($CDCl_3$) δ 8.68 (s, OH), 4.11 (q, J = 7.1, 4 H, CH_3CH_2O), 3.25 (s, 2 H, $H_2C(2)$), 2.91–2.47 (m, 4 H, CH_2CH_2COO), 2.07 (s, 3 H, CH_3CO), 1.22 (t, J = 7.1, 6 H, CH_3CH_2O). Anal. Calcd for $C_{13}H_{20}O_6$ (272): C, 57.34; H, 7.40. Found: C, 57.38; H, 7.57.

To diketone **36** (1.52 g, 5.5 mmol) in 0.6 mL of ethanol was added carefully hydrazine hydrate (0.33 g, 6.6 mmol) at 5 °C. A further 0.4 mL of ethanol was added, and the reaction mixture was kept at rt for 4.5 h. Evaporation of the solvents yielded pure pyrazole diester (1.49 g, 100%): R_f (ether) 0.2, n 1.4837; UV 205 (4.2); IR (film) 3580, 3340, 3200, 3140, 3080, 2980, 2940, 1730, 1590, 1260, 1170; ^1H NMR ($CDCl_3$) δ 10.20 (s, NH), 4.02 (q J = 7.1, 4 H, CH_3CH_2O), 3.29 (s, 2 H, CH_2-C(4)), 2.82, 2.57 (t, 4 H, CH_2CH_2COO), 2.12 (s, 3 H, CH_3-C(5)), 1.15, 1.13 (t, J = 7.1, 6 H, CH_3CH_2O); ^{13}C NMR ($CDCl_3$) δ 172.7, 171.1 (COO), 145.5 (C(5)), 141.9 (C(3)), 107.8 (C(4)), 60.3, 60.1 (CH_3CH_2O), 33.1 (CH_2CH_2COO), 28.9 (CH_2-C(4)), 20.5 (CH_2CH_2COO); 13.7, 10.2 (CH_3CH_2O); EI-MS 269 (4), 268 (9, $M^{\bullet+}$), 223 (14), 222 (36), 195 (64), 194 (11), 151 (17), 150 (12), 149 (27), 123 (11), 122 (15), 121 (100). Anal. Calcd for $C_{13}H_{20}N_2O_4$ (268): C, 58.19; H, 7.52; N, 10.44. Found: C, 57.45; H, 7.89; N, 10.56.

The pyrazole diester (0.5 g, 1.9 mmol) was refluxed for 10 h in 1 mL of ethanol containing 1.84 g of a 15% potassium hydroxide solution. The cold solution was diluted with water (2 mL) and acidified to pH 3.5 with 2 M HCl. The precipitate was filtered and washed with cold water and diethyl ether. Crystallization from water/ethanol yielded pure **19** (0.32 g, 81%): mp 225 °C; UV 222 (4.0); IR (KBr) 3260, 3100, 2980, 2940, 1710, 1580, 1520, 1220; ^1H NMR (DMSO-d_6) δ 3.43 (s, 2 H, CH_2-C(4)), 2.92–2.88, 2.66–2.62 (m, 4 H, CH_2CH_2COO), 2.28 (s, 3 H, CH_3-C(5)); ^{13}C NMR (DMSO-d_6) δ 174.2, 173.2 (COO), 145.4 (C(5)), 140.8 (C(3)), 108.5 (C(4)), 33.6 (CH_2CH_2COO), 29.2 (CH_2-C(4)), 21.1 (CH_2CH_2COO), 10.4 (CH_3-C(5)); EI-MS 213 (3), 212 (23, $M^{\bullet+}$), 168 (14), 167 (63), 166 (15), 150 (20), 149 (32), 125 (20), 123 (19), 122 (16), 121 (100). Anal. Calcd for $C_9H_{12}N_2O_4$ (212): C, 50.94; H, 5.70; N, 13.20. Found: C, 50.70; H, 5.69; N, 13.15.

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Notes

A Highly Selective Methodology for the Direct Conversion of Acetals to Esters

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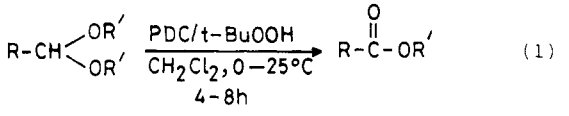
The acetal funtionality is the most commonly used protecting group for aldehydes,[1] and the direct conversion of cyclic and acyclic acetals to the corresponding esters is a useful synthetic methodology in organic synthesis. Systems utilizing molecular oxygen,[2] ozone,[2,3] dinitrogen tetroxide,[2] alkylhydroperoxides[2,4,5] halogen-based reagents,[6] *tert*-butyl hydroperoxide in the presence of palladium(II) catalyst,[7] potassium permanganate under phase-transfer conditions,[8] and electrochemical oxidation[9] have all been shown to bring about this transformation with varying degrees of flexibility.

Ozonolysis appears to be superior to all other methods in this category if yield and generality of the reaction are singled out as the important criteria. However, even this methodology is not effective in cases where the acetals contain carbon–carbon multiple bonds, and none of the above-mentioned procedures has been successfully used for acetals derived from α,β-unsaturated carbonyl compounds.

We now report that the 1:1.5 molar mixture of PDC and *tert*-butyl hydroperoxide that we had shown earlier to be an effective reagent for allylic and benzylic oxidations[10] as well as oxidative rearrangement of enol ethers[11] is also a superior reagent for the direct conversion of acetals to the corresponding esters.

Treatment of a wide variety of acetals with PDC/*t*-BuOOH (1:1.5) in dichloromethane led to the formation of the corresponding esters in high yield under mild reaction conditions (0–25 °C; 4–8 h) (eq 1). The results of this oxidation are summarized in Table I.



(1)

Unlike other reported procedures[2,9] acyclic acetals reacted with equal facility as the cyclic acetals. Five-membered ring acetals **1**, **3**, **5**, and **7** bearing alkyl and aromatic substituents gave the monoesters of ethylene glycol in good yields (entries 1–4). Similarly, six-membered cyclic acetals **9** and **11** gave good yields of the corresponding monoesters of propane-1,3-diols (entries 5 and 6).

It is interesting to note that the cyclic acetals (entries 1–7) gave the corresponding hydroxy esters without accompanying oxidation of the hydroxy groups. Cyclic acetal

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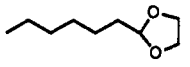
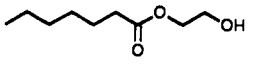
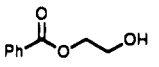
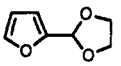
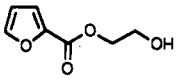
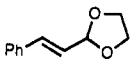
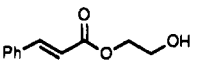
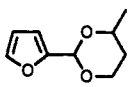
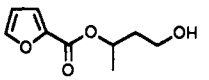
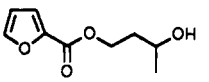
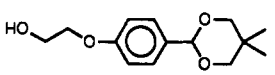
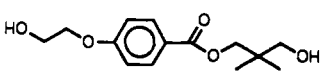
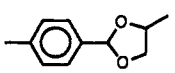
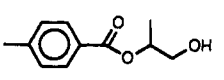
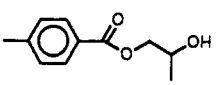
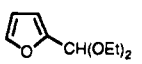
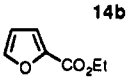
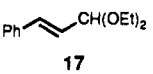
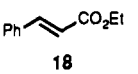
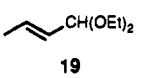
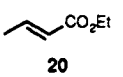
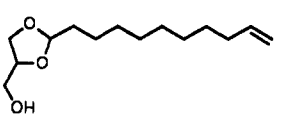
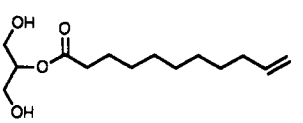
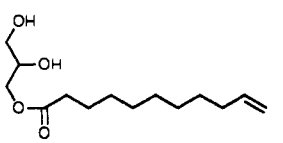
0022-3263/92/1957-5013$03.00/0

Table I.

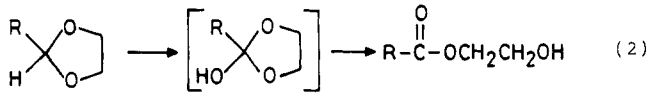
entry	substrate	time (h)	product(s)[a]	yield[b] (%)
1	 1[c]	8	 2	82
2	 3	5	 4	76
3	 5	4	 6	85
4	 7	5	 8	85
5	 9[c]	7	 10a + (1.2:1)[d]  10b	78
6	 11	5.5	 12	81
7	 13	6	 14a + (1.13:1)[d]  14b	73
8	 15	5	 16	74
9	 17	6	 18	72
10	 19	7	 20	67
11	 21	6	 22a + (1:1)[d]  22b	75

[a] All the products gave satisfactory spectral and analytical data. [b] Yields refer to pure isolated products and are also based on the starting material recovered (2–20%). [c] In these reactions the substrate–PDC–*t*-BuOOH ratio of 1:4:6 was employed whereas in all other cases the ratio was 1:2:3. [d] The ratio of the products was estimated by ^{1}H-NMR integration.

11 (entry 6), which contains a primary hydroxy group, underwent selective oxidation of the acetal to give the hydroxy ester 12 in 81% yield. Glycol monoesters such as those of ethylene glycol have been used as cross-linking agents for polyesters or as fungicides. The major drawback to the preparation of these compounds from diols is the concurrent formation of diester, necessitating a tedious separation procedure.[12] The present method indirectly

provides a useful means for the selective monoprotection of some symmetrical diols. Unsymmetrical cyclic acetals **9**, **13**, and **21** (entries 5, 7, and 11), however, yielded a mixture (approximately 1:1) of two esters corresponding to cleavage of either of the two acetal C–O bonds. Special mention must be made of the oxidation of acetals of α,β-unsaturated carbonyl compounds **7**, **17**, and **19**. All of these compounds underwent smooth oxidation to give the corresponding esters **8**, **18**, and **20**, respectively (entries 4, 9, and 10), in good yield. To our knowledge, this constitutes the first satisfactory method for the direct conversion of acetals of α,β-unsaturated aldehydes to α,β-unsaturated esters. The reaction of acetal **21**, containing an isolated carbon–carbon double bond (entry 11), gave a mixture of isomeric esters **22a** and **22b** (75%) with the double bond remaining intact. This example illustrates the superiority of the present methodology over the ozonolysis procedure[2,3] which obviously cannot be applied to such compounds.

No attempt has been made to probe the mechanism of the reaction. Nevertheless, we believe that radical-assisted C–H bond cleavage of the acetal center gives the hemiorthoester which is cleaved further to yield the product (eq 2).



(2)

In conclusion, the present methodology of direct conversion of acetals to esters mediated by PDC/*t*-BuOOH shows a high degree of chemoselectivity and hopefully will find wide application in organic synthesis.

Experimental Section

General Remarks. ^{1}H NMR spectra were recorded at 90 MHz, in $CDCl_3$. TLC was performed on 0.25-mm E. Merck precoated silica gel plates (60F-254). All products were purified by column chromatography, and were obtained mostly as oils. The melting points reported are uncorrected. Silica gel (60–120 mesh) was used for column chromatography. The starting materials were prepared following the reported procedures[1,13] (for compound **11** See refs 13 and 14).

Representative Procedure: 2-Hydroxyethyl 3-Phenyl-2-propenoate[15] (8). Pyridinium dichromate (3.76 g, 10 mmol) was dissolved in 8 mL of dry CH_2Cl_2 and cooled to 0 °C. *tert*-Butyl hydroperoxide (70% solution, 2 mL, 15 mmol) previously dried over 4-Å molecular sieves was added and allowed to react for 15 min. The resulting red supernatant solution was decanted into a flask immersed in an ice bath, washed twice with 5-mL portions of CH_2Cl_2, and filtered through a cotton plug to the same flask. The acetal **7** (0.88 g, 5 mmol) in 5 mL of CH_2Cl_2 was admitted into this flask containing a clear red solution. The reaction was carried out in an ice bath and allowed to warm to room temperature over a period of 5 h. The reaction mixture was filtered with a sintered-glass funnel through a pad of Celite and silica gel (TLC grade). Solvent was evaporated, and the product was purified by column chromatography (eluant: 5% ethyl acetate in hexanes). Yield: 0.816 g, 85%. IR ($CHCl_3$): ν 3484, 2944, 1713, 1638, 1446, 1161, 1074, and 981 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.6 (br, s, 1 H), 3.9 (t, J = 5.1 Hz, 2 H), 4.3 (t, J = 5.1 Hz, 2 H), 6.4 (dd, J = 15.4 and 2.1 Hz, 1 H), 7.4 (complex m, 6 H). MS: m/z 192 (M^+), 148, 131, 122, 103, 77. HRMS: calcd for $C_{11}H_{12}O_3$ = 192.0786, observed = 192.0784.

1,3-Butanediol Mono-2-furancarboxylate (10a and 10b). IR (thin film): ν 3418, 2968, 1713, 1584, 1479, 1398, 1302, 1185, 1122, and 765 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.24 (d, J = 6.4 Hz, 3 H), 1.36 (d, J = 6.4 Hz, 3 H), 1.86 (m, 4 H), 2.13 (s, exchangeable, 2 H), 3.67 (t, J = 5.9 Hz, 2 H), 3.93 (br, q, J = 6.4 Hz, 1 H), 4.44 (m, 2 H), 5.3 (q, J = 6.4 Hz, 1 H), 6.5 (dd, J = 3.5 and 1.7 Hz, 2 H), 7.16 (d, J = 3.5 Hz, 2 H), and 7.56 (s, 2 H). ^{13}C NMR ($CDCl_3$): δ 20.10 (q), 23.35 (q), 37.76 (t), 38.74 (t), 58.46 (t), 62.14 (t), 64.41 (d), 69.29 (d), 111.76 (d), 117.94 (d), 144.59 (s), 146.33 (d), 158.77 (s). MS: m/z 183 $(M - H)^+$, 167, 154, 139, 113, 101 (base peak), 95, 83, 72, 61, 52.

4-[(2-Hydroxyethyl)oxy]benzoic Acid, Monoester of 2,2-Dimethyl-1,3-propanediol (12). IR (thin film): ν 3466, 2950, 2848, 1731, 1602, 1476, 1395, 1365, 1113, and 1044 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.875 (s, 3 H), 1.25 (s, 3 H), 2.58 (br, s, exchangeable, 2 H), 4.04 (m, 8 H), 7.37 (d, J = 7.5 Hz, 2 H), and 7.75 (d, J = 7.5 Hz, 2 H). MS: m/z 251 $(M - 17)$, 191, 166, 121 (base peak), 115, 105, 95, 87, 77, 69, 65, 55, 45, and 41. HRMS: calcd for $C_{14}H_{19}O_4$ $(M - 17)$ = 251.1283, observed = 251.1284.

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Registry No. **1**, 1708-34-5; **2**, 16179-38-7; **3**, 936-51-6; **4**, 94-33-7; **5**, 1708-41-4; **6**, 142564-33-8; **7**, 5660-60-6; **8**, 17773-43-2; **9**, 6413-31-6; **10**, 142564-34-9; **10b**, 142564-37-2; **11**, 142564-35-0; **12**, 142564-36-1; **13**, 58244-29-4; **14a**, 142564-39-4; **14b**, 142564-40-7; **15**, 13529-27-6; **16**, 614-99-3; **17**, 7148-78-9; **18**, 103-36-6; **19**, 10602-34-3; **20**, 10544-63-5; **21**, 142564-38-3; **22a**, 142564-41-8; **22b**, 62285-15-8; PDC, 20039-37-6; *t*-BuOOH, 75-91-2.

Supplementary Material Available: Spectral data of the compounds **2**, **4**, **6**, **14a** + **14b**, **16**, **18**, **20**, and **22a** + **22b**, as well as the ^{1}H and/or ^{13}C NMR spectra for compounds **8**, **10a**, **10b**, and **12** (7 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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Enhancement of Reductive Carbon–Sulfur Bond Cleavage by Ultrasonically Dispersed Potassium in the Presence of a Proton Source

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A wide variety of reagents can be activated by ultrasound irradiation.[1] Among these, ultrasonically dispersed potassium (UDP)[2] is selective and effective to promote the Dickmann condensation of diesters,[2] enolate formation of ketones,[2] C–S bond scission of cyclic sulfones,[3,4] extrusion of SO_2 from 3-sulfolenes,[4] and other reactions.[5] Recently we found it interesting that a controlled amount of H_2O significantly accelerates the UDP-induced C–S bond cleavage of saturated cyclic sulfones.[6] Furthermore, the combination of UDP with H_2O (UDP/H_2O) causes C–S bond cleavage on systems which are inactive under anhydrous conditions. These findings broaden the synthetic usefulness of UDP.

The treatment of a 2-substituted 2-sulfolene with UDP under anhydrous conditions followed by treatment with MeI produces a γ,δ-unsaturated sulfone.[4] This reaction is highly regio- and stereoselective; however, the yields are normally below 50%. We were therefore interested in examining if this reaction can be improved. Thus, 2-

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