Table I. Relative Rate of Decomposition of 3 in Refluxing Glyme (85 °C)

Hydrazone	% hydrazone remaining[a] t = 15 min	1 h	2 h	4 h
3a	94	87	*b*	60
3b	91	84	*b*	54
3c	49	15	0.4	<0.1

[a] Determined by HPLC as described in the Experimental Section. [b] Not determined.

three cases, **5** is formed with <2% camphene as an impurity. The reaction can be conveniently run in glyme or even THF, solvents much easier to purify and separate from product than diglyme. This dramatic decrease in reaction temperature should be of special value in the production of unstable carbene-derived products.[12] The enhanced rate of this elimination and those reported earlier[3,11] reflect steric destabilization of **3c** by the bulky ortho substituents.

Experimental Section[13]

Camphor Trifluoromethanesulfonylhydrazone (2b). Camphor hydrazone was prepared as described elsewhere[10] using 12.8 g (0.40 mol) of anhydrous hydrazine, 20 mL of ethanol, and 15.2 g (0.10 mol) of camphor. The concentrated crude product was not purified but simply dissolved in 100 mL of dichloromethane and 10.0 g (0.10 mol) of triethylamine. The temperature was lowered to −78 °C and 28.2 g (0.10 mol) of trifluoromethanesulfonic anhydride was added to the stirred solution. After addition was complete, the reaction mixture was allowed to warm to room temperature and then washed with 1 N HCl, water, and brine, dried over magnesium sulfate, and concentrated in vacuo. The resulting crude oil was taken up in 50 mL of heptane, heated on a steam bath, filtered hot, and allowed to crystallize in the refrigerator for 2 days. The prismatic crystals were washed with cold hexane and dried overnight to give 10.0 g (34%) of **2b**, mp 85–89 °C. One recrystallization from hexane raised the melting point to 88–90 °C: NMR δ 0.75, 0.95, 1.03 (3 s, 3 H each), 1.2–2.8 (m, 7 H), 7.95 (br s, 1 H); IR (cm^{-1}) 3320 (N–H), 1670 (C=N), 1410, 1135 ($-SO_2$), 1225, 1205, 1000.

Anal. Calcd for $C_{11}H_{17}F_3N_2O_2S$: C, 44.29; H, 5.74; N, 9.39. Found: C, 44.32; H, 5.82; N, 9.31.

Thermal Decomposition. General Procedure. The camphor sulfonylhydrazones **2** (1.0 mmol) were dissolved in 10 mL of freshly distilled solvent (diglyme, glyme, or THF). To the stirred solution was then added 4.0 mmol of sodium methoxide. The resulting milky mixture was heated under reflux for the appropriate time, as shown for the glyme experiments in Table I. The disappearance of **2** was conveniently followed by HPLC analysis on a Waters Associates 3.9 mm × 30 cm μ-Porsil column (hexane/chloroform/methanol solvent) using aliquots which were acidified with 1 N HCl and taken to known volume with ether. The results for glyme as solvent are shown in Table I. Product mixtures were worked up by extracting with 1 N NaOH and were analyzed by GLC on a ¼ in. × 10 ft 15% FFAP on Chromosorb W column at 120 °C, using *o*-xylene as internal standard. Tricyclene was the major product observed in all cases (75–95% yield), with camphene detected in trace quantity (≤2%).

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Registry No.—**2a** Na, 63866-11-5; **2b**, 63866-12-6; **2b** Na, 63866-13-7; **2c** Na, 63866-14-8; **5**, 508-32-7; camphor hydrazone, 770-53-6; trifluoromethanesulfonic anhydride, 358-23-6.

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The Acetyl Function As a Protecting Group for Phenols

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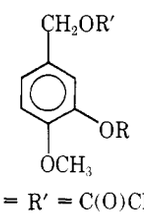
In the course of our current investigation of intramolecular phenolic coupling reactions[1] a number of diphenolic esters were required (e.g., **8** and **10**). While we were considering methods by which the phenolic groups could be protected during preparation of the ester linkages, our attention was drawn to a report concerning the reduction of phenyl esters.[2] In this study it was found that substituted phenyl esters of 3-phenylpropionic acid were reduced at least an order of magnitude more rapidly than the methyl ester. This observation suggested that the acetyl function might be useful as a protecting group for phenols. Although acetyls have been utilized for this purpose previously, they normally have been removed by treatment with aqueous acid or base.[3] The acid or base cleavage of phenols suffers from the disadvantage of not always being selective in the presence of other ester functional groups. A procedure for the selective removal of the acetyl group from phenols by reductive methods would greatly extend its utility as a protecting group.

The procedure was initially tested on the readily available diacetate **1**. Treatment of **1** with $NaBH_4$ in dimethoxyethane



1, R = R′ = C(O)CH_3
2, R = H; R′ = C(O)CH_3
3, R = C(O)CH_3; R′ = H

(DME) for 18 h at 40 °C afforded an 87% yield of the monoacetate **2**. The structure of **2** was assigned by comparison of its NMR spectrum with spectra of related compounds. The resonances due to the benzyl protons appear at δ 4.90 in the diacetate **1** and at δ 4.36 and 4.56 in alcohol **3** and isovanillin alcohol, respectively. Since the corresponding resonance occurs at δ 4.93 in **2**, **2** must be a benzyl acetate.

When *p*-acetoxybenzyl acetate (**4**)[4] was treated in the same manner, *p*-cresol was obtained in quantitative yield. No *p*-hydroxybenzyl acetate (**5**) could be isolated. Hayaski and Oka

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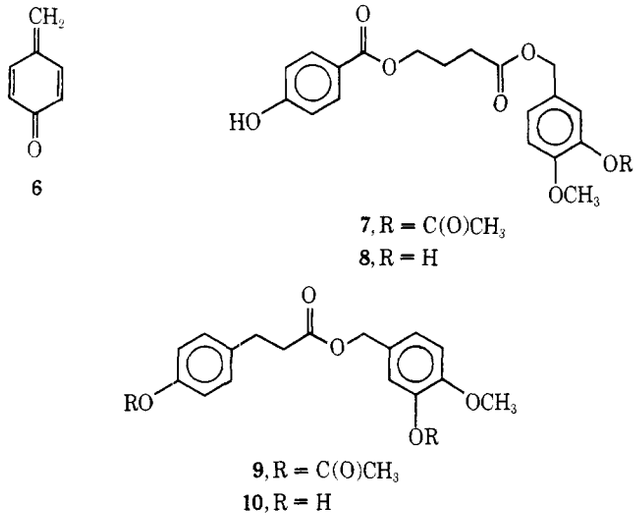
found that **4** gave good yields of *p*-hydroxybenzyl compounds when treated with nucleophiles.[5] Similar results were obtained with *o*-acetoxybenzyl acetate. The quinone methide (**6**) (or the ortho analogue) was postulated to be an intermediate in these reactions. Under the reduction conditions, **6** would be expected to be reduced to *p*-cresol. Since a quinone methide intermediate cannot be readily obtained from 3-acetoxybenzyl acetates, **2** would be expected to cleave without further reduction.

Monoacetate **3**, prepared by selective acetylation[6] of isovanillyl alcohol,[7] was converted into triester **7**.[8] Selective reduction of the triester with excess $NaBH_4$ produced the diphenol in 77% yield. Diacetate **9** was prepared from **3** by acylation with 3-(*p*-acetoxyphenyl)propionyl chloride.[9] Deacetylation of **9** afforded the diphenol **10** in 50% overall yield.



The procedure may be used to selectively cleave phenyl acetates in the presence of unsaturated esters. Thus, methyl *p*-acetoxycinnamate (**11**)[11] was converted to methyl *p*-hydroxycinnamate[11] in 90% yield.

These results indicate that a phenyl acetate may be reduced selectively in the presence of benzyl esters, benzoates, and cinnamates. Thus, $NaBH_4$ cleavage, in combination with selective acetylation, makes the acetyl group a very useful protecting group for phenols. Its utility in the hydroxybenzyl alcohol series is limited to those cases in which the hydroxyl group is in the 3 position.

Experimental Section

Representative examples of the acetate reduction and monoacetylation procedures are given here.

Reduction of Phenyl Acetates. 3-Hydroxy-4-methoxybenzyl Acetate (2). To a solution of 238 mg (1 mmol) of isovanillin alcohol diacetate (**1**)[4] in 5 mL of DME was added 200 mg (5.4 mmol) of sodium borohydride. The rapidly stirred suspension was heated at 45 °C for 18 h. After cooling in an ice–methanol bath, the reaction mixture was cautiously diluted with 5 mL of saturated aqueous NH_4Cl. The mixture was then diluted with 15 mL of ether and the organic layer was washed with saturated NH_4Cl (2 × 10 mL) and saturated NaCl (2 × 10 mL). After drying (Na_2SO_4) the organic layer was concentrated (in vacuo) to a pale yellow oil. Preparative TLC on silica gel (5% 2-propanol–benzene) afforded 171 mg (76% yield) of **2**: IR (film) 3420 (vb), 1750 (b), 1620 cm^{-1}; NMR ($CDCl_3$) δ 2.03 (s, 3 H, $-C(O)CH_3$), 3.80 (s, 3 H, $-OCH_3$), 4.93 (s, 2 H, $-CH_2Ar$), 5.73 (brs, 1 H, –OH), 6.7–6.9 (m, 3 H, aryl).

Anal. Calcd for $C_{10}H_{12}O_4$: C, 61.22; H, 6.16. Found: C, 61.41; H, 6.25.

Monoacetylation. 3-Acetoxy-4-methoxybenzyl Alcohol (3). Isovanillin alcohol (4.6 g, 30 mmol) was dissolved in aqueous potassium hydroxide (7 mL, 45 mmol). To this vigorously stirred solution was added 15 g of ice followed by 3.84 g (37 mmol) of acetic anhydride.[12] After the temperature had risen to 20 °C, an additional 250 mL of water was added and the mixture stirred for 0.5 h. The aqueous solution was then extracted with ether (3 × 30 mL). The combined extracts were washed with water (2 × 20 mL) and 20 ml of aqueous NaCl, dried (Na_2SO_4), and concentrated (in vacuo) to a pale yellow oil. Distillation of this oil [195–196 °C (0.25 Torr)] afforded 4.9 g (85% yield) of **3** along with a small amount of **1**. Separation of **3** from **1** could also be achieved in 37% yield by formation of the hexane-insoluble complex of **3** with $CaCl_2$.[13]

An analytical sample of **3** was obtained by preparative TLC (silica gel; 10% ether–benzene) followed by bulb-to-bulb distillation (Kugelrohr). **3**: IR (film) 3395, 1765, 1620 cm^{-1}; NMR ($CDCl_3$) δ 2.20 (s, 3 H, $-C(O)CH_3$), 3.40 (brs, 1 H, –OH), 3.70 (s, 3 H, $-OCH_3$), 4.36 (s, 2 H, $-CH_2Ar$), 6.8 (m, 3 H, aryl).

Anal. Calcd for $C_{10}H_{12}O_4$: C, 61.22; H, 6.16. Found: C, 61.41; H, 6.01.

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Supplementary Material Available: Detailed procedures for the treatment of **4** with $NaBH_4$ and for the preparation of compounds **1**, **8**, and **10** (3 pages). Ordering information is given on any current masthead page.

Registry No.—**1**, 63866-99-9; **2**, 63867-04-9; **3**, 63867-05-0; **4**, 2937-64-6; **7**, 63867-01-6; **8**, 63867-02-7; **10**, 63876-03-8; isovanillin alcohol, 4383-06-6; acetic anhydride, 108-24-7; acetyl chloride, 75-36-5; 3-(*p*-acetoxyphenyl)propionyl chloride, 63867-00-5.

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Triphase Catalysis. C-Alkylation of Nitriles

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In two recent papers[1,2] Regen introduced the new concept of triphase catalysis to describe a process of phase-transfer catalysis in which the ammonium salt was supported on a polymer insoluble in the reaction medium (e.g., anion-exchange resins). Two reactions were tested: the cyanide displacement on 1-bromooctane and 1-chlorooctane and the generation of dichlorocarbene from chloroform. In both cases, the reaction proceeds normally (e.g., as expected in two-phase catalysis[3–6]), but at higher temperatures and with longer reaction time. Also, almost at the same period anion-exchange resins were used in the synthesis of esters,[7] tetrahydropyrimidines,[8] and other reactions.[9–11]

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