.55	5.57t[8], 3.73d[8], 7.98m(2H), 7.45m(3H).
Φ_2CHCH[COMe]$_2$ **3f**	7.04	6.43	3.69	5.64d[12](1H), 5.33d[12](1H), 2.04s(6H).
Φ_2CHCH(CH$_2$CH$_2$CH$_2$CH$_2$)CO **3g**	7.05 6.98	6.42 6.41	3.64 3.62	5.08d[11](1H), 3.99dt[12][4](1H), 2.5m(1H), 2.33d[11](1H), 2.1br(1H), 1.7m(5H), 1.36m(1H), 1.19d[6](1H).
Φ_2CHCHMeCHO **3h**	7.09 7.07	6.49 6.45	3.67	9.64d[2](1H), 5.16d[10](1H), 3.53m(1H), 0.99d[7](3H).
Φ_2CHCHEtCHO **3i**	7.08 7.05	6.48 6.44	3.67	9.56d[2](1H), 5.27d[10](1H), 3.3—3.4m (1H),[f] 1.7—1.4m(2H), 0.89t[7.5](3H).
Φ_2CO **4**	7.20	6.46	3.65	
Φ_2CHOMe **5a**	7.12	6.50	3.71	6.29s(1H), 3.42s(3H)
Φ_2CH$_2$ **6**	7.06	6.49	3.69	4.01s(2H).
Φ_2CHNHCOMe **7a**	7.09	6.48	3.76	7.61d[9](1H), 7.21d[9](1H), 1.96s(3H).
Φ_2CHNHCOEt **7b**	7.09	6.49	3.77	7.75d[9](1H), 7.24d[9](1H), 2.21q[7](2H), 1.14t[7](3H).
8	7.08	6.50	3.47	6.74d[9](1H, 6′-*H*), 6.32dd[9][2](1H, 5′-*H*), 6.32s(1H, *central C–H*), 3.75s(3H, 2′-*MeO*), 3.62s(3H, 4′-*MeO*).
9	6.98	6.36[g]	3.54	6.41s(1H), 6.35?,[g] 6.33s(2H, *central C–H*), 3.59s(6H).
(2-MeOC$_6$H$_4$)$_2$CHOH	7.25dt[8][2] and 7.23dt[8][2] (2H, 4-*H* and 5-*H*), 6.92d[7](1H, 6-*H*), 6.68d[7](1H, 3-*H*), 6.35d[5](1H, *central C–H*), 3.81s(6H, *MeO*), 3.53d[5](1H, *OH*).			
(2-MeOC$_6$H$_4$)$_2$CHOMe	7.3—6.8m(9H), 6.03s(1H), 3.52s(6H), 3.39s(3H).			
(2-MeOC$_6$H$_4$)$_2$CHOEt	7.3—6.8m(10H), 6.14s(1H), 3.76s(6H), 3.56q[7](2H), 1.23t[7](3H).			
(2-MeOC$_6$H$_4$)$_2$CHOPr-*i*	7.3—7.2m(4H), 6.9—6.8m(4H), 6.27s(1H), 3.77s(6H), 3.65m(1H), 1.21d[6](6H).			

a) In CDCl$_3$; s = singlet, d = doublet, t = triplet, q = quartet, dd = double doublets, dq = double quartets, m = multiplet, and br = broad. b) Doublet with J_H = 8—9 Hz. c) Doublet with J_H = 8—9 Hz. d) Singlet. e) The coupling constants J_H given in square brackets in Hz. f) ABX$_3$ pattern. g) Overlapped.

recrystallized from methanol to give **4** in 70—80% yield; mp 203—204 °C (reported, 204 °C,[3] 205—206 °C,[17] 212—214 °C;[18] IR 1680 cm^{-1} (C=O). This compound is soluble in hot methanol, ethanol, 2-propanol, acetone, tetrahydrofuran, and benzene, and poorly soluble in diethyl ether, hexane and water.

Reactions of Φ_2CHOH (1) with Carbonyl Compounds. To a solution of **1** (1 mmol) in acetone (10 ml) was added 12 M (1 M = 1 mol dm^{-3}) hydrochloric acid (0.1—0.2 ml). After the mixture was stirred at room temperature for 15 h, water was added to form white crystals of Φ_2CHCH$_2$COMe (**3a**) in 70—80% yield; mp 128—129 °C (from ethanol); IR 1720 cm^{-1} (C=O). Found: C, 69.52; H, 7.06%. Calcd for $C_{20}H_{24}O_5$: C, 69.75; H, 7.02%. In the place of hydrochloric acid, trifluoroacetic acid and 60% aqueous perchloric acid could be used to give analogous results.

In an analogous manner in diethyl ketone, white crystals of Φ_2CHCHMeCOEt (**3b**) were obtained in 81% yield; mp 144—146 °C (from 2-propanol); IR 1720 cm^{-1} (C=O). Found: C, 70.64; H, 7.64%. Calcd for $C_{22}H_{28}O_5$: C, 70.94; H, 7.58%.

In analogous manners in ethyl methyl ketone at 4, 20, and 50 °C, ca. 80 : 20 mixtures of Φ_2CHCHMeCOMe (**3c**) and Φ_2CHCH$_2$COEt (**3d**) were obtained in 80—90% yield; mp 167—170 °C (90 : 10 mixture after recrystallization from 2-propanol). Found: C, 69.89; H, 7.39%. Calcd for $C_{21}H_{26}O_5$: C, 70.37; H, 7.31%.

In an analogous manner, a solution of **1** (1 mmol) and acetophenone (1 ml) in methanol (10 ml) containing 12 M hydrochloric acid (0.1 ml) gave white crystals of Φ_2CHCH$_2$COPh (**3e**) upon cooling the solution to −30 °C; yield 60%; mp 157—158 °C (from 2-propanol); IR 1680 cm^{-1} (C=O); MS *m/z* (rel intensity) 406 (M$^+$; 15), 151 (ΦCH_2^+; 100). Found: C, 73.69; H, 6.43%. Calcd for $C_{25}H_{26}O_5$: C, 73.87; H, 6.45%.

In an analogous manner, a solution of **1** and 2,4-pentanedione in *t*-BuOH containing 1 M hydrochloric acid heated at 60 °C for 2 h gave white crystals of Φ_2CHCH[COMe]$_2$ (**3f**) in 87% yield; mp 159—160 °C; IR 1730 and 1700 cm^{-1} (C=O); MS *m/z* (rel intensity) 386 (M$^+$; 5) 343 (M$^+$−MeCO; 99), 151 (ΦCH_2^+; 100) 151. Found: C, 68.16; H, 6.93%. Calcd for $C_{22}H_{26}O_6$: C, 68.38; H, 6.78%.

In an analogous manner, a solution of **1** and cyclohexanone in *t*-BuOH containing 1 M hydrochloric acid gave white crystals of

Table 2. ^{13}C NMR Spectral Data[a] for 2,6-Dimethoxyphenyl and 2-Methoxyphenyl Derivatives

Compounds	δ
Φ_2CHOH **1**	158.4, 127.7,[b] 120.7, 104.6,[b] 56.0; 64.5.[c]
Φ_2CHCH_2COMe **3a**	158.8, 126.4, 121.2, 104.6, 55.7; 207.9, 46.6,[d] 29.1,[e] 18.4[f]
$\Phi_2CHCHMeCOMe$ **3b**	159.1 and 158.9, 126.7 and 126.2, 121.0 and 119.7, 104.4 and 104.0, 55.7 and 55.3; 211.8, 48.1, 35.6, 27.5, 16.7.
Φ_2CHCH_2COEt **3c**	Not well-characterized due to the minority
$\Phi_2CHCHMeCOEt$ **3d**	159.1 and 158.9, 126.7 and 126.1, 121.0 and 119.9, 104.4 and 104.1, 55.7 and 55.3; 214.2, 47.5, 35.2, 32.7, 17.1, 7.8
Φ_2CHCH_2COPh **3e**	158.8, 128.0, 121.5, 104.6, 55.8; 199.0, 137.9, 132.0, 127.9, 126.4, 41.3, 29.1.
$\Phi_2CHCH[COMe]_2$ **3f**	158.6, 127.2, 118.5, 104.2, 55.5; 204.7, 70.1, 32.9, 29.0.
$\Phi_2CHCH(CH_2CH_2CH_2CH_2)CO$ **3g**	159.1 and 158.9, 126.5 and 125.7, 121.6 and 120.4, 104.4, 56.0 and 55.6; 213.1, 52.3, 42.6, 34.1, 33.7, 29.9, 26.1.
$\Phi_2CHCHMeCHO$ **3h**	159.0, 127.0 and 126.9, 120.0 and 118.5, 104.4 and 104.1, 55.7 and 55.3; 206.0, 55.6, (47.3?), 35.0, 13.8.
$\Phi_2CHCHEtCHO$ **3i**	159.2 and 158.9, 127.0, 118.7 and 119.7, 104.4 and 104.1, 55.7 and 55.3; 206.1, 54.5, 33.2, 21.9, 12.0.
Φ_2CO **4**	158.6, 130.9, 122.2, 104.7, 56.3.
Φ_2CHOMe **5a**	159.0, 127.9, 118.6, 104.5, 56.1; 72.4, 56.6.
Φ_2CH_2 **6**	158.9, 126.1, 119.3, 104.4, 56.1; 17.6.[d]
$\Phi_2CHNHC(O)Me$ **7a**	158.7, 127.6, 118.9, 104.6, 56.0; 168.4, 42.8, 23.8,
$\Phi_2CHNHC(O)Et$ **7b**	158.7, 127.6, 119.0, 104.6, 56.1; 171.7, 42.6, 30.1, 9.6.
8	159.4, 125.8, 122.7, 105.8, 56.4; 159.3, 158.4, 129.3, 126.3, 103.3, 97.9, 55.6, 55.2, 32.9($Ar_3\mathit{C}H$).
9	159.5, 125.8, 123.2, 105.4, 56.6; 155.6, 131.3, 124.2, 95.9, 56.0, 32.5($Ar_3\mathit{C}H$).
$(2\text{-}MeOC_6H_4)_2CHOH$	156.9, 131.1, 127.9, 128.6, 120.6, 110.5, 55.4; 67.4.
$(2\text{-}MeOC_6H_4)_2CHOMe$	157.3, 130.0, 128.3, 127.9, 120.4, 110.8, 55.7; 73.4, 57.3.
$(2\text{-}MeOC_6H_4)_2CHOEt$	157.3, 130.6, 128.2, 128.0, 120.4, 110.8, 55.7; 71.3, 64.9, 15.5.
$(2\text{-}MeOC_6H_4)_2CHOPr\text{-}i$	157.2, 130.9, 128.2, 128.1, 120.3, 110.6, 55.5; 69.9, 68.7, 22.5.

a) In $CDCl_3$; $\Phi = 2,6\text{-}(MeO)_2C_6H_3$; in order of phenyl carbons (C-2,6, C-4, C-1, C-3,5) of 2,6-dimethoxyphenyl group, $2,6\text{-}(MeO)_2$; and others. b) Doublet with $J_H = 158$—160 Hz. c) Doublet with $J_H = 148$ Hz. d) Triplet with $J_H = 130$ Hz. e) Quartet with $J_H = 131$ Hz. f) Very weak.

$\Phi_2CHCH(CH_2CH_2CH_2CH_2)CO$ (**3g**) in 81% yield; mp 157—158 °C; IR 1710 cm^{-1} (C=O); MS *m/z* (rel intensity) 384 (M^+; 12), 215 ($M^+ - \Phi H - MeCO$; 100).

In an analogous manner, a solution of **1** and propanal in *t*-BuOH containing 1 M hydrochloric acid heated at 60 °C for 1 d gave white crystals of $\Phi_2CHCHMeCHO$ (**3h**) upon cooling the solution at −30 °C; yield 67%; mp 137—138 °C; IR 1720 cm^{-1} (C=O); MS *m/z* (rel intensity) 344 (M^+; 7), 151 (ΦCH_2^+; 100). Found: C, 69.81; H, 7.03%. Calcd for $C_{20}H_{24}O_5$: C, 69.75; H, 7.02%.

In an analogous manner, a solution of **1** and butanal in *t*-BuOH containing 1 M hydrochloric acid heated at 60 °C for 1 d gave white crystals of $\Phi_2CHCHEtCHO$ (**3i**) upon cooling the solution at −30 °C; yield 56%; mp 123—124 °C after recrystallization from methanol; IR 1720 cm^{-1} (C=O); MS *m/z* (rel intensity) 358 (M^+; 2), 151 (ΦCH_2^+; 100). Found: C, 70.23; H, 7.35%. Calcd for $C_{21}H_{26}O_5$: C, 70.37; H, 7.31%.

Reactions of Φ_2CHOH (1) with Methanol in the Presence of Acid. After a mixture of **1** (1 mmol) and acetic acid (0.2, 1.0, or 2.0 mmol) in methanol (5 ml) was heated in a sealed glass tube at 80 °C for 24 h, water (15 ml) was added at 0 °C to precipitate colorless crystals of Φ_2CHOMe (**5a**) in 80—86% yield; mp 147—149 °C (from 2-propanol); MS (Me_2CO solution) *m/z* (rel intensity) 318 (M^+; 10), 151 (ΦCH_2^+; 100). Found: C, 67.85; H, 6.94%. Calcd for $C_{18}H_{22}O_5$: C, 67.91; H, 6.96%.

Reactions of Φ_2CHOH (1) with Alcohols in the Presence of Acid. To a suspension of **1** (5 mmol) in 2-butanol (50 ml) was added a drop (0.1—0.2 ml) of 12 M hydrochloric acid. After the resultant light-purple solution was kept at room temperature for 15 h, it was concentrated to ca. half volume. The UV spectrum of the distillate showed absorption at 273 nm, suggesting the formation of ethyl methyl ketone in 86% yield. The distillate was further treated with 2,4-dinitrophenylhydrazine to form yellow crystals of the hydrazone of ethyl methyl ketone in 69% yield. To the residue of distillation was added water to precipitate white crystals of Φ_2CH_2 (**6**) in 89% yield; mp 135—137 °C (reported,[19] 135—138.5 °C); MS *m/z* (rel intensity) 288 (M^+; 95), 151 (ΦCH_2^+; 100). Found: C, 70.51; H, 6.96%. Calcd for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99%.

An analogous solution treated in 2-propanol for 15 h was cooled to −30 °C to give **6** in 90% yield. The filtrate was distilled to ca. half volume, and acetone was detected based on the UV spectrum (273 nm) of the distillate in 90% yield and by the formation of 2,4-dinitrophenylhydrazone in 52% yield.

In analogous manners to the above, the reactions of **1** in ethanol, 1-butanol, and 1-octanol gave **6** in 93, 82, and 70% yields, respectively. Butanal and octanal, the by-products, were detected as the 2,4-dinitrophenylhydrazones in 64 and 54% yields, respectively.

Reactions of $(2\text{-}MeOC_6H_4)_2CHOH$ (1′) in Alcohols in the Presence of Acid. A colorless solution of **1′** (1 mmol) in methanol (10 ml) containing 1 M hydrochloric acid (0.2—1.0 ml) was kept at room temperature for 1—6 h. Water (10 ml) was added at 0 °C to give white precipitates of $(2\text{-}MeOC_6H_4)_2CHOMe$ in 80—90% yield; mp 43—44 °C; MS *m/z* (rel intensity) 258 (M^+; 40), 121

(ArCH$_2^+$; 100). Found: C, 74.39; H, 7.05%. Calcd for $C_{16}H_{18}O_3$: C, 74.40; H, 7.02%.

In an analogous manner to above in ethanol, (2-MeOC_6H_4)$_2$CHOEt was obtained in 91% yield; mp 79—81 °C; MS *m/z* (rel intensity) 272 (M$^+$; 20), 135 (ArCO$^+$; 100). Found: C, 74.80; H, 7.45%. Calcd for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40%.

In an analogous manner to above in 2-propanol, (2-MeOC_6H_4)$_2$CHOPr-*i* was obtained in 85% yield; mp 94—95 °C; MS *m/z* (rel intensity) 286 (M$^+$; 29), 135 (ArCO$^+$; 100).

Reactions of Φ_2CHOH (1) with Ethers. To a suspension of **1** (5 mmol) in tetrahydrofuran (50 ml) was added a catalytic amount of 60% perchloric acid (0.02—0.2 ml) to give a clear solution within a few minutes. After the mixture was stirred at room temperature for 15 h, an aliquot was analyzed based on the GC-MS spectrum to detect the formation of 2,3-dihydrofuran. To the reaction mixture was added water to form white precipitates of **6** in 82—92% yield.

To a suspension of **1** (1 mmol) in diethyl ether (10 ml) was added 12 M hydrochloric acid (0.1 ml). After the resultant pink suspension was stirred at room temperature for 15 h, a colorless solid was collected by filtration to give **6** in 84% yield.

Reactions of Φ_2CHOH (1) with Nitriles. After a suspension of **1** (1 mmol) in acetonitrile (10 ml) containing 12 M hydrochloric acid (0.1 ml) was stirred at room temperature for 15 h, water was added at 0 °C to precipitate colorless crystals of Φ_2CHNHCOMe (**7a**) in 75% yield; mp 176—179 °C; IR 3450 (N–H) and 1660 cm^{-1} (C=O). Found: C, 65.98; H, 6.68; N, 3.82%. Calcd for $C_{19}H_{23}O_5N_1$: C, 66.07; H, 6.71; N, 4.06%.

In an analogous manner in propiononitrile, Φ_2CHNHCOEt (**7b**) was obtained in 60—90% yield; mp 177—178 °C (from methanol–water); IR 3450 (N–H) and 1660 cm^{-1} (C=O). Found: C, 66.66; H, 6.98; N, 3.61%. Calcd for $C_{20}H_{25}O_5N_1$: C, 66.83; H, 7.01; N, 3.90%.

Reactions of Φ_2CHOH (1) in Dimethyl Sulfoxide. A suspension of **1** (1 mmol) in dimethyl sulfoxide (10 ml) containing 12 M hydrochloric acid (3 ml) was heated at 60 °C for 6 h. The ^{1}H NMR spectrum of the resultant precipitates showed the presence of 2, 4-dimethoxyphenylbis(2,6-dimethoxyphenyl)methane (**8**) and 1,3-dimethoxy-4,6-bis[bis(2,6-dimethoxyphenyl)methyl]benzene (**9**) in 25 : 75 ratio. The GC-MS spectrum of the filtrate showed the presence of 2,6-dimethoxybenzaldehyde, ΦCHO; MS *m/z* (rel intensity) 166 (M$^+$; 77), 76 ($C_6H_4^+$; 100). The pure isolations of **8** and **9** are described below.

Reactions of Φ_2CHOH (1) with 1,3-Dimethoxybenzene. In 1,3-Dimethoxybenzene. To a suspension of **1** (5 mmol) in 1,3-dimethoxybenzene (20 ml) was added trifluoroacetic acid (0.4 ml, 5.5 mmol) at room temperature. The resulting dark-red solution was heated at 60 °C for 0.5 h, and then was cooled at −30 °C to give colorless crystals of **8** in 58% yield; mp 161—162 °C (methanol); MS *m/z* (rel intensity) 424 (M$^+$; 67), 151 (ΦCH$_2^+$; 100). Found: C, 70.48; H, 6.66%. Calcd for $C_{25}H_{28}O_6$: C, 70.74; H, 6.65%.

In 2-Methyl-2-propanol. A suspension containing **1** (5 mmol), 1,3-dimethoxybenzene (0.39 ml, 3 mmol), and 1 M hydrochloric acid (1.1 ml) in 2-methyl-2-propanol (10 ml) was heated at 60 °C for 36 h. To the resultant yellow suspension was added hexane (30 ml); the mixture was then cooled at −30 °C to give colorless crystals of **9** in 88% yield; mp 264—265 °C (2-propanol). Found: C, 70.86; H, 6.50%. Calcd for $C_{42}H_{46}O_{10}$: C, 70.97; H, 6.52%.

This work was supported by the Grant-in-Aid for Scientific Research No. 08455492 from the Ministry of Education, Science and Culture.

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