(s, 1, 2-H), 7.61 (d, 1, $J_{4,5}$ = 9.6 Hz, 4-H); IR 2110 (N_3) cm^{-1}; UV (95% ethanol) λ_{max} 214 nm (log ϵ 4.31), 247 (4.34), 289 (3.99); UV (0.1 N HCl) λ_{max} 210 nm (log ϵ 4.30), 244 (4.34), 285 (3.99); UV (pH 7.0 buffer) λ_{max} 210 nm (log ϵ 4.28), 242 (4.35), 287 (4.00); UV (0.1 N NaOH) λ_{max} 220 nm (log ϵ 4.12), 245 (4.29), 289 (3.92); FDMS, m/e 245 (M^+).

Anal. Calcd for $C_{11}H_{11}N_5O_2$: C, 53.87; H, 4.52; N, 28.56. Found: C, 53.70; H, 4.57; N, 28.40.

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Registry No. **1**, 606-20-2; **2**, 79476-53-2; **3**, 87586-68-3; **4a**, 5192-23-4; **4b**, 5192-03-0; **4c**, 5318-27-4; **4d**, 2462-30-8; **5a**, 81524-73-4; **5b**, 81524-74-5; **5c**, 81524-75-6; **5d**, 81524-70-1; **6**, 19727-83-4; **7a**, 4769-96-4; **7b**, 46885-76-1; **8**, 73-22-3; $(CH_3)_2NCH(OCH_3)_2$, 4637-24-5; $NH_2NHCONH_2$·HCl, 563-41-7.

Reaction of Dimethyloxosulfonium Methylide with Epoxides. Preparation of Oxetanes

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Methods for the preparation of oxetanes include the cyclization of 1,3-halohydrins with alkali, the light-catalyzed 1,2-cycloaddition of olefins and carbonyl compounds,[1] the thermal decomposition of tributyltin derivatives,[2] and the reaction of sulfoximide anion with carbonyl compounds.[3] The analogous azetidines have been prepared by reaction of dimethyloxosulfonium methylide with aziridines.[4] We now report on a convenient synthesis of oxetanes by reaction of dimethyloxosulfonium methylide (1) with epoxides and with carbonyl compounds.

Results and Disscussion

The ylide 1 is an efficient methylene-transfer reagent in reactions with epoxides **3a–e**, affording the corresponding oxetanes **3a–e** in yields of 83–97% on standing at 50 °C for 3 days (Table I). We propose the following pathway for the reaction:

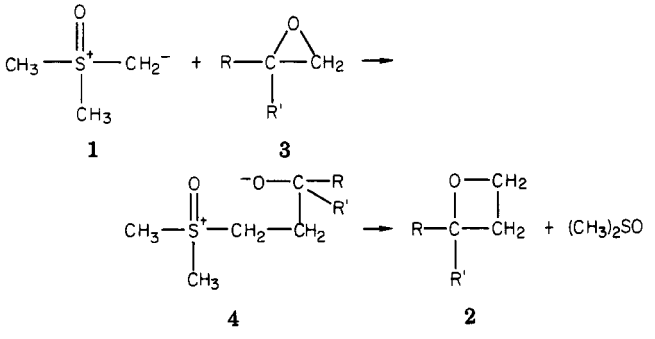


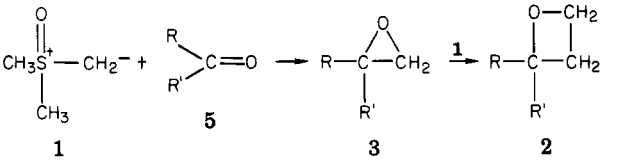
Table I. Preparation of Oxetanes from Epoxides

compd	R	R′	compd	yield,[a] %	yield,[b] %
3a	H	C_6H_5	**2a**	65	94
3b	C_6H_5	C_6H_5	**2b**	55[c]	99
3c	H	*p*-ClC_6H_4	**2c**	23[c]	88
3d	CH_3	C_6H_5	**2d**	24[c]	85
3e	cyclohexanone		**2e**	81	83

[a] 10 mol % excess ylide; reflux 4 h. [b] 100 mol % excess ylide; 50 °C, 3 days. [c] Unreacted epoxide recovered in yields of 25%, 45%, and 50%, respectively.

The reaction of epoxides with 1 differs from those reported with related reagents. Thus, anions of *N*-(*p*-tolylsulfonyl)sulfoximines are nucleophilic alkylidene transfer reagents in reactions with ketones, imines, and α,β-unsaturated ketones, affording epoxides, aziridines, and cyclopropanes, respectively.[5] However, reaction of this anion with epoxides yields only the corresponding γ-hydroxy sulfoximines. Likewise, reaction of epoxides with α-lithio *tert*-butyl sulfoxide gives γ-hydroxy sulfoxides.[6]

Since oxosulfonium ylides are practical reagents for the synthesis of epoxides from carbonyl compounds, we explored the reaction of 2 equiv of 1 with carbonyl compounds. As shown in Table II, oxetanes **2** were obtained in 80–97% yields by carrying out the reaction at 50 °C for 3 days.



The reported synthesis of oxetanes by reaction of *N*-(*P*-tolylsulfonyl)sulfoximide anion with carbonyl compounds is quite sensitive to temperature.[3] For example, oxetane **2i** was obtained in 69% yield at a reaction temperature of 40 ± 2 °C. However, at a reaction temperature of 45 ± 2 °C, 2-(4-*tert*-butylcyclohexenyl)ethanol was formed as a byproduct in 17% yield. The reaction with 1 does not require such rigidly controlled reaction conditions; reaction with benzophenone gave **2b** in yields of 97% (50 °C, 3 days) or 88% (reflux, 1 day).

The use of dimethyloxosulfonium methylide as a nucleophilic methylene-transfer reagent to epoxides has advantages over most known oxetane synthesis methods: the reaction conditions are mild and convenient; yields of the products are much higher than those reported by the procedures of Deric (40%),[1] Biggs (20–40%),[2] and Welch (46–96%).[3]

Experimental Section

The aldehydes and ketones used as starting materials were reagent grade (>95% pure) and were used as received unless otherwise specified. Epoxides were prepared by the reaction of dimethylsulfonium methylide with carbonyl compounds.[7,8] ^1H

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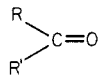
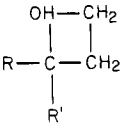
Table II. Preparation of Oxetanes from Carbonyl Compounds[a]





compd	R	R'	compd	yield, %	bp, °C (mmHg)
5a	H	C_6H_5	2a	93	37-38 (0.016)
5b	C_6H_5	C_6H_5	2b	97	111-115 (0.013)
5c	H	p-ClC_6H_4	2c	90	60-64 (0.018)
5d	CH_3	C_6H_5	2d	90	31-35 (0.009)
5e	cyclohexanone		2e	88	31-33 (0.013)
5f	H	p-$CH_3C_6H_4$	2f	80	44-47 (0.007)
5g	C_2H_5	C_6H_5	2g	96	44-48 (0.022)
5h	4-methylcyclohexanone		2h	80	24-26 (0.072)
5i	4-*tert*-butyl cyclohexanone		2i	87	63-65 (0.040)

[a] Reactions carried out at 50 °C for 3 days.

NMR spectra were measured with a JEOL PMX-60 spectrometer or a JEOL FX-200 spectrometer. Mass spectra were recorded of a JEOL DX-300 mass spectrometer.

Methylene-Transfer Reaction. Oxetane 2a from Epoxide 3a. To a solution of 4.40 g (20 mmol) of trimethyloxosulfonium iodide in 40 mL of *t*-BuOH was added a solution of 2.24 g (20 mmol) of *t*-BuOK in 25 mL of *t*-BuOH at 50 °C. After 30 min of stirring, 1.20 g (10 mmol) of **3a** (freshly distilled) in 20 mL of *t*-BuOH was added dropwise to this solution. After 3 days of stirring, the resulting suspension was evaporated, washed with water, and extracted three times with *n*-hexane. The combined extract was dried over $MgSO_4$ and evaporated to give oxetane **2a** (1.26 g, 9.4 mmol) in 94% yield. Without further purification, resulting **2a** was spectroscopically pure: ^1H NMR ($CDCl_3$) δ 2.33-3.43 (m, 2 H), 4.20-5.20 (m, 2 H), 5.73 (t, 1 H, J = 7.2 Hz), 7.30 (s, 5 H); HRMS, m/e 134.0731 ($C_9H_{10}O$ requires 134.0721).

2b-e were prepared in a similar manner from 10 mmol of epoxide; yields are shown in Table I. **2b**: mp 41-43 °C; ^1H NMR ($CDCl_3$) δ 3.17 (t, 2 H, J = 8.0 Hz), 4.63 (t, 2 H, J = 8.0 Hz), 7.07-7.63 (m, 10 H); HRMS, m/e 210.1044 ($C_{15}H_{14}O$ requires 210.1045). Anal. Calcd for $C_{15}H_{14}O$: C, 85.71; H, 6.67. Found: C, 85.73; H, 6.61. **2c**: ^1H NMR ($CDCl_3$) δ 2.33-3.23 (m, 2 H), 4.40-5.06 (m, 2 H), 5.70 (t, 1 H, J = 8.0 Hz), 7.07-7.63 (m, 10 H); HRMS, m/e 168.0342, 170.0312 (C_9H_9OCl requires 168.0342, 170.0312). **2d**: ^1H NMR ($CDCl_3$) δ 1.73 (s, 3 H), 2.75 (t, 2 H, J = 7.8 Hz), 4.55 (dt, 2 H, J = 1.8, 8.0 Hz), 7.35 (s, 5 H); HRMS, m/e 148.0888 ($C_{10}H_{12}O$ requires 148.0888). **2e**: ^1H NMR δ 1.0-2.0 (m, 10 H), 2.27 (t, 2 H, J = 7.8 Hz), 4.43 (t, 2 H, J = 7.8 Hz); HRMS, m/e 124.1043 ($C_8H_{14}O$ requires 126.1045).

Double Methylene-Transfer Reaction. Oxetane 2b from 5b. To a solution of 8.80 g (40 mmol) of trimethyloxosulfonium idodide in 80 mL of *t*-BuOH was added a solution of 4.48 g (40 mmol) of *t*-BuOK in 50 mL of *t*-BuOH at 50 °C. After 30 min of stirring, 1.82 g (10 mmol) of benzophenone (**5b**) in 20 mL of *t*-BuOH was added dropwise. After 3 days of stirring, the resulting suspension was evaporated, washed with water, and extracted three times with *n*-hexane. The combined extract was dried over $MgSO_4$ and evaporated to give oxetane **2b** (2.04 g, 9.7 mmol) in 97% yield. Without further purification, **2b** was spectroscopically pure: mp 41-43 °C.

2a,c-i were prepared in a similar manner from 10 mmol of ketone; yields are shown in Table II **2f**: ^1H NMR ($CDCl_3$) δ 2.32 (s, 3 H), 2.40-3.33 (m, 2 H), 4.37-4.93 (m, 2 H), 5.72 (t, 1 H, J = 7.8 Hz), 7.17 (s, 4 H); HRMS, m/e 148.0888 ($C_{10}H_{12}O$ requires 148.0888). **2g**: ^1H NMR ($CDCl_3$) δ 0.82 (t, 3 H, J = 7.3 Hz), 1.63-2.23 (m, 2 H), 2.73 (dt, 2 H, J = 3, 8 Hz), 4.52 (t, 2 H, J = 7.7 Hz), 7.28 (s, 5 H); HRMS, m/e 162.1045 ($C_{11}H_{14}O$ requires 162.1045). **2h**: ^1H NMR ($CDCl_3$) δ 0.57-2.03 (m, 11 H), 1.80-2.53 (m, 1 H), 2.28 (t, 2 H, J = 7.8 Hz), 4.43 (t, 2 H, J = 7.8 Hz); HRMS, m/e 140.1183 ($C_9H_{16}O$ requires 140.1201). **2i**: ^1H NMR ($CDCl_3$) δ 0.85 (s, 9 H), 1.00-1.83 (m, 8 H), 2.00-2.40 (m, 1 H), 2.28 (t, 2 H, J = 8.0 Hz), 4.42 (t, 2 H, J = 8.0 Hz); HRMS, m/e 182.1691 ($C_{12}H_{22}O$ requires 182.1671).

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Registry No. 1, 5367-24-8; **2a**, 4436-23-1; **2b**, 884-73-1; **2c**, 17492-23-8; **2d**, 19352-10-4; **2e**, 185-18-2; **2f**, 5583-71-1; **2g**, 87597-07-7; **2h**, 87597-08-8; **2i**, 87597-09-9; **3a**, 96-09-3; **3b**, 882-59-7; **3c**, 2788-86-5; **3d**, 2085-88-3; **3e**, 185-70-6; **5a**, 100-52-7; **5b**, 119-61-9; **5c**, 104-88-1; **5d**, 98-86-2; **5e**, 108-94-1; **5f**, 104-87-0; **5g**, 93-55-0; **5h**, 589-92-4; **5i**, 98-53-3.

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Synthesis of a Conjugated Nitrile from a Benzylic Ketone via a Cyanotrimethylsilane Adduct: 3,4-Dihydro-6-methoxynaphthalene-1-carbonitrile

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6-Methoxynaphthalene-1-carbonitrile (**4**) and its 3,4-dihydro derivative **3** are useful intermediates for the synthesis of steroids and the oxidized metabolites of carcinogenic hydrocarbons.[1-4] The fully aromatic nitrile **4** is commonly prepared from 6-methoxy-1-aminonaphthalene via diazotization and the Sandmeyer reaction.[1] However, preparation of the starting compound entails a multistep synthesis and affords relatively poor overall yields. The 3,4-dihydro compound **3** is presently available through addition of diethylaluminum cyanide to 6-methoxy-1-tetralone followed by dehydration.[5] Since diethylaluminum cyanide is a relatively expensive and hazardous reagent, and large solvent volumes are required, this method is impractical for larger scale preparations.

We now report a convenient one-pot synthesis of **3** from 6-methoxytetralone (**1**) and dehydrogenation of **3** directly to **4** (Scheme I). Boron trifluoride-catalyzed addition of cyanotrimethylsilane[6] to **1** yields the adduct **2** which on

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