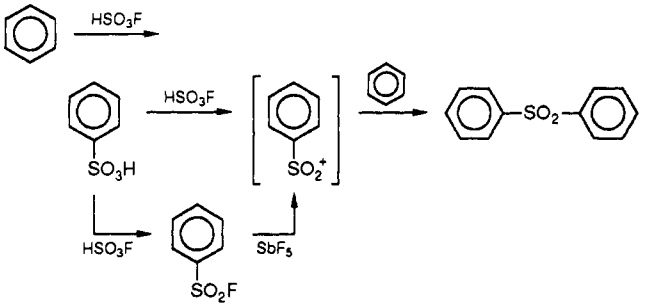
action path of diphenylsulfone can be represented as follows:



Furthermore, we found out that HSO_3F became an extremely strong sulfonation reagent by the addition of SbF_5 in disulfonyl compounds synthesis from arylsulfonyl fluorides and diaryl sulfones.[9]

In summary, the HSO_3F–SbF_5 system was useful for a one-pot synthesis of diaryl sulfones and disulfonation of aromatic compounds under mild conditions.

Experimental Section

All aromatic starting materials, HSO_3F (Moritakagaku), and SbF_5 (Aldrich) were of highest available purity and were used without further purification. A Yanagimoto G-3800 and G-6800 gas chromatography equipped with an on-line automatic integrator was used for GC analysis. A 25-m capillary column (OV-1701) and a 1.5-m packed column (FFAP) were used for isomer separation, whereas a 1.5-m packed column (OV-17) was utilized for yield determination. MS analysis (GC–MS) was performed on a Hitachi M-2000 fitted with a 50-m capillary column (OV-1701). ^{1}H-NMR spectra were recorded on a Hitachi R-24B, and ^{13}C-NMR spectra were recorded on a Nihondenshi FX-200. Infrared analysis was accomplished on a Nihonbunko IRA-1.

Sulfonation Procedures. The required amount of HSO_3F and SbF_5 were added into a 300-mL three-necked flask under temperature control, and then aromatic compounds were added with vigorous stirring into the mixture of HSO_3F and SbF_5. After the reaction was over, the reaction mixture was quenched in ice–water and extracted by benzene. Products were characterized by IR, ^{1}H-NMR, ^{13}C-NMR, and mass spectroscopy and elemental analysis, and the yields of them were determined by GC using internal standards. Products isolation was carried out by vacuum distillation or recrystallization in acetone–*n*-hexane system.

Supplementary Material Available: Spectral data for diaryl sulfones and disulfonyl compounds and the results of disulfonyl compound synthesis experiments (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.

(9) Refer to supplementary material.

A Preparation of Unsymmetrical α-Diketones

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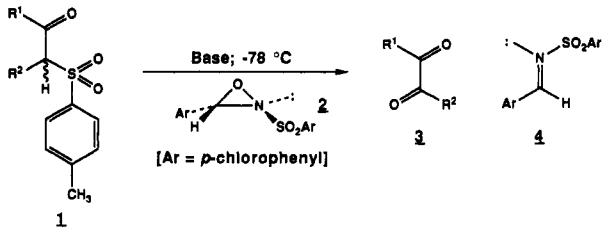
An efficient preparation of unsymmetrical α-diketones has long been of interest,[1] and several important methods have been developed.[2,3] We have sought to uncover a general and convergent strategy which would provide formation of the central carbon bond between two unsymmetrical carbonyl segments. Such a scheme would provide an efficient pathway for ongoing studies in the construction of highly oxygenated spiro ketal natural products.[4,5] In the course of our investigations, it became clear that the numerous routes for preparation of α-sulfonyl ketones, as well as the stable nature of these substances, would make them ideal starting materials. Furthermore, the direct oxidative desulfonation of alkyl, allylic, and benzylic sulfones was recently reported.[6] Herein, we wish to report a convenient procedure which allows conversion of readily available α-sulfonyl ketones **1** to the corresponding α-diketones **3** through a mild oxidative desulfonylation utilizing 2-[(*p*-chlorophenyl)sulfonyl]-3-(*p*-chlorophenyl)oxaziridine (**2**).



Pioneering efforts of Franklin Davis have documented the utility of *N*-sulfonyloxaziridines as a new family of oxidants.[7] These reagents have been used for epoxidations of alkenes,[8] heteroatom (S, Se, N) oxidations,[9] and the synthesis of alcohols and phenols from organometallic intermediates.[10] More recently this methodology has been developed as a practical route for the direct oxidation of ketone, ester, and amide enolates.[11] Furthermore, the

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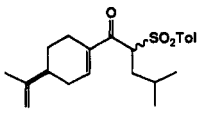
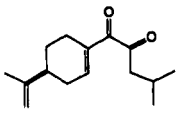
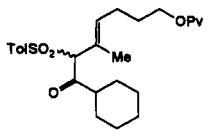
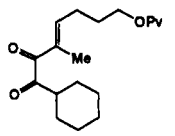
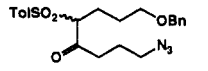
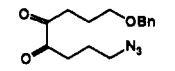
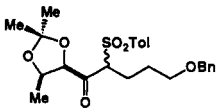
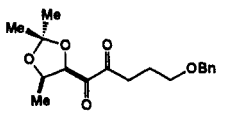
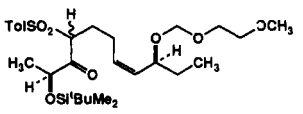
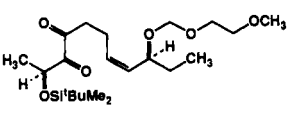
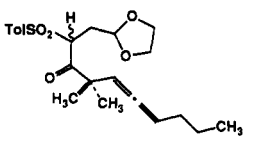
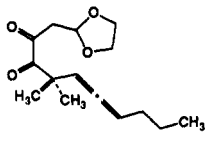
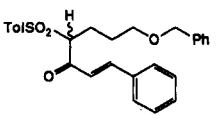
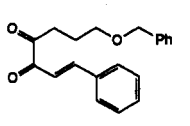
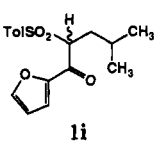
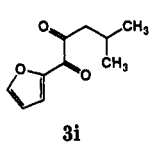
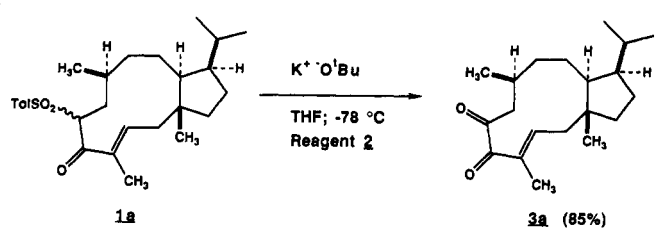
Table I. Formation of α-Diketones in THF at -78 °C

starting sulfone	product[a]	yield (%)
 1b	 3b	81
 1c	 3c	67[b]
 1d	 3d	89
 1e	 3e	83
 1f	 3f	82
 1g	 3g	81[c]
 1h	 3h	82
 1i	 3i	78[c,d]

[a] All reactions were run at -78 °C for 30 min. [b] Starting sulfone 1c was recovered (22%). [c] Solubility is achieved with THF/HMPA, ratio 4:1 by volume. [d] Solubility is achieved by addition of 18-crown-6 (1 equiv).

reagent-controlled asymmetric oxidations of enolates using chiral nonracemic *N*-sulfonyloxaziridines has been achieved.[12] Mechanistic studies have shown that the reagents transfer oxygen via a S_N2 displacement with formation of an intermediate hemiaminal,[13] and a relative rate study in a series of aryl-substituted 2-sulfonyloxaziridines has been described.[14]

We have illustrated the effectiveness of this approach with the high yielding oxidation of **1a** to afford the novel 11-membered diterpene enedione **3a**. Application of our technique to a series of functionalized α-sulfonyl ketones led to the sensitive 1,2-diketones as compiled in Table I. Potassium *tert*-butoxide in dry tetrahydrofuran (THF) generally gave the best results with formation of yellow solutions of enolates for low temperature addition of THF solutions of oxaziridine. Purified yields following flash chromatography on silica were typically in the range of 78–85%.



1a 3a (85%)

As illustrated by the examples of Table I, the reaction can be carried out in the presence of remote or conjugating alkenes, including the more reactive allenic and furanyl components (**3g** and **3i**). Conjugating olefins of enedione products may initially be present in the form of either an allylic sulfone or an α,β-unsaturated carbonyl component (examples **1a**, **1b**, **1c**, and **1h**). Additionally, no evidence for isomerization of double bond geometry has been ob-

(12) Davis, F. A.; Weismiller, M. C. *J. Org. Chem.* **1990**, *55*, 3715. Davis, F. A.; Haque, M. S.; Prezeslawski, R. M. *J. Org. Chem.* **1989**, *54*, 2021 and references therein.

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served in these products. The procedure is also tolerant of the usual ether and acetal protecting units, and no side products arising from β-eliminations of the 1,3-dioxolanes of **3e** and **3g** were observed. While the bulky pivaloate ester **1c** survived the base conditions, acetate and benzoate esters were not compatible owing to deprotections during deprotonations. Incorporation of the azido functionality (**3d**) permits masking of a basic nitrogen into these α-diketones as an entry for alkaloid synthesis. Remarkably, no evidence for epimerization of the additional α-asymmetry of **3e** or **3f** was detected.

Unfortunately, all of our oxidation attempts were not uniformly successful. The use of lithium or sodium bases led to greatly depressed yields. It has been shown that lithium enolates undergo aldol condensations with the byproduct *N*-sulfonimine (**4**) in competition with hydroxylation.[11d] In addition, enolate insolubility has occasionally led to serious problems. For some of these cases, the inclusion of hexamethylphosphoric triamide (HMPA) or addition of 18-crown-6 was beneficial in overcoming such difficulties. In one example (**1c** of Table I) the recovered starting ketone failed to exhibit deuterium incorporation upon D_2O quench subsequent to the introduction of oxaziridine **2**. However, the ketone enolate was readily deuterated in the absence of the oxaziridine. Further speculation of this point requires a more detailed mechanistic study. Recognizing that many aryl-substituted oxaziridines have been described in the literature, we can confirm that the parent 2-(phenylsulfonyl)-3-phenyloxaziridine[15] gave similar results and yields as obtained with **2** (as examined for examples **1b**, **1d**, and **1h**). Unfortunately the stable and commercially available (+)- and (−)-(camphorylsulfonyl)oxaziridines suffered from a lack of sufficient reactivity and solubility under our conditions.

In summary, this mild oxidative desulfonylation allows for the formation of functionalized, unsymmetrical α-diketones with complete regiocontrol. The procedure is applicable to both cyclic and acyclic systems. It is a useful addition to the methodology previously reported and broadens the scope of synthetic strategies which utilize the condensations of α-sulfonyl carbanions with a variety of carbonyl derivatives.

Experimental Section

General Methods. ^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ (300 MHz for ^1H and 75.5 MHz for ^{13}C). THF was distilled from sodium benzophenone ketyl under Ar. Precoated glass plates 60F-254 (E. Merck, 0.25 or 0.50 mm thickness) were used for preparative TLC. All reactions were run under Ar for 0.5 h. All yields are reported for purified products isolated after flash chromatography on silica gel (E. Merck 60; 230–400 mesh). HRMS data were collected under the same conditions as reported for the corresponding low resolution spectrum for each substance. The product diketones were insufficiently stable when stored at rt to send for elemental combustion analysis. All products were obtained as oils which were pure as indicated by TLC and ^{13}C NMR data.

Preparation of 2-[(*p*-Chlorophenyl)sulfonyl]-3-(*p*-chlorophenyl)oxaziridine (2). A mixture of *p*-chlorobenzaldehyde (10.3 g, 73.3 mmol), *p*-chlorosulfonamide (14.0 g, 73.3 mmol), powdered 5-Å molecular sieves (11 g), Amberlyst 15 ion-exchange resin (200 mg), and toluene (120 mL) was heated at reflux for 16 h. Water was removed by a Dean–Stark trap. Upon cooling to rt, the mixture was filtered and concentrated to a yellow solid which was triturated with pentanes. This crude sulfonimine **4** was characterized and used without further purification: ^1H NMR δ 9.02 (s, 1 H), 7.94 (d, J = 8.7 Hz, 2 H), 7.87 (d, J = 8.7 Hz, 2 H), 7.53 (d, J = 8.4 Hz, 2 H), 7.48 (d, J = 8.4 Hz, 2 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 129.46, 129.50, 129.66, 130.58, 132.45, 136.50, 140.38, 141.80, 169.48.

The *N*-sulfonimine **4** (3.00 g, 9.55 mmol), toluene (140 mL), K_2CO_3 (28 g, 200 mmol), and water were combined with vigorous stirring. Oxone (potassium peroxymonosulfate, 29 g, 47 mmol, 5 equiv) was added in small portions over 30 min. The reaction mixture was stirred at rt for 2 h and then transferred to a separatory funnel. The aqueous layer was removed and washed with toluene (80 mL). The organic layers were combined, washed with aqueous 10% Na_2SO_3 (100 mL), dried (Na_2SO_4), filtered, and concentrated below 40 °C to a thick oil, which was purified by flash chromatography (silica gel; toluene/hexanes 7:3 v/v). The oxaziridine **2** was triturated with hexanes to provide a fine white solid (2.43 g, 77% yield), which was judged to be pure on the basis of melting point (mp 107.5–108 °C) and NMR data: ^1H NMR δ 7.96 (d, J = 8.7 Hz, 2 H), 7.59 (d, J = 8.4 Hz, 2 H), 7.36 (s, 4 H), 5.49 (s, 1 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 75.70, 128.75, 129.05, 129.52, 129.74, 130.69, 132.94, 137.69, 142.02. Oxaziridine **2** prepared in this manner was routinely dried in vacuo (1.5 h), placed under argon, and stored in the freezer (−20 °C) until needed.[16]

Preparation of α-Sulfonyl Ketone 1a. A Representative Swern Oxidation Procedure. Addition of dimethyl sulfoxide (7 μL, 85 mg, 1.08 mmol) to a solution of oxalyl chloride (47 μL, 68 mg, 0.54 mmol) in CH_2Cl_2 (2 mL) at −78 °C resulted in vigorous formation of a white precipitate. After 10 min, a solution of a 1:1 mixture of diastereomeric β-hydroxy sulfones corresponding to **1a** (200 mg, 0.45 mmol) in CH_2Cl_2 (2 mL) was added. The reaction was stirred at −78 °C for 20 min, treated with triethylamine (188 μL, 136 mg, 1.35 mmol), and allowed to warm to rt. The mixture was diluted with EtOAc (10 mL) and washed with saturated aqueous NH_4Cl (2 × 5 mL). The organic phase was dried (Na_2SO_4) and purified by flash chromatography (silica gel, 20% EtOAc/Hexanes) to provide a 1:1 ratio of epimeric α-sulfonyl ketones **1a** as a foamy white solid (190 mg, 95%): mp 181–182 °C; $[\alpha]^{24}_D$ +3.6° (*c* 0.7, $CHCl_3$); IR ($CHCl_3$) 2950, 1665, 1600, 1450, 1380, 1305, 1235, 1135 cm^{-1}; ^1H NMR (diastereoisomer A) δ 7.81 (d, J = 8.0 Hz, 2 H), 7.34 (d, J = 8.0 Hz, 2 H), 6.70 (m, 1 H), 4.72 (dd, J = 9.8 Hz, J = 2.3 Hz, 1 H), 2.45 (s, 3 H), 2.28 (AB of ABX, J_{AB} = 12.0 Hz, J_{AX} = 9.0 Hz, J_{BX} = 2.7 Hz, $\Delta\nu_{AB}$ = 83.5 Hz, 2 H), 1.88 (m, 1 H), 1.75 (s, 3 H), 1.80–1.15 (m, 11 H), 1.00 (m, 2 H), 0.96 (d, J = 6.2 Hz, 3 H), 0.87 (d, J = 6.2 Hz, 3 H), 0.86 (d, J = 6.2 Hz, 3 H), 0.80 (s, 3 H); MS (CI, NH_3) *m/e* (relative intensity) 445 (1), 290 (56), 137 (71), 109 (100), 95 (99), 81 (93); HRMS *m/e* calcd for $C_{27}H_{41}O_3S$ (M^+ +1) 445.2778, found 445.2773; ^1H NMR (diastereoisomer B) δ 7.82 (d, J = 7.5 Hz, 2 H), 7.35 (d, J = 7.5 Hz, 2 H), 6.80 (m, 1 H), 5.06 (dd, J = 12.5 Hz, J = 3.9 Hz, 1 H), 2.45 (s, 3 H), 2.28 (AB of ABX, J_{AB} = 12.9 Hz, J_{AX} = 13.1 Hz, J_{BX} = 3.3 Hz, $\Delta\nu_{AB}$ = 49.1 Hz, 2 H), 1.85 (m, 1 H), 1.76 (s, 3 H), 1.62–0.96 (m, 13 H), 1.23 (s, 3 H), 0.85 (d, J = 6.2 Hz, 3 H), 0.82 (d, J = 5.5 Hz, 3 H), 0.73 (d, J = 5.5 Hz, 3 H); MS (CI, NH_3, 25 eV) *m/e* (relative intensity) 445 (3), 289 (51), 271 (7), 157 (21), 151 (20), 123 (55), 95 (89), 81 (100); HRMS *m/e* calcd for $C_{27}H_{40}O_3S$ (M^+) 444.2700, found 444.2684.

This standard Swern oxidation protocol[17] has been used to generate high yields of the starting α-sulfonyl ketones **1b**, **1c**, **1d**, **1f**, and **1g** of Table I from their corresponding alcohols.

Preparation of α-Sulfonyl Ketone 1j. A Representative Acylation of Sulfone Stabilized Carbanions. An ethereal solution (2 mL) of 1-[(*p*-methylphenyl)sulfonyl]-3-methylbutane (500 mg, 2.21 mmol) was added dropwise to a 1 M solution of *N*-lithiohexamethyldisilazide (2.2 mL) in THF. After 5 min, methyl 2-furoate (0.12 mL, 1.2 mmol) was added dropwise in dry ether (1 M solution). At approximately 5-min intervals, a second aliquot of lithium hexamethyldisilazide (1.1 mL) and methyl

(15) For a preparation of 2-(phenylsulfonyl)-3-phenyloxaziridine: Vishwakarma, L. C.; Stringer, O. D.; Davis, F. A. *Org. Synth.* **1987**, *66*, 203. However, our material was prepared using the Oxone method described in the Experimental Section. See also our ref 17.

(16) Samples of our reagent oxaziridine **2** gave much more consistent oxidation results when prepared according to the Oxone method as compared to material from sulfonimine oxidation with *m*-chloroperbenzoic acid. Davis, F. A.; Chattopadhyay, S.; Towson, J. C.; Lal, S.; Reddy, T. *J. Org. Chem.* **1988**, *53*, 2087. Reagent **2** could be stored at −20 °C under argon for several months without an appreciable decrease in reactivity.

(17) Mancuso, A. J.; Huang, S.-L.; Swern, D. J. *J. Org. Chem.* **1978**, *43*, 2480.

furoate solution (0.06 mL, 0.6 mmol) were added. This sequential addition was repeated one additional time (1 M lithium hexamethyldisilazide, 1.1 mL, and 1 M methyl furoate, 0.06 mL) with subsequent stirring for 15 min followed by aqueous NH_4Cl quench (14 mL). The organic layer was separated, dried ($MgSO_4$), filtered, and concentrated to a thick brown oil. Purification by flash chromatography (silica gel; 10% Et_2O/30% CH_2Cl_2/60% Hex; R_f = 0.25) afforded 540 mg (1.69 mmol, 76% yield) of the keto sulfone **1i** as a white crystalline solid: mp 118–119 °C (CH_2Cl_2); IR (Nujol mull) 2910, 2850, 1650, 1455, 1375, 1300, 1200, 1130 cm^{-1}; ^1H NMR δ 7.67 (d, J = 9.0 Hz, 2 H), 7.61 (d, J = 1.5 Hz, 1 H), 7.28–7.31 (m, 3 H), 6.56 (dd, J = 3.3 Hz, J = 1.5 Hz, 1 H), 4.97 (dd, J = 12.0 Hz, J = 3.0 Hz, 1 H), 2.40 (s, 3 H), 2.08 (ddd, J = 13.0 Hz, J = 12.0 Hz, J = 5.1 Hz, 1 H), 1.86 (ddd, J = 13.0 Hz, J = 9.0 Hz, J = 3.0 Hz, 1 H), 1.47–1.56 (m, 1 H), 0.86 (d, J = 6.6 Hz, 3 H), 0.84 (d, J = 6.3 Hz, 3 H); ^{13}C NMR δ 180.1, 152.5, 147.7, 145.0, 143.6, 129.3 (two overlapping signals), 119.3, 112.9, 68.9, 35.3, 25.7, 22.8, 21.3 (two signals); HRMS (CI, NH_3) m/e calcd for $C_{17}H_{21}O_4S$ (M^+) 321.1161, found 321.1131.

This standard acylation method was used to afford starting ketones **1e**, **1h**, and **1i** from Table I in yields ranging from 47 to 76%. Alternatively, the α-sulfonyl ketones can be routinely prepared via the oxidation of β-keto sulfides or by the alkylations of enolates derived from α-sulfonyl ketones.[18]

Representative Oxidation Procedure with Oxaziridine 2. (3*E*)-(1*R*,8*S*,11*S*,12*R*)-1,4,8-Trimethyl-12-isopropylbicyclo[9.3.0]tetradec-3(4)-ene-5,6-dione (3a). A solution of the α-sulfonyl ketone **1a** (274 mg, 0.62 mmol) in THF (7 mL) was added dropwise via syringe to a suspension of potassium *tert*-butoxide (92 mg, 0.82 mmol) in THF (3 mL) at 22 °C. The resulting bright yellow solution was stirred at rt for 0.5 h and then cooled to −78 °C. A solution of oxaziridine **2** (432 mg, 1.31 mmol) in dry THF (1.5 mL) was added dropwise to the solution of α-sulfonyl anion at −78 °C. After 0.5 h, the reaction was quenched by the addition of saturated aqueous NH_4Cl (5 mL) and allowed to warm to rt. The mixture was diluted with H_2O (10 mL), and the aqueous phase was extracted with EtOAc (4 × 10 mL). The combined organic phase was dried (Na_2SO_4) and concentrated to a thick oil. Purification by flash chromatography on silica gel (5% EtOAc/hexanes) provided the pure diketone **3a** as a viscous yellow oil (161 mg, 86%): IR (neat) 2950, 1705, 1665, 1635, 1450, 1380, 1375, 1210, 1000 cm^{-1}; UV ($CHCl_3$) λ_{max} 360 (63); ^1H NMR δ 6.64 (m, 1 H), 2.47 (AB of ABX, J_{AB} = 12.9 Hz, J_{AX} = 12.5 Hz, J_{BX} = 2.7 Hz, $\Delta\nu_{AB}$ = 184.5 Hz, 2 H), 2.34 (AB of ABX, J_{AB} = 14.1 Hz, J_{AX} = 11.6 Hz, J_{BX} = 4.1 Hz, $\Delta\nu_{AB}$ = 26.7 Hz, 2 H), 1.85 (s, 3 H), 1.80 (m, 1 H), 1.62–1.32 (m, 7 H), 1.31–1.12 (m, 4 H), 1.09 (s, 3 H), 0.98 (d, J = 7.0 Hz, 3 H), 0.87 (d, J = 5.9 Hz, 3 H), 0.81 (d, J = 5.9 Hz, 3 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 208.0, 199.2, 153.2, 134.6, 53.5, 49.4, 45.7, 45.4, 44.7, 41.4, 34.1, 28.3, 27.7, 26.4, 23.8, 22.2, 22.1, 21.0, 20.9, 10.1; MS (CI, NH_3) m/e (relative intensity) 305 (11), 304 (19), 289 (17), 262 (19), 261 (100), 233 (35), 215 (52), 195 (28); HRMS m/e calcd for $C_{20}H_{33}O_2$ (M^+ + 1) 305.2482, found 305.2477.

Spectral data for the representative examples of Table I are listed below.

(4*S*)-1-(4-Methyl-2-oxopentanoyl)-4-isopropenylcyclohex-1-ene (3b): 281 mg, 1.20 mmol (81%); IR (neat) 2950, 1700, 1655, 1630, 1445, 1250, 1140, 890 cm^{-1}; UV ($CHCl_3$) λ_{max} 374 (23); ^1H NMR δ 6.95 (m, 1 H), 4.75 (m, 2 H), 2.47 (m, 2 H), 2.19 (m, 4 H), 1.94 (m, 1 H), 1.75 (s, 3 H), 1.55–1.40 (m, 3 H), 0.97 (d, J = 6.6 Hz, 6 H); MS (CI, NH_3) m/e (relative intensity) 150 (11), 149 (100), 93 (32), 81 (10), 79 (22); HRMS m/e calcd for $C_{15}H_{22}O_2$ (M^+) 234.1621, found 234.1627.

(*E*)-1-Cyclohexyl-3-methyl-7-[(2,2-dimethylpropanoyl)oxy]hept-3-ene-1,2-dione (3c): 160 mg, 0.50 mmol (67%); IR (neat) 2940, 2860, 1730, 1710, 1660, 1635, 1450, 1285, 1155, 1035 cm^{-1}; UV ($CHCl_3$) λ_{max} 376 (28); ^1H NMR δ 6.48 (m, 1 H), 4.07 (t, J = 6.6 Hz, 2 H), 2.87 (m, 1 H), 2.39 (m, 2 H), 1.84 (s, 3 H), 1.84–1.70 (m, 6 H), 1.36–1.20 (m, 6 H), 1.21 (s, 9 H); MS (CI, NH_3) m/e (relative intensity) 127 (100), 109 (44), 85 (31), 83 (97), 81 (61); HRMS m/e calcd for $C_{19}H_{30}O_4$ (M^+) 323.2223, found 323.2216.

8-Azido-1-(benzyloxy)octane-4,5-dione (3d): 18 mg, 0.062 mmol (89%); IR (neat) 2920, 2860, 2100, 1710, 1455, 1400, 1360, 1275, 1100, 955 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.32–7.28 (m, 5 H), 4.41 (m, 2 H), 3.50 (t, J = 5.9 Hz, 2 H), 3.21 (t, J = 6.9 Hz, 2 H), 2.81 (t, J = 6.8 Hz, 2 H), 2.66 (t, J = 7.3 Hz, 2 H), 1.97 (m, 2 H), 1.77 (m, 2 H); ^{13}C NMR δ 191.6, 128.4, 127.8, 127.7, 72.9, 69.9, 50.6, 33.5, 32.9, 24.6, 22.5; MS (CI, NH_3, 40 eV) m/e (relative intensity) 231 (5), 181 (10), 131 (14), 112 (11), 91 (100); HRMS m/e calcd for $C_{15}H_{19}N_3O_2 - C_4H_6N_3O$ ($M^+ - C_4H_6N_3O$) 177.0916, found 177.0916.

(4*R*,5*S*)-4-[5-(Benzyloxy)-1,2-dioxopentyl]-2,2,5-trimethyl-1,3-dioxolane (3e): 65 mg, 0.203 mmol (83%); IR (neat) 2930, 1715, 1600, 1450, 1380, 1095, 695 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.35–7.20 (m, 5 H), 5.16 (d, J = 7.8 Hz, 1 H), 4.64 (dq, J = 7.8 Hz, J = 6.4 Hz, 1 H), 4.44 (s, 2 H), 3.48 (m, 2 H), 2.85 (m, 2 H), 1.96 (m, 2 H), 1.06 (d, J = 6.4 Hz, 3 H); MS (CI, NH_3) m/e (relative intensity) 181 (5), 177 (3), 169 (3), 115 (44), 91 (100); HRMS m/e calcd for $C_{18}H_{24}O_5 - C_3H_6O$ (M^+ − acetone) 262.1205, found 262.1210.

(6*Z*)-(1*S*,8*S*)-1-[(*tert*-Butyldimethylsilyl)oxy]-8-[(2-methoxyethoxy)methoxy]-1-methyl-6-decene-2,3-dione (3f): 50 mg, 0.088 mmol (82%); IR (neat) 2940, 2890, 2865, 1716, 1465, 1255, 1105, 1040, 840, 780 cm^{-1}; ^1H NMR δ 5.56 (m, 1 H), 5.38 (m, 1 H), 4.67 (AB, J_{AB} = 6.9 Hz, $\Delta\nu$ = 45.8 Hz, 2 H), 4.33 (dt, J = 6.7 Hz, J = 9.4 Hz, 1 H), 3.85–3.55 (m, 5 H), 3.51 (s, 3 H), 2.9 (m, 1 H), 2.65 (m, 1 H), 2.40 (m, 2 H), 1.68 (m, 1 H), 1.48 (m, 1 H), 1.06 (d, J = 6.9 Hz, 3 H), 0.91 (t, J = 7.4 Hz, 3 H), 0.83 (s, 9 H), 0.01 (s, 6 H); ^{13}C NMR δ 202.4, 199.2, 131.25, 131.23, 92.6, 72.3, 71.8, 66.8, 65.3, 59.0, 41.9, 41.8, 36.2, 28.4, 25.7, 21.1, 18.2, 12.2, 9.8, 2.23, 2.18; MS (CI, NH_3) m/e (relative intensity) 325.2 (10), 283.1 (6), 267.1 (8), 201.1 (10), 193.1 (9), 131.0 (15), 89.1 (100); HRMS m/e calcd for $C_{19}H_{35}O_5Si$ (M^+ + 1 − C_2H_5O) 371.2282, found 371.2254.

1-Dioxolanyl-4,4-dimethyl-5,6-decadiene-2,3-dione (3g): 40 mg, 0.098 mmol (81%); IR (neat) 2980, 2950, 2890, 1935, 1775, 1712, 1455, 1390, 1140, 1035, 950, 918 cm^{-1}; ^1H NMR δ 5.36 (m, 1 H), 5.27 (m, 2 H), 3.97 (m, 2 H), 3.87 (m, 2 H), 3.07 (d, J = 5.0 Hz, 2 H), 1.97 (m, 2 H), 1.40 (m, 2 H), 1.33 (d, J = 4.8 Hz, 6 H), 0.92 (t, J = 7.3 Hz, 3 H); ^{13}C NMR δ 203.7, 202.1, 197.5, 100.4, 95.8, 94.5, 64.9, 45.5, 43.5, 30.7, 24.5, 24.5, 22.3, 13.7; MS (CI,NH_3) m/e (relative intensity) 267.2 (2), 151.1 (48), 123.1 (23), 81.1 (40), 73.0 (100); HRMS m/e calcd for $C_{15}H_{23}O_4$ (M^+ + 1) 267.1597, found 267.1596.

(1*E*)-7-(Benzyloxy)-1-phenyl-1-heptene-3,4-dione (3h): 30 mg, 0.067 mmol (82%); IR ($CHCl_3$ film) 3075, 3040, 2940, 2870, 1715, 1685, 1655, 1605, 1580, 1455, 1100, 990 cm^{-1}; ^1H NMR δ 7.78 (d, J = 16.1 Hz, 1 H), 7.60–7.20 (m, 11 H), 4.45 (s, 2 H), 3.52 (t, J = 5.9 Hz, 2 H), 2.95 (t, J = 7.0 Hz, 2 H), 2.0 (m, 2 H); ^{13}C NMR δ 200.9, 187.3, 147.2, 138.1, 134.5, 131.2, 130.4, 129.4, 128.95, 128.9, 128.7, 128.2, 127.7, 127.62, 127.56, 118.6, 72.9, 69.2, 33.9, 24.2; MS (CI, NH_3) m/e (relative intensity) 201.1 (12), 132.0 (10), 131.0 (100), 103.0 (12), 91.1 (63); HRMS m/e calcd for $C_{20}H_{21}O_3$ (M^+ + 1) 309.1491, found 309.1491.

2-(4-Methyl-2-oxopentanoyl)furan (3i): 41 mg, 0.128 mmol (78%); IR (neat) 3170, 2980, 2890, 1790, 1720, 1670, 1565, 1460, 1400, 1030, 890, 780 cm^{-1}; ^1H NMR δ 7.74 (d, J = 1.2 Hz, 1 H), 7.63 (d, J = 3.5 Hz, 1 H), 6.60 (dd, 1.6, J = 3.5 Hz, 1 H), 2.78 (d, J = 6.87 Hz, 2 H), 2.20 (m, 1 H), 0.97 (d, J = 6.6 Hz, 6 H); ^{13}C NMR δ 200.2, 176.8, 149.2, 148.8, 124.5, 112.9, 46.1, 24.2, 22.5; MS (CI, NH_3) m/e (relative intensity) 181.1 (72), 180.1 (56), 138.1 (35), 131.0 (24), 85.1 (100); HRMS m/e calcd for $C_{10}H_{13}O_3$ (M^+ + 1) 181.0865, found 181.0864.

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Registry No. **1a** (isomer 1), 141375-05-5; **1a** (isomer 2), 141434-75-5; **1a** (alcohol), 141375-07-7; **1b** (isomer 1), 141375-08-8; **1b** (isomer 2), 141375-09-9; **1b** (alcohol), 141375-11-3; **1c**, 141375-12-4; **1c** (alcohol), 141375-14-6; **1d**, 141375-15-7; **1d** (al-

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cohol), 141375-17-9; **1e** (isomer 1), 141375-18-0; **1e** (isomer 2), 141375-19-1; **1f** (isomer 1), 141375-21-5; **1f** (isomer 2), 141434-76-6; **1f** (alcohol), 141375-23-7; **1g** (isomer 1), 141375-24-8; **1g** (isomer 2), 141375-25-9; **1g** (alcohol), 141375-27-1; **1h**, 141375-28-2; **1i**, 141375-30-6; **2** (Ar = *p*-chlorophenyl), 141375-32-8; **3a**, 141375-06-6; **3b**, 141375-10-2; **3c**, 141375-13-5; **3d**, 141375-16-8; **3e**, 141375-20-4; **3f**, 141375-22-6; **3g**, 141375-26-0; **3h**, 141375-29-3; **3i**, 141375-31-7; **4** (Ar = *p*-chlorophenyl), 141375-33-9; $4\text{-}ClC_6H_4CHO$, 104-88-1; $4\text{-}ClC_6H_4SO_2NH_2$, 98-64-6; $PhCH_2O(CH_2)_4Ts$, 141375-34-0; $Ts\text{-}(CH_2)_2CH(CH_3)_2$, 91485-21-1; methyl furoate, 611-13-2.

Supplementary Material Available: Proton and carbon NMR spectra for products (15 pages). Ordering information is given on any current masthead page.

Synthesis and Alkali Metal Binding Properties of "Upper Rim" Functionalized Calix[4]arenes[1]

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Introduction

The calixarenes are receiving considerable attention as starting materials for the preparation of novel hosts, ligands, and pores.[3-6] Of special interest, in this regard, has been the use of the *cone*-conformer of calix[4]arenes. Previous studies have shown that certain lower rim (phenolic side) ester and amide derivatives of calix[4]arene cones are effective in extracting alkali metal picrates from water into chloroform and that sodium salts are strongly favored.[3,4,7-9] To date, no effort has been made to examine the extracting behavior of upper-rim analogs. Because of the splay that is inherent in the calix[4]arene framework, one might expect that placement of ligands on the upper rim could result in stronger binding toward larger metal ions and that extraction of potassium or cesium salts might be favored. The fact that calix[4]arenes have moderate flexibility, however, makes it difficult to predict their precise complexation and selectivity features.[10] In order to probe this issue, we have synthesized calixarenes **I-III**, and have compared their extracting behavior with those previously reported for a lower-rim functionalized ester (**IV**).[7] This paper reports our principal findings.

Scheme I

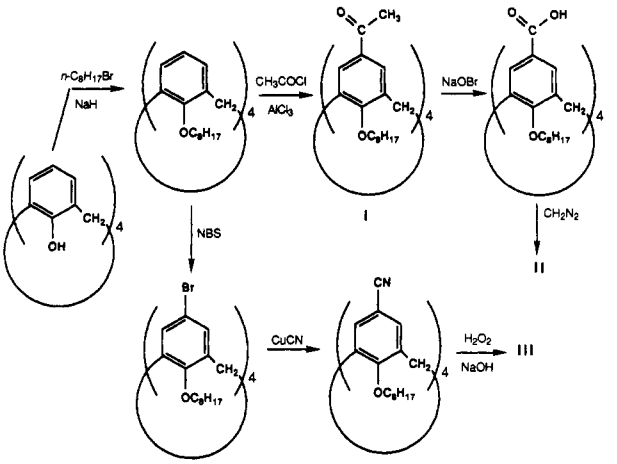
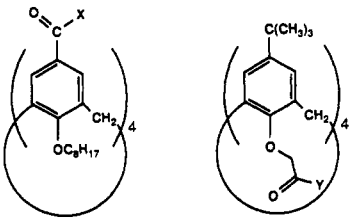


Table I. Extraction Equilibrium Constants for Picrate Salts by I-III

	$10^{-5} K_e$[a]			
calixarene	Li^+	Na^+	K^+	Cs^+
I	0.122 ± 0.011	1.411 ± 0.088	0.686 ± 0.054	0.109 ± 0.008
II	0.152 ± 0.007	0.842 ± 0.078	1.295 ± 0.142	0.102 ± 0.014
III	0.062 ± 0.007	1.463 ± 0.029	1.084 ± 0.139	0.489 ± 0.066
IV[b]	0.056	11.3	0.1	0.11

[a] Average of three to five independent experiments, using [calixarene] = 1×10^{-3} M; $[Li^+] = 8.4 \times 10^{-3}$; $[Na^+] = [K^+] = 1.0 \times 10^{-3}$; $[Cs^+] = 4.8 \times 10^{-3}$; error values represent one standard deviation of the mean. [b] See ref 7.



Results and Discussion

Alkylation of 25,26,27,28-tetrahydroxycalix[4]arene[11] with 1-bromooctane afforded the corresponding tetrakis(*n*-octyloxy) ether, which was readily isolated as the cone isomer. Friedel-Crafts acylation (CH_3COCl) of this tetraether afforded **I**; subsequent haloform oxidation, and esterification (CH_2N_2), yielded **II**. Calixarene **III** was prepared by bromination of the starting tetrakis(*n*-octyloxy) ether (NBS), followed by sequential displacement with cyanide and hydrolysis (Scheme I).

Specific methods that we have used for extracting alkali metal picrates from water into chloroform were similar to those previously described.[7,12] Extraction constants (K_e), which define the equilibrium shown in eq 1, were calculated using eq 2. Here, M^+_{aq} and Pi^-_{aq} represent the alkali cation and picrate anion that is present in the aqueous phase, and L_{org} and $\{LM^+,PI^-_{org}\}$ are the ligand and ligand-metal picrate complex in chloroform, respectively; the activity coefficients, γ^2, that have been used to calculate K_e values were 0.88 and 0.95, when employing 5×10^{-3} and 1×10^{-3} M picrate solutions, respectively.[12]

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