while substitution occurs principally by inversion (70–81%), significant racemization results under the reaction conditions even in the presence of added $NaHCO_3$ to neutralize any generated acid.[10] Saturated alkyl chlorides react only with reluctance (entries 9 and 10), but displacement of allylic chlorides occurs readily with only meager rearrangement (2%, entry 13). Terminal epoxides (entries 27 and 28) are cleaved, thus providing a mild process for the formation of 1,2-diols. In these cases superior results were obtained with $NaHCO_3$ present.[10,11] Finally, alcohols in place of water also effect substitution to the corresponding ethers (entries 29–31).

Experimental Section

General Reaction Procedure. The process was straightforward for all examples. A solution of the compound (5 mmol) in 15% (v/v) aqueous HMPA or NMP (25 mL) was heated at 100–130 °C (Table I) and the reaction progress monitored by GC or TLC. After completion, the mixture was cooled, diluted with water (50 mL), and extracted with two portions of ether or pentane. The organic phase was washed with three portions of water, dried ($MgSO_4$), and concentrated on a rotary evaporator. Recrystallization or bulb-to-bulb distillation afforded the products, which were analyzed by GC and/or NMR comparisons with authentic samples.

Registry No. $1\text{-}C_{12}H_{25}I$, 4292-19-7; $C_6H_5COCH_2Br$, 70-11-1; $(E)\text{-}CH_3(CH_2)_6CH{=}CHCH_2Cl$, 70-11-1; $2\text{-}C_8H_{17}I$, 557-36-8; $1\text{-}C_8H_{17}I$, 629-27-6; $1\text{-}C_{12}H_{25}Br$, 143-15-7; $1\text{-}C_8H_{17}Br$, 111-83-1; $1\text{-}C_8H_{17}Cl$, 111-85-3; $2\text{-}C_8H_{17}Br$, 557-35-7; $2\text{-}C_{10}H_{21}Br$, 39563-53-6; $C_6H_5COCHBrC_6H_5$, 1484-50-0; $2\text{-}C_8H_{17}OTS$, 1028-12-2; (−)-$2\text{-}C_8H_{17}OTs$, 27770-99-6; $1\text{-}C_{12}H_{25}OH$, 112-53-8; $1\text{-}C_8H_{17}OH$, 111-87-5; $C_6H_5COCH_2OH$, 582-24-1; $(E)\text{-}CH_3(CH_2)_6CH{=}CHCH_2OH$, 18409-18-2; $CH_3(CH_2)_6CHOHCH{=}CH_2$, 51100-54-0; $2\text{-}C_8H_{17}OH$, 123-96-6; $2\text{-}C_{10}H_{21}OH$, 1120-06-5; $C_6H_5COCHOHC_6H_5$, 119-53-9; (−)-$2\text{-}C_8H_{17}OH$, 5978-70-1; (+)-$2\text{-}C_8H_{17}OH$, 6169-06-8; $1\text{-}C_{12}H_{25}OCH_3$, 3482-63-1; $2\text{-}C_8H_{17}OCH_3$, 1541-09-9; H_2O, 7732-18-5; $PhCOCH_2Br$, 70-11-1; $NaHCO_3$, 144-55-8; HCO_3^-, 71-52-3; CH_3OH, 67-56-1; HMPA, 680-31-9; NMP, 872-50-4; 2-(4-bromobutyl)furan, 66356-49-8; 2-bromocyclodecanone, 31236-94-9; *exo*-2-bromocamphor, 30462-54-5; menthol tosylate, 7212-65-9; 1-dodecene epoxide, 2855-19-8; 2-methyl-1-undecene epoxide, 54125-40-5; 4-furylbutanol, 19958-66-8; 2-hydroxycyclododecanone, 19025-38-8; cyclododecanol, 1724-39-6; 1,2-dodecadiol, 1119-87-5; 2-methyl-1,2-undecadiol, 84988-54-5; (*Z*)-cyclododecene, 1129-89-1; (*E*)-cyclododecene, 1486-75-5; cyclododecyl tosylate, 27092-44-0.

(10) For acid-sensitive substrates, 1 or 2 equiv of $NaHCO_3$ may be added to neutralize acid generated. Except for epoxides, this had no effect on yields.

(11) Aqueous bicarbonate has been reported to displace benzylic and allylic halides: Pinck, L. A.; Hilbert, G. E. *J. Am. Chem. Soc.* **1946**, *68*, 751. Burgstahler, A. W.; Nordm, J. C. *Ibid.* **1961**, *83*, 198.

Alkylation of Enolates from β-Dicarbonyl Compounds with Sulfonium Salt Electrophiles

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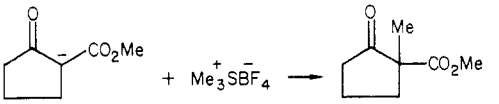
The alkylation of anions generated from β-dicarbonyl compounds has been extensively investigated.[1] Judicious choice of the electrophile and cation has often permitted selective reaction at oxygen or carbon. Sulfonium salts have not been included in this group of electrophiles[2-4] despite the obvious biological analogue, *S*-adensylmethionine.[5] We recently used the reaction of *S*-ethylthiolanium fluoborate with three enolates from β-keto esters to form 1,5-keto mercaptans.[6] In this note, we report on the potentially useful application of sulfonium salts as electrophiles for the alkylation of β-dicarbonyls that undergo O-alkylation.



1 2 3

Application of a sulfonium salt electrophile offers some unique advantages. Since the leaving group portion, a thioether, is as soft and polarizable as iodide, these electrophiles should promote selective reaction at the soft center of an ambident nucleophile. With asymmetric sulfonium salts, the potential competitive alkyl transfers may be controlled by the choice of sulfur appendages. For instance, cyclic sulfonium salts might undergo alkyl transfer to regenerate a cyclic thioether or might suffer ring opening to provide an ω-keto thioether. Finally, a sulfonium salt cation–electrophile and an enolate anion in a nonpolar solvent represent a new "phase-transfer" type arrangement without any water present.[7,8] This combination has now been examined for the effect on C- vs. O-alkylation.

These sulfonium salts do possess three apparent limitations. First, the electrophilic sulfur appendages should be chosen to facilitate the S_N2 reaction. Secondly, the counterion of the sulfonium salt must be nonnucleophilic to minimize decomposition of the salt. Finally, the ambident nucleophile is limited to species that are not basic enough to generate an ylide from the sulfonium salt.

A recent report indicates that methyl 2-oxocyclopentanecarboxylate undergoes both carbon and oxygen alkylation with a variety of electrophiles.[9] The sodium enolate from this compound affords only carbon alkylation with trimethylsulfonium fluoborate (**2**), *S*-ethylthioxanium fluoborate (**4**), *S*-ethylthiolanium fluoborate (**6**), and *S*-ethyl 5,6-dihydro-4-methyl-2*H*-thiapyranium fluoborate (**8**; Table I). Although the percentage of carbon alkylation is somewhat higher than that in other reports,[9,10] this observation is probably not significant.

(1) (a) House, H. O. "Modern Synthetic Reactions", 2nd ed.; W. A. Benjamin: Menlo Park, CA, 1972; pp 510–542. (b) Jackman, L. M.; Lange, B. C. *Tetrahedron* **1977**, *33*, 2737–2769. (c) DePalma, V. M.; Arnett, E. M. *J. Am. Chem. Soc.* **1978**, *100*, 3514–3525. (d) Stowell, J. C. "Carbanions in Organic Synthesis"; Wiley: New York, 1979; pp 198–202, 205–207. (e) Le Noble, W. J. *Syntheses* **1970**, 1–6.

(2) For the only examples of C-alkylation, see: (a) Reference 55 cited ref 1b; Lange, B. C. unpublished results. (b) Badet, B.; Julia, M.; Ramirez-Munoz, M. *Syntheses* **1980**, 926–929; Table 3, entry 6.

(3) For a competing reaction process, see: Morel, G.; Marchand, E.; Foucaud, A. *Tetrahedron Lett.* **1978**, 3719–3722.

(4) For other alkylations with sulfonium and selenonium salts, see: (a) Yamauchi, K.; Tanabe, T; Kinoshita, M. *J. Org. Chem.* **1979**, *44*, 638–639. (b) Yamauchi, K.; Nakamura, K.; Kinoshita, M. *Tetrahedron Lett.* **1979**, 1787–1790. (c) Yamauchi, K.; Nakamura, K.; Kinoshita, M. *J. Org. Chem.* **1978**, *43*, 1593–1595.

(5) For models, see: Knipe, J. O.; Coward, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 4339–4348. Mihel, I.; Knipe, J. O; Coward, J. K.; Schowen, R. L. *Ibid.* **1979**, *101*, 4349–4358. Hegazi, M. F.; Borchardt, R. T.; Schowen, R. L. *Ibid.* **1979**, *101*, 4359–4365.

(6) Garst, M. E.; Johnson, A. T. *Tetrahedron Lett.* **1980**, 4811–4814. Garst, M. E.; McBride, B. J.; Johnson, A. T. *J. Org. Chem.* **1981**, *46*, 8–16.

(7) Durst, H. D.; Liebeskind, L. *J. Org. Chem.* **1974**, *39*, 3271–3273.

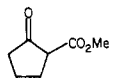
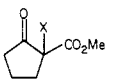
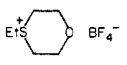
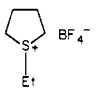
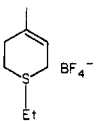
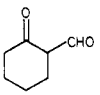
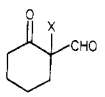
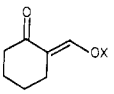
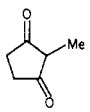
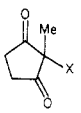
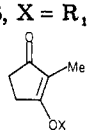
(8) Noyori, R.; Nishida, I.; Sakata, J. *J. Am. Chem. Soc.* **1981**, *103*, 2106–2108.

(9) Singh, J. *J. Org. Chem.* **1980**, *45*, 3368–3369.

(10) See footnote 10 in ref 9. Mayer, R. "Newer Methods of Preparative Organic Chemistry"; Foerst, W., Ed.; Academic Press: New York, 1961; Vol. 2, pp 101–132. Ide, J.; Sakai, K. *Tetrahedron Lett.* **1976**, 1367–1370.

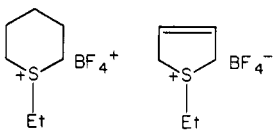
0022-3263/83/1948-1362$01.50/0

Table I. Alkylation of β-Dicarbonyl Compounds

ketone	sulfonium salt	products[a] (% yield[b])	method[c]	ketone	sulfonium salt	products[a] (% yield[b])	method[c]
 1	$Me_3S^+BF_4^-$ 2	 3, X = R_1 (88)	A (THF)	15	4	18, X = R_2 (38)	A or B
				15	6	19, X = R_3 20, X = R_3 (65)	A (C_7H_8)
1	 4	5, X = R_2 (62)	A (THF)	15	8	21, X = R_4 (32) 22, X = R_4 (3)	A (C_7H_8)
1	 6	7,[d] X = R_3 (88)	A (THF)	 23	2	 24, X = R_1 (82)	B
1	 8	9,[d] X = R_4 (98)	A (THF)			 25, X = R_1 (8)	
 10	2	 11, X = R_1 (17)	A (THF)	23	4	26, X = R_2 (20) 27, X = R_2 (20)	B
		 12, X = R_1 (20)		23	6	 28, X = R_3 (14) 26, X = R_2 (7)	
						 29, X = R_3 (14) 27, X = R_2 (7)	A (C_8H_{10})
10	2	11 (35) 12 (0)	B				
10	4	13, X = R_2 (11) 14, X = R_2 (27)	A (C_6H_8)				
 15	2	 16, X = R_1 (64)	B				
		 17, X = R_2 (6)					

[a] R_1 = Me; R_2 = Et, R_3 = $(CH_2)_4SEt$; R_4 = $CH_2CHCCH_3(CH_2)_2SEt$. [b] Isolated yield. [c] See Experimental Section. [d] The details of these compounds are reported in a full account of epoxyannulation (ref 6).

The ring opening vs. dealkylation competition is evident with salts **4**, **6**, **8**, and *S*-ethylthianium fluoborate (**30**). As Eliel[11] observed for the methyl analogues of **6** and **30**, ring opening predominates in five-membered rings and dealkylation in six-membered rings. The dealkylation reaction using 1,4-thioxane as the alkyl carrier should permit the ready transfer of any primary alkyl group. To promote ring opening in six-membered rings, the desired S_N2 reaction was enhanced by making it an allylic displacement as in **8**. The geometrical requirements for this process have been examined by Bartlett[12] and King.[13] Salt **8** possesses enough π-overlap to yield only ring-opened products. We also treated *S*-ethyl 2,5-dihydrothiophonium fluoborate (**31**)[14] with the anion from **1** and with cyanide. In each instance, only 1-(1,3-butadienyl)ethyl thioether was formed, via the expected elimination reaction.



30 **31**

A more rigorous test for selective carbon alkylation is found with 2-formylcyclohexanone. Salt **2** affords clean C-methylation, while the more hindered salt **4** provides comparable amounts of C- and O-alkylated products as previously noted for this enolate with alkyl halides.[14]

The enolates from **15** and **23** are uniquely designed to favor O-alkylation. Steric hinderance at carbon and the nonchelating "W" geometry of the enolate promote O-alkylation in β-diketones.[1a] These enolates are completely insoluble in most solvents except dipolar aprotics and water, methanol, etc. The former solvents enhance O-alkylation, while the latter often provide side products

(11) Eliel, E. L.; Hutchins, R. O.; Mebane, R.; Willer, R. L. *J. Org. Chem.* **1976**, *41*, 1052–1057.
(12) Bartlett, P. D.; Trachtenberg, E. N. *J. Am. Chem. Soc.* **1958**, *80*, 5808–5812.
(13) King, J. F.; Tsang, G. T. Y. *J. Chem. Soc., Chem. Commun.* **1979**, 1131–1132.
(14) Johnson, W. S.; Posvic, H. *J. Am. Chem. Soc.* **1947**, *69*, 1361–1366.

from the insoluble electrophile or from retro-Claisen reactions. C-Alkylation of **15** and **23** with methyl iodide in protic solvents or allylic halides in water proceeds without complication in 60–80% yield.[15-17] Apparently, alkylation of **15** and **23** with nonactivated electrophiles affords less than 10% of C-alkylation.[18] Our results with sulfonium salts in hydrocarbon solvents represent an improvement in all instances. These solvents were chosen to promote the soft nucleophile–soft electrophile interaction. Although some increased carbon alkylation was noted, clearly competing O-alkylation remains a problem with these enolates.

These experiments demonstrate the potential utility of sulfonium salts as electrophiles for the alkylation of β-dicarbonyl anions. These electrophiles may be valuable in transferring primary alkyl groups or in preparing ω-functionalized carbonyl systems.

Experimental Section

Infrared spectra were recorded on a Beckman IR 18 AX, a Perkin-Elmer Infracord, a Pye-Unicam SP 1000, or a Pye-Unicam SP 3-200 spectrophotometer; bands yielding structural information are reported in reciprocal centimeters (cm^{-1}), using polystyrene calibration. Nuclear magnetic resonance spectra were recorded on a Varian EM 390 instrument at 25 °C in deuteriochloroform, and the peak positions are reported in parts per million from tetramethylsilane internal standard, using multiplet (m), quartet (q), triplet (t), doublet (d), or singlet (s) to describe the multiplicity. Carbon magnetic resonance spectra were recorded on a JEOL CFT-100 instrument in deuteriochloroform, and the peak positions are assigned relative to the chloroform resonances at 78.161, 76.900, and 75.619 ppm. The low-resolution mass spectra were obtained on a Finigan 4000 GCMS DS instrument with sample introduction via direct probe or through a 6-ft GC column containing 3% Dexil 300 on Supelcoport. High-resolution spectra were performed at the Biomedical Mass Spectrometry Resource, University of California, San Francisco, with sample introduction by direct probe.

GC analysis was performed on a Varian 3700 gas chromatograph with an FID detector outfitted with a 6 ft × 0.25 in. glass column containing 3% Dexil 300 on 100/120 Supelcoport or 3% SE 30 on 100/120 Supelcoport.

The β-dicarbonyls were commercially available[19] and the sulfonium salts prepared by standard routes.[20]

General Procedure A. A dry sodium enolate of the β-dicarbonyl (10^{-2} mol) prepared from dicarbonyl and sodium hydride in tetrahydrofuran (THF) and evaporation of the solvent. The enolate and 1.3×10^{-2} mol of the sulfonium salt were suspended in 20 mL of THF or aromatic hydrocarbon solvent (distilled from calcium hydride). This suspension was heated at reflux for 24 h. Most of the solvent was removed under vacuum, and the residue was poured onto a silica gel column. Elution with hexane afforded the solvent; hexane:ether (1:1), the "C"-alkylation product; and hexane:ether (1:3), the "O"-alkylation product.

General Procedure B. The dry sodium enolate and the sulfonium salt were mixed in the same proportions and distilled from a Kugelrohr apparatus at 0.013 kPa. The products were separated by the same method.

Methyl 1-[4-(Ethylthio)butyl]-2-oxocyclopentanecarboxylate (7): 88% yield; IR 1750, 1720 cm^{-1}; NMR δ 1.2 (t, $J \sim$ Hz, 3), 2.2 (m, 10), 2.6 (m, 6), 3.7 (s, 3); HRMS observed m/z 240.1204, $C_{13}H_{22}O_3S$ (-18) requires 240.1184.

Methyl 1-[3-Methyl-5-(ethylthio)-(*Z*)-2-pentenyl]-2-oxocyclopentanecarboxylate (9): 98% yield; bp 50 °C at 0.013 kPa; IR 2980, 1760, 1735, 1450, 1335, 1160 cm^{-1}; NMR δ 1.27 (t, J = 12 Hz, 3), 1.71 (s, 3), 2.2 (m), 2.43 (q, J = 12 Hz, 2), 3.68 (s, 3), 5.10 (t, 1); HRMS observed m/z 284.144064, $C_{15}H_{24}O_3S$ requires 284.1442.

2-Methyl-2-[4-(ethylthio)butyl]cyclopentane-1,3-dione (19) and 2-Methyl-3-[4-(ethylthio)butoxy]cyclopent-2-en-1-one (20). 19: IR 2920, 1715, 1620, 1445, 1338, 1110 cm^{-1}; NMR δ 1.10–1.80 (m, 12 H), 2.33–2.80 (m, 4 H), 2.87 (s, 4 H); HRMS observed m/z 228.1187, $C_{12}H_{20}O_2S$ requires 228.1176.

20: IR 2920, 1685, 1625, 1380, 1340, 1115 cm^{-1}; NMR δ 1.22 (t, 3 H, J = 8 Hz), 1.50 (s, 3 H), 1.63–2.00 (m, 4 H), 2.20–2.76 (m, 8 H), 4.20 (t, J = 8 Hz, 2 H); HRMS observed m/z 228.1182, $C_{12}H_{20}O_2S$ requires 228.1176.

2-Methyl-2-[5-(ethylthio)-3-methyl-(*Z*)-pentenyl]cyclopentane-1,3-dione (21) and 2-Methyl-3-[5-(ethylthio)-3-methyl-(*Z*)-2-pentenoxy]cyclopent-2-en-1-one (22). 21: IR 2980, 2940, 2880, 1762, 1725, 1455, 1422, 1380, 1315, 1268, 1078 cm^{-1}; NMR δ 1.02 (s, 3 H), 1.24 (t, J = 8 Hz, 3 H), 1.68 (s, 3 H), 2.05–2.58 (m, 8 H), 2.62 (s, 4 H), 4.90 (t, J = 8 Hz, 1 H); ^{13}C NMR δ 215.75, 215.75, 137.73, 118.59, 56.08, 34.91, 34.91, 34.03, 31.39, 29.21, 25.41, 22.79, 17.96, 14.24; HRMS observed m/z 254.1348, $C_{14}H_{22}O_2S$ requires 254.1345.

22: IR 2978, 2940, 2880, 1692, 1630, 1448, 1395, 1380, 1338, 1118, 970 cm^{-1}; NMR δ 1.30 (t, 3 H, J = 8 Hz), 1.60 (s, 3 H), 1.86 (s, 3 H), 2.20–2.70 (m, 10 H), 4.70 (d, J = 8 Hz, 2 H), 5.48 (brd t, J = 8 Hz, 1 H); MS (70 eV), m/z 254 (M^+); HRMS observed m/z 254.1345, $C_{14}H_{22}O_2S$ requires 254.1345.

2-Methyl-2-[4-(ethylthio)butyl]cyclohexane-1,3-dione (28) and 2-Methyl-3-[4-(ethylthio)butoxy]cyclopent-2-en-1-one (29). 28: IR 2940, 2885, 1730, 1698, 1455, 1380, 1266, 1135, 1026 cm^{-1}; NMR δ 1.12–1.33 (m, 6 H), 1.33–2.10 (m, 8 H), 2.20–2.80 (m, 8 H); HRMS observed m/z 242.1341, $C_{13}H_{22}O_2S$ requires 242.1334.

29: IR 2920, 1610, 1380, 1355, 1098 cm^{-1}; NMR δ 1.23 (t, 3 H, J = 8 Hz), 1.67 (s, 3 H), 1.70–2.18 (m, 9 H), 2.20–2.70 (m, 8 H), 4.02 (t, 2 H, J = 6 Hz); HRMS observed m/z 242.1329, $C_{13}H_{22}O_2S$ requires 242.1334.

Registry No. **1**, 10472-24-9; **2**, 676-88-0; **3**, 30680-84-3; **4**, 85098-51-7; **5**, 25684-00-8; **6**, 696-98-0; **7**, 83705-56-0; **8**, 83705-60-6; **9**, 83705-61-7; **10**, 1193-63-1; **11**, 37709-42-5; **12**, 15839-18-6; **13**, 61783-91-3; **14**, 15839-65-3; **15**, 765-69-5; **16**, 3883-58-7; **17**, 25112-86-1; **18**, 25112-87-2; **19**, 85098-52-8; **20**, 85098-53-9; **21**, 85098-54-0; **22**, 85098-55-1; **23**, 1193-55-1; **24**, 562-13-0; **25**, 25112-91-8; **26**, 25112-82-7; **27**, 20643-20-3; **28**, 85098-56-2; **29**, 85098-57-3.

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An Improved α-Chlorination of Carboxylic Acids

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Although the Hell–Volhard–Zelinksy (HVZ) α-bromination of carboxylic acids was discovered a century ago,[1] extension of this chemistry to α-chlorination has occurred only recently. The propensity of chlorine to undergo competing free radical reactions under HVZ conditions

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