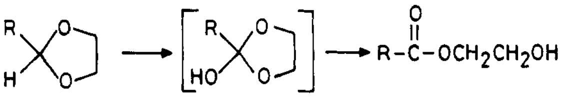
provides a useful means for the selective monoprotection of some symmetrical diols. Unsymmetrical cyclic acetals **9**, **13**, and **21** (entries 5, 7, and 11), however, yielded a mixture (approximately 1:1) of two esters corresponding to cleavage of either of the two acetal C–O bonds. Special mention 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.

Acknowledgment. The authors wish to thank DST and UGC New Delhi for financial support.

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

Ta-shue Chou* and Sheng-Yueh Chang

Institute of Chemistry, Academia Sinica, Taipei, Taiwan,
and Department of Chemistry, National Taiwan University,
Taipei, Taiwan, ROC

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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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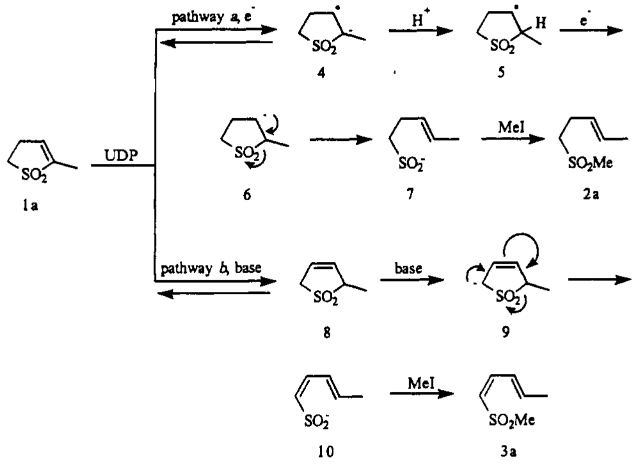
* Address correspondence to this author at Academia Sinica.

Scheme I



methyl-2-sulfolene (**1a**) was reacted with UDP in anhydrous toluene at 50 °C for 2 h followed by MeI treatment. The MeI used in the final stage was to convert the very water-soluble sulfinate intermediate to the more isolable methyl sulfone. In order to have a better understanding of how this reaction proceeds, the reaction was rapidly worked up and purified. The yield of the desired product **2a** (44%) was almost identical to that obtained within a shorter period of reaction time (40%).[4] In addition to **2a**, we could identify another product **3a** formed in an equal amount. Compound **3a** polymerized rapidly upon standing even at temperatures below 0 °C. In our early study,[4] no efforts were made to isolate or to identify this unstable compound. On the basis of the formation of **2a** and **3a** and their stereochemistry, a mechanism is proposed for this reaction (Scheme I).

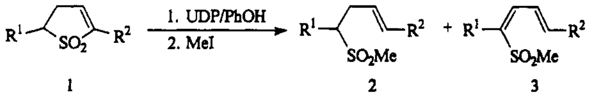
The formation of **2a** involves two steps of electron transfer with a protonation reaction in between and the net change is a reduction (pathway *a*). A reason for the regio- and stereoselectivity was offered.[4] Product **3a** is formed from a sequence of double-bond migration, deprotonation, and anionic cycloreversion (pathway *b*), and no electron transfer is involved. Several facts support this proposal. First, it is known that 2-sulfolenes are in equilibrium with 3-sulfolenes under basic conditions,[7] although **1a** is predominantly favored over **8**.[8] Second, a strong base is known to deprotonate **8** regioselectively at the 5-position giving the anion **9**.[9] Third, in the absence of an electrophile, a 3-sulfolenyl carbanion instantaneously undergoes a stereoselective ring-opening reaction above −78 °C to produce the corresponding 1,3-dienylsulfinate with the C_1–C_2 double bond in the *Z*-configuration.[10] The radical anion **4** formed in pathway *a* should serve as the base required for the double-bond migration and anionic cycloreversion in pathway *b*. Thus, for the formation of each molecule of **5** from **4** leading to **2a**, a molecule of **8** must be deprotonated leading to **3a** eventually. In the absence of an exotic proton source, pathways *a* and *b* should proceed to the same extent so that the yield of **2a** could not exceed 50%. The mechanism shown in Scheme I satisfactorily explains not only the formation and the stereochemistry of the products but also their distribution.

Table I. Reactions of 2-Methyl-2-sulfolene (1a) with UDP in the Presence of a Proton Source To Give 2a and 3a

entry	proton source (molar concn, M)[a]	temp (°C)	time	yield[d,e] (%) and ratio (2a:3a)
1		rt[b]	1 h	no reaction
2		50	2 h	88 (1:1)
3	*t*-BuOH (0.4)	rt	5 min[c]	79 (1.5:1)
4	MeOH (0.3)	rt	7 min[c]	82 (2:1)
5	H_2O (0.3)	rt	7 min[c]	68 (4:1)
6	PhOH (0.2)	rt	10 min[c]	75 (12:1)
7	AcOH (0.08)	rt	12 min[c]	20 (>99:1)

[a] The proton source was added as a dilute solution in THF dropwise to the reaction mixture of **1a** and UDP in toluene. [b] The reaction temperature was kept at room temperature by adding crushed ice to the ultrasound bath periodically. Otherwise, the bath temperature increased to 50 °C within 20 min. [c] The reaction time indicated is the time period of the slow addition of the proton source. [d] Products **2a** and **3a** were obtained after MeI treatment of the potassium sulfinates **7** and **10**, respectively. [e] The molar ratios of the reactants **1a**-UDP-proton source were kept at 1:3:3 for all entries.

Table II. Reactions of 2-Sulfolenes with UDP Using Phenol as the Proton Source



entry	2-sulfolene	products and yields (%)	lit.[a] (%)
1	R^1 = H, R^2 = Me, **1a**	**2a** (69.2) + **3a** (5.8)	**2a** (40)
2	R^1 = H, R^2 = Et, **1b**	**2b** (71.5) + **3b** (8.7)	**2b** (43)
3	R^1 = R^2 = Me, **1c**	**2c** (86.0) + **3c** (2.0)	**2c** (45)
4	R^1 = R^2 = Et, **1d**	**2d** (74.0) + **3d** (5.7)	**2d** (72)
5	R^1 = R^2 = *n*-Bu, **1e**	**2e** (72.0) + **3e** (3.2) + **11** (10.2)	**2e** (40)
6	R^1 = R^2 = *n*-heptyl, **1f**	**2f** (38.6) + **3f** (19.6) + **12** (8.5)	**2f** (48)

[a] See ref 4. The 2-sulfolenes were reacted with UDP under anhydrous conditions and only **2a**–**2f** were identified.

According to the analysis of the reaction pathways, it was thought that the introduction of H_2O to the reaction should improve the yield of **2a** because the radical anion **4** would abstract a proton from H_2O faster than from the α-position of **8**. Indeed, the reaction of **1a** with UDP/H_2O produced **2a** and **3a** in a 4:1 ratio (68% yield). When operating this reaction, it is essential to add H_2O slowly as a dilute solution in THF (0.3 M) to the reaction mixture so that the H_2O does not consume the potassium too fast. Otherwise, the destruction of potassium becomes a serious problem and the desired reaction is blocked. When *t*-BuOH, instead of H_2O, was used as the proton source in this reaction, products **2a** and **3a** were formed in a 1.5:1

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ratio. This number is somewhat better than that from the reaction performed under anhydrous conditions (1:1) but not as good as that using H_2O as the proton source (4:1). It was reasoned that the acidity of the proton source may have influence on the competitive proton abstraction reactions. We therefore studied this reaction using different proton sources, and the results are summarized in Table I.

As the acidity of proton source changes from $pK_a \simeq 19$ for *t*-BuOH to $pK_a \simeq 5$ for AcOH, the product ratio shifts from 1.5:1 to more than 99:1 showing an excellent correlation between the product ratio and the acidity. Although the relative yield of **2a** to **3a** was the best when acetic acid was used (entry 7), the overall yield was poor (20%). The poor yield must be due to rapid destruction of potassium by the very acidic AcOH. The attempts to use a larger excess of potassium and acetic acid failed to improve the overall yield. Apparently, acetic acid is not the choice of proton source even though it can block the pathway *b* almost entirely. The most satisfactory proton source in our study is phenol (entry 6) which can hinder the pathway *b* without lowering the overall yield by much.

The reactions of a series of 2-alkylated 2-sulfolenes and 2,5-disubstituted 2-sulfolenes with UDP using PhOH as the proton source were studied and summarized in Table II.

The yields of the reduction products **2a–2f** are mostly better than those obtained under anhydrous conditions. In some cases (entries 3 and 5), the yields of the side products (**3c** and **3e**) are almost negligible. In addition to the fact that the yields are improved, the major advantages of this modified procedure are that the reactions can be performed at room temperature and that the C–S bond cleavage step is so rapid that it is completed immediately after the proton source has been added to the mixture. The observation of the minor products **11** and **12** (entries 5 and 6),

11 R = n-Bu
12 R = n-heptyl

which must have been formed from the SO_2 extrusion of the corresponding 3-sulfolenes,[12] supports the proposal in Scheme I that the 3-sulfolene **9** is involved as an intermediate.

In summary, we have illustrated herein that the combination of UDP with a proton source can be used to greatly enhance the selective C–S bond cleavage reactions of 2-substituted 2-sulfolenes. The acidity of the proton source has a determining influence on the results of the reactions. The moderately acidic phenol can be used as the proton source without destroying the potassium to a significant extent. Other possible applications of UDP-induced reactions in the presence of a proton source are under investigation.

Experimental Section

General. ^1H NMR spectra were recorded on a Bruker AC-200 NMR spectrometer as solutions in $CDCl_3$. IR spectra were measured on a Perkin-Elmer 290 IR spectrophotometer. Mass spectra were measured on a VG 70-250-S mass spectrometer. A transsonic T570/H ultrasonic cleaning bath (Elma, West Germany) was used. Anhydrous toluene was freshly distilled from sodium before use.

Typical Reaction Procedure. To a suspension of ultrasonically dispersed potassium[2] (61 mg, 1.56 mmol) in anhydrous toluene (10 mL) was added 2-methyl-sulfolene (**1a**) (69 mg, 0.52 mmol) in toluene (10 mL), and the mixture was irradiated in an ultrasonic cleaning bath for 20 min. A solution of PhOH/THF (0.2 M, 1.56 mmol) was added dropwise over a period of 10 min whereupon the reaction was completed. The solvent was evaporated under reduced pressure, MeI (1.2 mL), H_2O (1.5 mL), and THF (20 mL) were added, and the resulting mixture was heated at reflux for 3 h. The excess THF was removed under reduced pressure, and the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with saturated $Na_2S_2O_3$, dried ($MgSO_4$), and concentrated under reduced pressure. The crude was purified by HPLC (LiChrosorb column, hexane/EtOAc (1:1)) to give **2a** and **3a**.

The same procedure was used for all other reactions, and the products and yields are summarized in Table II. The spectral data of products **2a–2f**,[4] **11**,[13] and **12**[4] are identical with those reported in the literature. The dienyl sulfones **3a–3f** polymerized rapidly so that elemental analyses were not obtained. The ^1H NMR spectral data revealed the purity of these products to be better than 95%.

(1*Z*,3*E*)-1-(Methylsulfonyl)-1,3-pentadiene (3a): colorless oil; IR (neat) 3057, 3012, 2928, 1687, 1638, 1507, 1374, 1293, 1130, 959, 794 cm^{-1}; ^1H NMR δ 1.92 (dd, 3 H, $J = 6.9$, 1.2 Hz), 2.99 (s, 3 H), 6.02 (d, 1 H, $J = 15.0$ Hz), 6.20 (dq, 1 H, $J = 11.0$, 6.9 Hz), 6.97 (dd, 1 H, $J_1 = J_2 = 11.0$ Hz), 7.02–7.27 (m, 1 H); MS *m/z* 146 (M^+), 131, 101, 82, 81, 67, 66 (100); $C_6H_{10}O_2S$ requires 146.0399, found 146.0401.

(1*Z*,3*E*)-1-(Methylsulfonyl)-1,3-hexadiene (3b): colorless oil; IR (neat) 3056, 2969, 2931, 1635, 1290, 1217, 1126, 993, 790 cm^{-1}; ^1H NMR δ 1.07 (t, 3 H, $J = 7.3$ Hz), 2.26 (dq, 2 H, $J = 6.5$, 7.3 Hz), 2.99 (s, 1 H), 6.02 (d, 1 H, $J = 11.0$ Hz), 6.21 (dt, 1 H, $J = 15.1$, 6.5 Hz), 6.68 (dd, 1 H, $J_1 = J_2 = 11.0$ Hz), 7.05–7.27 (m, 1 H); MS *m/z* 160 (M^+), 145, 101, 97, 81, 80, 79 (100); $C_7H_{12}O_2S$ requires 160.0556, found 160.0558.

(2*Z*,4*E*)-2-(Methylsulfonyl)-2,4-hexadiene (3c): colorless oil; IR (neat) 3030, 2976, 2875, 1632, 1598, 1270, 1142, 992, 780 cm^{-1}; ^1H NMR δ 1.87 (d, 3 H, $J = 6.6$ Hz), 2.12 (s, 3 H), 2.92 (s, 3 H), 6.02 (dq, 1 H, $J = 14.9$, 7.6 Hz), 6.50 (d, 1 H, $J = 11.6$ Hz), 7.00–7.15 (m, 1 H); MS *m/z* 160 (M^+), 108, 97, 79 (100), 69; $C_7H_{12}O_2S$ requires 160.0556, found 160.0561.

(3*Z*,5*E*)-3-(Methylsulfonyl)-3,5-octadiene (3d): colorless oil; IR (neat) 3075, 2966, 1699, 1680, 1290, 1118, 961, 904, 758 cm^{-1}; ^1H NMR δ 1.07 (t, 3 H, $J = 6.2$ Hz), 1.20 (t, 3 H, $J = 6.2$ Hz), 2.22 (dq, 2 H, $J = 6.9$, 6.2 Hz), 2.47 (q, 2 H, $J = 6.2$ Hz), 2.94 (s, 3 H), 6.09 (dt, 1 H, $J = 14.8$, 6.9 Hz), 6.50 (d, 1 H, 11.4 Hz), 7.01 (ddt, 1 H, $J = 14.8$, 11.4, 1.5 Hz); MS *m/z* 188 (M^+), 129, 125, 108, 93 (100), 79; $C_9H_{16}O_2S$ requires 188.0871, found 188.0866.

(5*Z*,7*E*)-5-(Methylsulfonyl)-5,7-dodecadiene (3e): colorless oil; IR (neat) 3068, 2957, 1633, 1579, 1300, 1128, 1020, 979, 953 cm^{-1}; ^1H NMR δ 0.86–0.97 (m, 6 H), 1.28–1.60 (m, 8 H), 2.20 (dt, 2 H, $J = 6.9$, 6.7 Hz), 2.41 (t, 2 H, $J = 7.0$ Hz), 2.93 (s, 3 H), 6.03 (dt, 1 H, $J = 14.9$, 6.9 Hz), 6.49 (d, 1 H, $J = 11.3$ Hz), 7.03 (ddt, 1 H, $J = 14.9$, 11.3, 1.5 Hz); MS *m/z* 244 (M^+), 229, 215, 201, 189, 176, 135, 121, 107, 93, 79 (100); $C_{13}H_{24}O_2S$ requires 244.1515, found 244.1497.

(8*Z*,10*E*)-8-(Methylsulfonyl)-8,10-octadecadiene (3f): colorless oil; IR (neat) 3031, 2944, 1694, 1307, 1127, 960, 795 cm^{-1}; ^1H NMR δ 0.88 (t, 6 H, $J = 6.9$ Hz), 1.26–1.62 (m, 20 H), 2.19 (dt, 2 H, $J = 6.9$, 6.7 Hz), 2.41 (t, 2 H, $J = 7.2$ Hz), 2.93 (s, 3 H), 6.02 (dt, 1 H, $J = 15.0$, 6.9 Hz), 6.49 (d, 1 H, $J = 11.4$ Hz), 7.02 (dd, 1 H, $J = 11.4$, 15.0 Hz); MS *m/z* 328 (M^+), 265, 248, 221, 204, 195, 165, 149, 124, 106 (100), 87, 79; $C_{19}H_{36}O_2S$ requires 328.2436, found 328.2431.

Acknowledgment. We thank the National Science Council of the Republic of China for financial support (NSC 81-0208-M-001-33).

Supplementary Material Available: Proton NMR spectra of **3a–3f** (6 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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