Figure 2. ^{13}C NMR spectra of the uranyl tricarbonate–bicarbonate–carbonic acid system. Scale is shown on the a spectrum. The d and e samples are identical.

broaden, collapsing to a 164.77-ppm singlet at 58 ± 2 °C.[6] When the room temperature δ values are used, the position of the fast exchange singlet can be calculated from eq 1, by using standard

$$\delta_{CO_3^{2-},av} = \delta_{HCO_3^-} + (1 - x_{HCO_3^-})(\delta_{UO_2(CO_3)_3^{4-}} - \delta_{HCO_3^-}) \quad (1)$$

NMR theory.[7] Assuming the complex is indeed the tricarbonate complex, its mole fraction $(1 - x_{HCO_3^-})$ would be 0.366. If the appropriate numbers are substituted in eq 1, the δ value for the collapsed singlet is given by

$$\delta_{CO_3^{2-},av} = 162.31 + 0.366(168.86 - 162.31) = 164.71$$

which is in excellent agreement with the measured value.

More extensive variable temperature studies were undertaken to gain a measure of the E_a for carbonate exchange. The spectra were obtained at pH 9.1 by using a 90% ^{13}C label. Theoretical spectra were calculated by assuming relaxation and instrumental broadening were negligible compared to the observed line widths. The derived rates were found by systematically adjusting the input exchange rates to reproduce the observed spectra. Trial values were obtained by using the slow and rapid line width (T$_2$) approximations[8] for the low- and high-temperature experimental cases. The program used was similar to that of Binsch.[9] Figure 1 shows examples of some of these experimental and theoretical curves. An Arrhenius plot gives an E_a value of 13.00 kcal with a preexponential factor of 9.24×10^{10}.

It was observed that carbonate transfer increased markedly with lowering of pH. This is illustrated in Figure 2. Note that at pH 7.06 at room temperature the spectrum is almost a singlet, but the separate peaks can be resolved at 16 °C. Also note the presence of dissolved CO$_2$ (125.8 ppm) at the lower pH's.

At pH <7 considerably more complex spectra are obtained. They feature a sharp peak at 169.9 ppm plus envelopes of broader peaks at smaller δ values. These spectra probably stem from uranyl carbonate dimers or trimers and will be the subject of our further investigations.

Concerted Ring-Opening Reaction of Cyclobutenes. The Extraordinary Accelerating Effects of Arylsulfoxy and Sulfonyl Carbanion Substituents

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Over the years, thermal ring opening of cyclobutenes has held the attention of physical organic chemists[1] and has proven to be

(6) Only insignificant changes were noted in the δ value of the ^{13}CH$_3$OH reference in the temperature range 7-70 °C.
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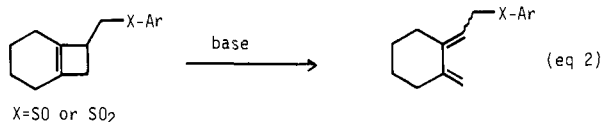
Table I. Ring-Opening Reactions of Cyclobutenes[a]

Entry	Cyclobutenes (Rf values)[b]	Products (%) (Rf values)[b]

Scheme I

[a] (i) Li, NH$_3$, THF, EtOH, -78 °C; (ii) ethylene glycol, p-TsOH, CH$_2$Cl$_2$, room temperature; (iii) TsCl, pyridine; (iv) NaI, THF, reflux; (v) sodium p-toluenesulfinate, DMF, 60 °C; (vi) PhSNa, THF, room temperature; (vii) 1 equivalent of MCPBA, CH$_2$Cl$_2$, room temperature.

Scheme II

[a] All reactions were carried out in THF at -30 °C for 10 min, using n-butyllithium as base, and the yield was not optimized. All compounds appearing in this table are fully characterized by analytical and spectral data. [b] R$_f$ values were taken on silica gel 60 F-254, developing with CH$_2$Cl$_2$:EtOAc (9:1). [c] Reference 11.

one of the most useful reactions for generating diene systems (eq 1) which have been widely used in the synthesis of natural products.[2]

(eq 1)
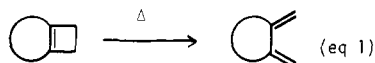
Herein we wish to report our observations on the exceptionally facile ring-opening reaction of cyclobutenes, facilitated by arylsulfoxy and sulfonyl carbanion.[3] The systems chosen for study were the (arylsulfoxy)- and (arylsulfonyl)methylcyclobutenes (eq 2), dienes generated from them constituting an essential part of the skeleton of the vitamin D series.[4]

(eq 2)

X = SO or SO$_2$

The syntheses of compounds **4-6**,[5] which were used for this

study, was straightforward (Scheme I). Birch reduction of (benzocyclobutenyl)methyl alcohol **1**,[6] followed by ketalization, afforded **2** which was subsequently treated with tosyl chloride in pyridine and sodium iodide to give iodide **3**. Compound **4** was prepared by treating **3** with sodium p-toluenesulfinate, and compounds **6** and **5** were derived from **3** by successive treatment with sodium thiophenolate and 1 and 2 equiv of m-chloroperbenzoic acid, respectively.

The butene ring-opening reaction was usually carried out at -30 °C by using n-butyllithium as a base (Table I). The following experimental procedure is representative of this reaction. To a stirred solution of 167 mg (0.5 mmol) of 3,3-(ethylenedioxy)-7-(p-toluenesulfonyl)methylbicyclo[4.2.0]oct-1(6)-ene (**4**) in 3 mL of tetrahydrofuran under nitrogen at -78 °C was added 0.4 mL (0.6 mmol) of a 1.5 M solution of n-butyllithium in hexane and the temperature was raised to -30 °C. After the mixture had been stirred for 10 min at this temperature, saturated aqueous ammonium chloride was added and the mixture was extracted with methylene chloride. The extract was washed with water and dried over anhydrous Na$_2$SO$_4$. The residue resulting from evaporation of solvent was chromatographed on silica gel, using benzene as eluant, to produce 150 mg (90%) of the diene **11**;[7]
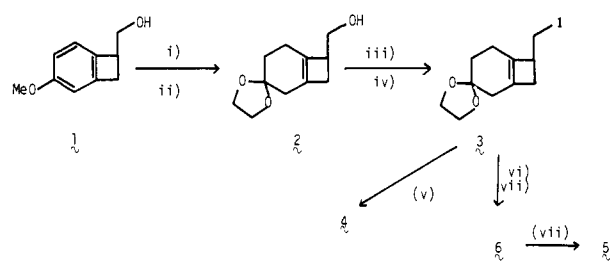
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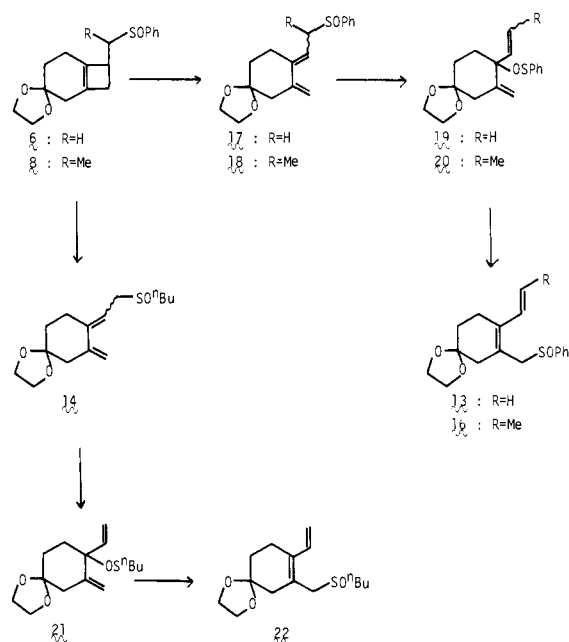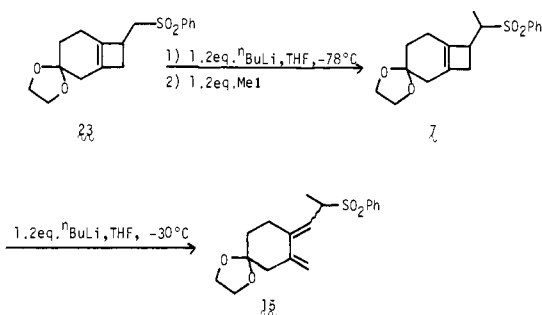
(5) **4**: mp 131-132 °C; NMR (CCl$_4$) δ 2.41 (s, 3 H), 3.1 (br s, 2 H), 3.80 (s, 4 H), 7.24 (d, *J* = 8 Hz, 2 H), 7.65 (d, *J* = 8 Hz, 2 H); *m/e* 334 (M$^+$). **6**: oil; NMR (CCl$_4$) δ 2.9 (m, 2 H), 3.85 (s, 4 H), 7.5 (br s, 5 H); *m/e* 304 (M$^+$). **5**: oil; NMR (CCl$_4$) δ 3.15 (br s, 2 H), 3.83 (s, 4 H), 7.4-8.0 (m, 5 H); *m/e* 320 (M$^+$).

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Scheme III

compound **10**[7] was obtained by a similar treatment of **5**.

In case of sulfoxy compounds **6** and **8**, the compounds which resulted from subjecting them to the same reaction conditions as **4** were **13**, **14**, and **16**,[8] respectively. The formation of **13** and **16** could be explained by the intervention of double [2.3] sigmatropic rearrangement of the initial products **17** and **18** via **19** and **20**. Actually compound **14**, which resulted from nucleophilic substitution of the phenyl group of compound **6** by *n*-butyl on treatment with *n*-butyllithium followed by ring opening, was transformed quantitatively into compound **22**[9] on standing at room temperature via **21** (Scheme II). In the case of compound **6** lithium diisopropylamide was also used as a base in place of *n*-butyllithium under the same conditions to give compound **13** (74.3%) as the sole product.[10]

A very attractive feature of this method of diene generation is that alkylation of **23** and **6**, involving essentially the same conditions as above, *n*-BuLi/THF, can be carried out at −78 °C, at which temperature the butene ring remains intact. Thus, compounds **7** and **8** were obtained in almost quantitative yields by using 1.2 equiv of *n*-butyllithium and 1.2 equiv of methyl iodide, 2.2 equiv of base and electrophile was used for **9** and **10**. Monomethylated compounds **7** and **8** were then subjected to a ring-opening reaction to give dienes **15** and **16**, respectively. Thus it can be seen that alkylation and/or ring-opening reactions of such butenes are readily brought about by control of the reaction temperature (Scheme III).

(7) **11**: UV (EtOH) (log ε) 238 nm (3.94); NMR (CCl₄) δ 2.45 (s, 3 H), 3.71 (d, *J* = 8 Hz, 2 H), 3.83 (s, 4 H), 4.6 (br s, 1 H), 4.86 (br s, 1 H), 5.4 (distorted t, *J* = 8 Hz, 1 H), 7.25 (d, *J* = 8 Hz, 2 H), 7.66 (d, *J* = 8 Hz, 2 H); *m/e* 334 (M⁺). To confirm its structure, **11** was treated with 10% hydrochloric acid in methanol to give **24**: IR (CHCl₃) 1665 cm⁻¹; NMR
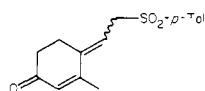
(CCl₄) δ 2.03 (s, 3 H), 2.43 (s, 3 H), 3.88 (d, *J* = 8 Hz, 2 H), 5.73 (s, 1 H), 5.85 (distorted t, *J* = 8 Hz, 1 H), 7.26 (d, *J* = 8 Hz, 2 H), 7.7 (d, *J* = 8 Hz, 2 H); *m/e* 290 (M⁺). **10**: oil; UV (EtOH) (log. ε) 237 nm (3.93); NMR (CCl₄) δ 3.76 (d, *J* = 8 Hz, 2 H), 3.84 (s, 4 H), 4.66 (br s, 1 H), 4.90 (br s, 1 H), 5.10 (distorted t, *J* = 8 Hz, 1 H), 7.40–8.0 (m, 5 H); *m/e* 320 (M⁺).

(8) **13**: oil; UV (EtOH) (ε) 243 nm (4.20); NMR (CCl₄) δ 3.4 (d, *J* = 12 Hz, 1 H), 3.7 (d, *J* = 12 Hz, 1 H), 3.85 (s, 4 H), 4.8 (d, *J* = 10 Hz, 1 H), 5.03 (d, *J* = 16 Hz, 1 H), 6.27 (dd, *J* = 10 and 16 Hz, 1 H), 7.43 (br s, 5 H); *m/e* 304 (M⁺). **14**: oil; UV (EtOH) (log ε) 235 nm (4.06); NMR (CCl₄) δ 3.38 (d, *J* = 9 Hz, 2 H), 3.9 (s, 4 H), 4.63 (br s, 1 H), 4.93 (br s, 1 H), 5.52 (t, *J* = 9 Hz, 1 H); *m/e* 284 (M⁺). **16**: oil; UV (EtOH) (log ε) 253 nm (4.09); NMR (CCl₄) δ 1.64 (d, *J* = 5 Hz, 3 H), 3.4 (d, *J* = 12 Hz, 1 H), 3.67 (d, *J* = 12 Hz, 1 H), 3.86 (s, 4 H), 5.56 (m, 1 H), 5.92 (d, *J* = 14 Hz, 1 H), 7.3–7.6 (m, 5 H); *m/e* 318 (M⁺).

(9) **22**: UV (EtOH) (log ε) 246 nm (4.17); NMR (CCl₄) δ 3.5 (br s, 1 H), 3.9 (s, 4 H), 5.05 (d, *J* = 11 Hz, 1 H), 5.2 (d, *J* = 16 Hz, 1 H), 6.68 (d, d, *J* = 11 and 16 Hz, 1 H); *m/e* 284 (M⁺).

(10) The formation of the initial product **17** was recognized in the NMR spectrum of the crude product from this experiment showing the typical olefinic signals, although this was very labile and spontaneously isomerized to give **13** on purification. **17**: oil; NMR (CDCl₃) δ 3.65 (d, *J* = 8 Hz, 2 H), 3.93 (s, 4 H), 4.66 (br s, 1 H), 4.90 (br s, 1 H), 5.39 (distorted t, *J* = 8 Hz, 1 H), 7.50 (br s, 5 H).

(11) **15**: oil; UV (EtOH) (log ε) 240 nm (3.97); NMR (CCl₄) δ 1.46 (d, *J* = 7 Hz, 3 H), 3.0–3.4 (m, 1 H), 3.87 (s, 4 H), 4.67 (br s, 1 H), 4.94 (br s, 1 H), 5.25 (d, *J* = 10 Hz, 1 H), 7.5–8.0 (m, 5 H); *m/e* 334 (M⁺).

It is clear that the presence of an active proton next to the arylsulfoxy or -sulfonyl group is critical for this new ring-opening reaction of butenes, since compounds **9** and **10**, which have no active protons, were recovered unchanged when subjected to the above treatment. We plan to report further studies on this reaction and its application to the synthesis of natural products in the near future.

Photochemistry of Metal–Metal Bonded Complexes: One-Electron Oxidation of Photogenerated Seventeen-Valence-Electron Radicals

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Though M–M bond homolysis according to eq 1 is generally

$$\text{>M–M<} \xrightarrow{h\nu} 2\cdot\text{M<} \tag{1}$$

the main result of photoexcitation[1] of metal–metal bonded complexes such as $M_2(CO)_{10}$ (M = Mn, Re)[2] and $(\eta^5\text{-}C_5H_5)_2W_2(CO)_6$,[3] efficient formation of metal carbonyl cations and anions has been observed upon irradiation of metal–metal bonded complexes in polar media.[4] We wish to report results that show that clean, 1-electron oxidation of photogenerated 17-valence-electron radicals can be an important thermal reaction pathway. Oxidation is thus added to halogen abstraction,[1–3,5] radical coupling,[1–3,6,7] radical trapping,[8] and ligand substitution[9,10] as reaction paths for the primary photoproducts from dinuclear metal–metal bonded

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