tooxygenated for 4 h, as described above for compound **8**. Activated charcoal was added and the suspension was filtered and concentrated. The crude product was purified by flash chromatography (25% ethyl acetate–hexane) to afford 370 mg (77.5%) of diketone **14** as an oil: IR (film) ν 2980, 1710 (vs, br), 1400, 1370, 1165 cm^{-1}; ^1H NMR δ 1.4 and 1.45 (s, *t*-Bu, rotamers), 1.6–2.2 (m, ring H-3s, H-4s), 2.36 (s, CH_3), 3.5 (br q, J = 6 Hz, ring H-5s), 4.8 (br m, ring H-2); $[\alpha]^{24}_D$ −42.0° (*c* 0.85, $CHCl_3$). Anal. Calcd for $C_{12}H_{19}NO_4$: C, 59.73; H, 7.94; N, 5.81. Found: C, 59.60; H, 7.80; N, 5.64.

Cleavage of Diketone 14. To a solution of 21 mg (0.087 mmol) of diketone **14** in 1 mL of 50% aqueous methanol was added 37 mg (0.16 mmol) of periodic acid. After 4 h the product was isolated with ethyl acetate, affording 15 mg (80%) of Boc-proline **10** (IR, ^1H NMR, TLC). This material showed $[\alpha]^{24}_D$ −72.7° (*c* 1.4, $CHCl_3$) and −77.0° (*c* 0.75, $CHCl_3$) vs. −89.2° (*c* 1.4, $CHCl_3$) and −94.5° (*c* 0.75, $CHCl_3$) for starting **10**. The optical purity of **10** derived from diketone **14** is therefore 81.5%.

(*S*)-1-(2-Pyrrolidinyl)-1,2-propanedione Hydrochloride (3·HCl). Boc-diketone **14** (46 mg, 0.19 mmol) was dissolved in 1 mL of 4 M hydrogen chloride in dioxane. After 1.2 h the solution was concentrated and the resulting oil was triturated with two portions of ether. The diketone **3** (33 mg, 98%) was thus obtained as a yellow solid, mp 128–130 °C dec; $[\alpha]^{24}_D$ −18° (*c* 0.45, $CHCl_3$); IR (film) ν 3650–3100 (br, vs) 3000 (br), 1725, 1355 cm^{-1}; ^1H NMR δ 2.45 (s, CH_3), 2.0 (br s, 4 H) and 3.5 (br s, 2 H) (ring CH_2), 5.1 (br s, H-2), 8.9, 10.2 (br s, NH_2^+). Anal. Calcd for $C_7H_{12}NO_2Cl$: C, 47.33, H, 6.81; N, 7.89. Found: C, 47.12; H, 7.06; N, 7.66.

5-Phenyl-2,3-pentanedione (2). To a stirred solution of 345 mg (2.0 mmol) of 3-phenylpropanoyl chloride (**15**) in 10 mL of THF was added 0.35 mL (2.0 mmol) of diisopropylethylamine followed at once by 0.43 mL (2.0 mmol) of enamine **18**. A precipitate formed after several minutes. The mixture was stirred overnight. Filtration and concentration gave crude enamino ketone **16**. This material was dissolved in 50 mL of CH_2Cl_2, 5 mg of bisacenaphthenethiophene was added, and the solution was photooxygenated for 2.2 h as described above for compound **8**. The crude product was purified by flash chromatography (10% ethyl acetate–hexane) to afford 184 mg (52%) of diketone **3** as a volatile yellow oil: IR (film) ν 2920 (w), 1720, 1710, 1350 cm^{-1}; ^1H NMR δ 2.3 (s, CH_3), 3.0 (m, CH_2s), 7.25 (s, Ph). Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.97; H, 6.87. Found: C, 75.06; H, 6.88.

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Lithiation of 2-Bromoketene Dithioacetals

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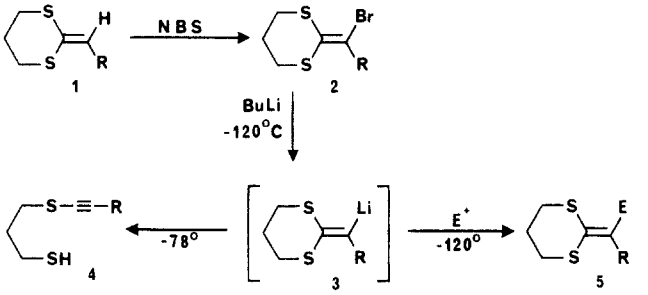
The preparation of tetrasubstituted ketene dithioacetals such as **5** can be carried out by using a number of standard methods.[1] Because several of those procedures either failed or were too lengthy for a particular derivative of interest to us, we sought a new route that would complement the others by converting a simple ketene dithioacetal (e.g., **1**) into a more highly functionalized one (**5**).

Table I. Reactions of Vinyllithium 3 with Electrophiles

entry	electrophile, E^+	product (5), E	yield, %
a	CH_3OD	−D	81[a]
b	$(CH_3)_3SiCl$	$-Si(CH_3)_3$	93[b]
c	CH_3I	$-CH_3$	84
d	$CH_3(CH_2)_2I$	$-(CH_2)_2CH_3$	74[c]
e	$CH_3(CH_2)_4CHO$	$-CH(OH)(CH_2)_4CH_3$	64
f	$HCON(CH_3)_2$	−CHO	71
g	$TolSO_2$ menthyl[7]		47

[a] MS and ^1H NMR indicate 94% deuterium incorporation. [b] Crude yield; decomposes during silica gel chromatography; homogenous by TLC. [c] Requires HMPA as cosolvent.



One possible approach would be to treat an electrophile with a vinyllithium derivative such as **3**. The successful utilization of this intermediate poses several challenges, however. First, trisubstituted ketene dithioacetals **1** undergo direct metalation (deprotonation) either in the allylic position or in the dithiane ring but not at the desired vinylic position.[2] Furthermore, even if **3** could be generated by some other means, it might be prone to undergo β-elimination of the trans heteroatom, by analogy with the well-known instability of *trans*-1-lithio-2-methoxyethene,[3] to give the alkyne **4** after workup. Bearing these potential problems in mind, we chose to attempt regioselective generation of the vinyllithium derivative via halogen–metal exchange. The required vinyl bromide precursor **2** is easily prepared by treating **1** with NBS in the presence of Et_3N for 5 min at 20 °C.[4] Standard aqueous workup followed by flash chromatography gives **2**, an oil that is reasonably stable in the dark at −20 °C, in 86% yield.

When **2** is metallated at −78 °C (2*t*-BuLi, −78 °C in THF), the major product isolated after quenching with MeOH is the elimination product **4**. At a lower temperature, however, the vinyllithium intermediate is stable. Thus, treatment of **2** in THF/ether/pentane (4:1:1)[5] with 2 equiv of *t*-BuLi at −120 °C cleanly generates **3** within 20 min. The addition of any of a variety of electrophiles gives the products derived from **3**, as shown in Table I, after reaction at −120 °C for 30 min, slow warming to room temperature, aqueous workup, and purification by flash chromatography.[6] Less reactive electrophiles such as

(1) Kolb, M. In "The Chemistry of Ketenes, Allenes, and Related Compounds"; Patai, S., Ed.; John Wiley: New York, 1980; Part 2, Chapter 16.

(2) Seebach, D.; Kolb, M. *Liebigs Ann. Chem.* **1977**, 811.

(3) Lau, K. S. Y.; Schlosser, M. *J. Org. Chem.* **1978**, *43*, 1595. Vinyllithium reagents similar to **3** have been generated and shown to undergo this elimination, but efficient trapping of electrophiles by the vinyl anion was not reported. Andersen, N. H.; Duffy, P. F.; Denniston, A. D.; Grothjahn, D. B. *Tetrahedron Lett.* **1978**, 4315.

(4) Vinyl bromides such as **2** are intermediates in the "oxidative solvolysis" of ketene dithioacetals to give α-halo esters: see ref 1, p 690.

(5) Gobrich, G; Trapp, H. *Chem. Ber.* **1966**, *99*, 680.

(6) All products gave satisfactory spectral data (see above). In addition, products **5c** and **5d** were identical spectrally (^1H NMR, IR, and MS) and chromatographically (TLC) with material prepared independently by procedures described in ref 2.

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epoxides are not useful in this reaction because decomposition of the vinyllithium species via elimination is faster than the desired nucleophilic substitution. Reaction of the acyclic dimethylketene dithioacetal analogous to **2** under the same conditions gave <10% elimination but suffered from lower yields in both the bromination and alkylation steps.

This convenient two-step procedure thus complements existing methods of ketene dithioacetal formation, and while it is limited to relatively reactive electrophiles, it nonetheless provides a convenient method of preparing and/or elaborating a wide variety of these synthetically useful derivatives.

Experimental Section

Preparation of 2. *N*-Bromosuccinimide (3.30 g, 18.5 mmol) was added in small portions to a solution of **1** (R = *n*-pentyl, 2.49 g, 12.3 mmol), triethylamine (3.40 mL, 24.4 mmol), and methylene chloride (15 mL). The resulting solution was stirred for 5 min and then poured into a mixture of ether and saturated aqueous $NaHCO_3$. The aqueous phase was extracted with ether, and the combined organic extracts were dried ($MgSO_4$) and concentrated in vacuo. Flash chromatography of the crude mixture (silica gel, petroleum ether/ether, 95:5) gave 3.00 g (86%) of **2** as an oil which is stable at −20 °C in the dark: IR (neat) 2920, 2860, 1560, 1420, 1250 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.90 (m, 4 H), 2.70 (t, J = 7.3 Hz, 2 H), 2.06 (m, 2 H), 1.50 (m, 2 H), 1.28 (m, 4 H), 0.86 (t, J = 6.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 126.8, 122.2, 38.5, 30.7, 29.8, 29.4, 28.0, 23.7, 22.5, 14.0; MS (EI, 70 eV), m/e (relative intensity) 282 (M^+ + 2, 20.5), 280 (M^+, 19.7), 225 (M^+ − 55, 100), 223 (M^+ − 57, 95.2), 201 (M^+ − 79, 55.1), 151 (M^+ − 129, 25.2), 149 (M^+ 131, 14.0), 145 (M^+ − 135, 58.0).

Conversion of 2 into 5. General Procedure. A solution of **2** (R = *n*-pentyl, 145 mg, 0.516 mmol) in THF/ether/pentane ((4:1:1), 0.5 mL) was added dropwise to a solution of *tert*-butyllithium (0.80 mL of a 1.67 M solution in pentane, 1.30 mmol) in 1.5 mL of THF/ether/pentane (4:1:1) at −120 °C. The resulting soltuion was stirred for 20 min, followed by addition of the electrophile as a cold THF solution. After 30 min, the reaction mixture was allowed to warm to 20 °C. Water (1 mL) was added, and the mixture was extracted with ether. The combined organic extracts were dried ($MgSO_4$) and concentrated. Flash chromatography of the crude mixture (silica gel, petroleum ether/ether mixtures) gave **5**. In the case of **5d**, 0.4 mL of HMPA was added before the electrophile was introduced. Yields for each electrophile are shown in Table I.

Spectral Data. 5a: (oil) IR (neat) 2920, 2560, 2860, 1580, 1420 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.83 (m, 4 H), 2.15 (m, 4 H), 1.27 (m, 6 H), 0.86 (t, J = 6.7 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 134.1, 125.8, 31.4, 30.4, 29.6, 29.3, 28.7, 25.5, 22.5, 14.0; MS (EI, 70 eV), m/e (relative intensity) 203 (M^+, 60.2), 146 (M^+ − 57, 100), 129 (M^+ − 74, 16.0). The ratio of 203/202 indicates 94% deuterium incorporation. Calcd for $C_{10}H_{17}DS_2$ (M^+) m/e 203.0912, found m/e 203.0905. This product was identical chromatographically with **1**. The ^1H NMR of this product is nearly identical with that of **1** except that the triplet signal at δ 5.95 ppm is ca. 6% of the integration of that in the ^1H NMR of **1**.

5b: (oil) ^1H NMR ($CDCl_3$) δ 2.90 (m, 4 H), 2.30 (m, 2 H), 2.10 (m, 2 H), 1.30 (m, 6 H), 0.88 (t, J = 6.8 Hz, 3 H), 0.20 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 144.1, 137.2, 34.4, 32.1, 30.6, 29.6, 29.3, 24.8, 22.6, 14.2, 0.6; MS (EI, 70 eV), m/e (relative intensity) 274 (M^+, 13.5), 259 (M^+ − 15, 8.87), 217 (M^+ − 57, 56), 200 (M^+ − 74, 11.4), 73 (M^+ − 201, 100). Calcd for $C_{13}H_{26}S_2Si$ (M^+) m/e 274.1245, found m/e 274.1236.

5c: (oil) IR (neat) 2940, 2860, 1580, 1420 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.82 (m, 4 H), 2.32 (m, 2 H), 2.11 (m, 2 H), 1.88 (s, 3 H), 1.28 (m, 6 H), 0.87 (t, J = 6.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 140.5, 119.3, 36.0, 31.7, 30.3, 30.2, 27.6, 25.2, 22.6, 20.2, 14.0; MS (EI, 70 eV), m/e (relative intensity) 216 (M^+, 23.2), 159 (M^+ − 57, 100), 145 (M^+ − 271, 13.2), 85 (M^+ − 131, 15.3). Calcd for $C_{11}H_{20}S_2$ (M^+) m/e 216.1006, found m/e 216.1000. This product was identical spectrally (^1H NMR, IR, MS, and chromatographically (TLC) with an authentic sample.[6]

5d: (oil) IR (neat) 2940, 2860, 1580, 1450 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.84 (m, 4 H), 2.30 (m, 4 H), 2.13 (m, 2 H), 2.25–2.50 (m, 8 H), 0.91 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 145.4, 120.3, 36.1, 34.1, 31.9, 30.5, 28.1, 25.3, 22.6, 21.7, 14.1; MS (EI, 70 eV), m/e (relative intensity) 244 (M^+, 36.8), 215 (M^+ − 29, 29.8), 187 (M^+ − 57, 100), 159 (M^+ − 85, 59.3), 85 (M^+ − 159, 19.5). Calcd for $C_{13}H_{24}S_2$ (M^+) m/e 244.1319, found m/e 244.1306. This product was identical spectrally (^1H NMR, IR, and MS) and chromatographically (TLC) with an authentic sample.[6]

5e: (oil) IR (neat) 3450, 2940, 2860, 1570, 1470 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.90 (m, 1 H), 2.75–3.05 (m, 4 H), 2.29 (m, 2 H), 2.13 (m, 2 H), 1.78 (d, J = 4.4 Hz, OH), 1.20–1.60 (m, 14 H), 0.89 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 145.5, 124.0, 72.6, 35.9, 32.4, 31.9, 30.2, 30.2, 29.8, 29.6, 25.7, 25.1, 22.7, 22.5, 14.1; MS (EI, 70 eV), m/e (relative itensity) 302 (M^+, 7.9), 284 (M^+ − 18, 1.6), 245 (M^+ − 57, 2.3), 231 (M^+ − 71, 100), 227 (M^+ − 75, 4.1), 213 (M^+ − 89, 2.0), 203 (M^+ − 99, 7.8). Calcd for $C_{16}H_{30}OS_2$ (M^+) m/e 302.1738, found m/e 302.1742.

5f: (oil) IR (neat) 2940, 2860, 1650, 1520, 1250 cm^{-1}; ^1H NMR ($CDCl_3$) δ 10.0 (s, 1 H), 3.07 (t, J = 6.7 Hz, 2 H), 2.98 (t, J = 7.1 Hz, 2 H), 2.39 (m, 2 H), 2.23 (m, 2 H), 1.29 (m, 6 H), 0.86 (t, J = 6.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 185.5, 161.0, 138.5, 31.9, 29.0, 28.6, 28.3, 27.8, 24.5, 22.5, 14.0; MS (EI, 70 eV), m/e (relative intensity) 230 (M^+, 26.5), 173 (M^+ − 57, 100), 145 (M^+ − 85, 19.0), 99 (M^+ − 131, 22.8). Calcd for $C_{11}H_{18}OS_2$ (M^+) m/e 230.0799, found m/e 230.0788.

5g: (oil) ^1H NMR ($CDCl_3$) δ 7.48 (d, J = 8.2 Hz, 2 H), 7.25 (d, J = 8.7 Hz, 2 H), 3.15 (m, 2 H), 2.90 (m, 2 H), 2.38 (s, 3 H), 2.20 (m, 4 H), 2.19 (m, 6 H), 0.78 (t, J = 3.4 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 141.5, 141.4, 141.1, 140.6, 129.7, 124.3, 32.0, 29.6, 28.7, 26.2, 24.3, 22.3, 21.4, 14.0; MS (CI, 100 eV), m/e (relative intensity) 341 (M^+ + 1, 100).

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Registry No. **1**, 73798-32-0; **2**, 100189-87-5; **5a**, 100189-88-6; **5b**, 100189-89-7; **5c**, 73813-65-7; **5d**, 100189-90-0; **5e**, 100189-91-1; **5f**, 100189-92-2; **5g**, 100189-93-3; tolyl menthyl sulfone, 3865-44-9.

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Modification of Chemical Reactivity by Cyclodextrins: Observation of Moderate Effects on Norrish Type I and Type II Photobehavior

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The photochemistry and photophysics of organic molecules in organized assemblies are being studied with great interest in order to understand the features controlling the selectivity in the photoreactions brought about by these media.[1] These studies have paved the way to an intriguing number of possibilities by which photoreactivity can be modified. In this connection, we have investigated the photobehavior of a number of phenyl alkyl ketones and α,α-dimethylphenyl alkyl ketones (Scheme I) incorporated in the hydrophobic interior of cyclodextrin cavities. It was

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