mixture was stirred for 20 h and then refluxed for 4 h.

The cooled solution was concentrated by flash evaporation and chromatographed on a 3 × 11 cm column of alumina with the following solvents: hexane (200 mL), CH_2Cl_2 (200 mL), *i*-PrOH (200 mL). The last 400 mL of solvents were combined and concentrated. Distillation of this residue afforded 600 mg of the desired crown (39.0% yield).

Acknowledgment. We thank Mr. Don Patterson for obtaining the mass spectra. We also express our sincere gratitude to Professor Mitsuo Okahara of Osaka University for his invaluable suggestions regarding this synthetic scheme and to Professor James E. Moore for his advice and patience.

Registry No. **1a**, 84812-01-1; **1b**, 84812-02-2; **1c**, 84812-03-3; **1d**, 84812-04-4; **1e**, 70069-04-4; **1f**, 84812-05-5; **2a**, 13483-49-3; **2b**, 71712-93-1; **2c**, 73692-54-3; **2d**, 106-92-3; **3a**, 84812-06-6; **3b**, 84812-07-7; **3c**, 84812-08-8; **3d**, 84812-09-9; $HOCH_2CH_2OMe$, 109-86-4; $HO(CH_2CH_2O)_2Me$, 111-77-3; $HO(CH_2CH_2O)_3Me$, 112-35-6; (chloromethyl)oxirane, 106-89-8; triethylene glycol, 112-27-6; 3-oxapentamethylene ditosylate, 7460-82-4.

Base-Induced Fragmentation of Ethanediyl *S,S*-Acetals Bearing Two Aromatic Substituents at C-2

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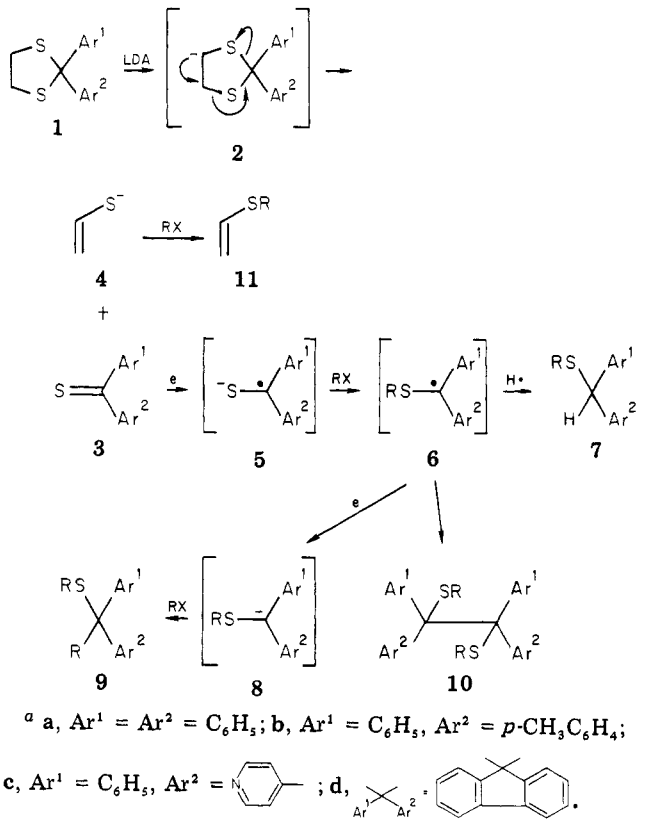
Several papers have appeared[1-6] in the literature which have dealt with the reaction involving cleavage of ethanediyl *S,S*-acetals to ethylene and dithiocarbonate. Recently, Wilson and co-workers have observed[7,8] the metalation of several ethanediyl *S,S*-acetals with *n*-butyllithium, which resulted in fragmentation to the corresponding thiocarbonyl compound and vinyl thiolate anion. The former has been further converted to thiols or sulfides via a process involving reduction, S-addition, C-addition, or double addition with excess *n*-butyllithium. We now report the fragmentation of ethanediyl *S,S*-acetals bearing two aromatic substituents at C-2 and the behavior of the resulting fragments, using the less nucleophilic lithium diisopropylamide (LDA),[9] which avoids nucleophilic butylation of the intermediate thiocarbonyl compound by *n*-butyllithium.

The reaction of the ethanediyl *S,S*-acetal of benzophenone or *p*-methylbenzophenone (**1a** or **1b**) with LDA in tetrahydrofuran proceeds via proton abstraction at C-4 followed by cycloelimination to afford the corresponding thioketone (**3a** or **3b**) and vinyl thiolate anion (**4**; Scheme I). The isolation of **3a** or **3b** was impossible, presumably because they are immediately converted to radical anions (**5**) by one-electron transfer[10] from LDA.

Scheme I[a]



[a] a, $Ar^1 = Ar^2 = C_6H_5$; b, $Ar^1 = C_6H_5$, $Ar^2 = p\text{-}CH_3C_6H_4$; c, $Ar^1 = C_6H_5$, Ar^2 = ; d, .

However, when the ethanediyl *S,S*-acetal of acetophenone[11] was submitted to similar fragmentation by LDA and subsequent protonation, the formation of thioacetophenone was evident from its characteristic color.

When the appropriate alkyl halide was added to the above reaction mixture containing **4** and **5**, the former was easily converted to the corresponding alkyl vinyl sulfide (**11**) and the latter to alkyl diarylmethyl sulfide (**7**). Though the exact mechanism is still in doubt, the radical anion **5** is thought to be alkylated with the alkyl halide to afford a radical species (**6**), which can produce the final product (**7**) by abstraction of a hydrogen radical from tetrahydrofuran.

Wilson and co-workers previously proposed[7,8] a very similar sequence for the reaction of the ethanediyl *S,S*-acetals of aliphatic ketones with *n*-butyllithium.

In this way a series of alkyl benzhydryl sulfides (**7a**) and their methylated compounds (**7b**) were produced in fairly good yields along with compounds **11** as byproducts (Table I).

When the same fragmentation–alkylation sequence was applied to the ethanediyl *S,S*-acetal of 4-benzoylpyridine (**1c**), a sulfide (**9c**) bearing a tertiary alkyl group was obtained in moderately good yields.

The sulfide **9c** may be produced in a process involving one-electron transfer[10] between **6c** similarly formed and LDA to afford an anion (**8c**), which on subsequent trapping by the remaining alkyl halide leads to **9c**.

An electron-withdrawing effect of the pyridyl group in **6c** would account for such the behavior of **6c**. In the case

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(10) The electron-donating abilities of triethylamine and **4** are also well-known.
(11) It has been found that the treatment of ethanediyl *S,S*-acetal of acetophenone with LDA under the similar conditions results in the formation of thioacetophenone and vinyl thiolate anion, and the former is deprotonated by LDA: Ikehira, H.; Tanimoto, S.; Oida, T.; Okano, M., unpublished report.

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Table I. Reaction Products from the Reaction of the Fragments of 1 with Various Electrophiles

starting substrate	electrophile	product[a]	yield, %	^{1}H NMR,[b] δ
1a	CH_3I	7a [R = CH_3]	97	1.85 (s, 3 H), 4.92 (s, 1 H), 7.00-7.50 (m, 10 H)
1a	C_2H_5I	7a [R = C_2H_5]	99	1.17 (t, 3 H, J = 7 Hz), 2.39 (q, 2 H, J = 7 Hz), 5.06 (s, 1 H), 7.00-7.50 (m, 10 H)
1a	$CH_3(CH_2)_3I$	7a [R = $CH_3(CH_2)_3$]	95	0.45-0.86 (m, 3 H), 0.87-1.55 (m, 4 H), 2.11 (t, 2 H, J = 6 Hz), 4.82 (s, 1 H), 6.80-7.30 (m, 10 H)
1a	$CH_3(CH_2)_3Br$	7a [R = $CH_3(CH_2)_3$]	97	
1a	$C_6H_5CH_2Br$	7a [R = $C_6H_5CH_2$]	96	3.47 (s, 2 H), 4.82 (s, 1 H), 7.05-7.40 (m, 10 H)
1b	CH_3I	7b [R = CH_3]	97	1.85 (s, 3 H), 2.25 (s, 3 H), 4.90 (s, 1 H), 6.95-7.48 (m, 9 H)
1b	C_2H_5I	7b [R = C_2H_5]	94	1.12 (t, 3 H, J = 7 Hz), 2.23 (q, 2 H, J = 7 Hz), 2.21 (s, 3 H), 4.98 (s, 1 H), 6.71-7.30 (m, 9 H)
1b	$CH_3(CH_2)_2Br$	7b [R = $CH_3(CH_2)_2$]	78	0.90 (t, 3 H, J = 6 Hz), 1.11-1.80 (m, 2 H), 2.21 (t, 2 H, J = 6 Hz), 2.21 (s, 3 H), 4.91 (s, 1 H), 6.73-7.32 (m, 9 H)
1b	$(CH_3)_2CHBr$	7b [R = $(CH_3)_2CH$]	40	1.17 (d, 6 H, J = 7 Hz), 2.25 (s, 3 H), 2.15-2.78 (m, 1 H), 5.00 (s, 1 H), 6.81-7.42 (m, 9 H)
1b	$CH_3(CH_2)_3I$	7b [R = $CH_3(CH_2)_3$]	93	0.67-1.09 (m, 3 H), 1.09-1.78 (m, 4 H), 2.13-2.47 (m, 2 H), 2.25 (s, 3 H), 4.49 (s, 1 H), 6.81-7.48 (m, 9 H)
1b	$CH_3(CH_2)_3Br$	7b [R = $CH_3(CH_2)_3$]	77	
1c	CH_3I	9c [R = CH_3]	67	1.73 (s, 3 H), 1.93 (s, 3 H), 7.00-7.45 (m, 7 H), 8.25-8.55 (m, 2 H)
1c	C_2H_5I	9c [R = C_2H_5]	85	0.75 (t, 3 H, J = 7 Hz), 0.98 (t, 3 H, J = 7 Hz), 1.98 (q, 2 H, J = 7 Hz), 2.23 (q, 2 H, J = 7 Hz), 6.85-7.50 (m, 7 H), 8.15-8.50 (m, 2 H)
1c	$CH_3(CH_2)_2I$	9c [R = $CH_3(CH_2)_2$]	91	0.50-1.50 (m, 10 H), 1.78 (t, 2 H, J = 6 Hz), 1.96 (t, 2 H, J = 6 Hz), 6.75-7.35 (m, 7 H), 8.10-8.40 (m, 2 H)
1c	$CH_3(CH_2)_3I$	9c [R = $CH_3(CH_2)_3$]	84	0.60-1.08 (m, 6 H), 1.08-1.75 (m, 8 H), 1.86-2.45 (m, 4 H), 6.97-7.48 (m, 7 H), 8.20-8.50 (m, 2 H)
1c	$CH_3(CH_2)_3Br$	9c [R = $CH_3(CH_2)_3$]	94	
1d	CH_3I	9d [R = CH_3]	37	1.19 (s, 3 H), 1.68 (s, 3 H), 7.02-7.68 (m, 8 H)
		10d [R = CH_3]	34	1.21 (s, 6 H), 6.90-7.48 (m, 16 H)
1d	C_2H_5I	9d [R = C_2H_5]	40	0.43 (t, 3 H, J = 7 Hz), 0.71 (t, 3 H, J = 7 Hz), 1.62 (q, 2 H, J = 7 Hz), 2.16 (q, 2 H, J = 7 Hz), 7.02-7.70 (m, 8 H)
		10d [R = C_2H_5]	33	0.80 (t, 6 H, J = 7 Hz), 1.51 (q, 4 H, J = 7 Hz), 6.82-7.43 (m, 16 H)
1d	$CH_3(CH_2)_3I$	9d [R = $CH_3(CH_2)_3$]	51	0.41-1.41 (m, 14 H), 1.41-1.76 (m, 2 H), 1.91-2.36 (m, 2 H), 7.05-7.78 (m, 8 H)
		10d [R = $CH_3(CH_2)_3$]	13	0.41-0.90 (m, 6 H), 0.90-1.32 (m, 8 H), 1.32-1.65 (m, 4 H), 6.85-7.36 (m, 16 H)
1d	$CH_3(CH_2)_3Br$	9d [R = $CH_3(CH_2)_3$]	75	
		10d [R = $CH_3(CH_2)_3$]	0	

[a] 7a, 7b, 9d, and 10d were isolated by column chromatography (silica gel, 10% ethyl acetate/hexane). 9c was isolated by column chromatography (silica gel, 25% ethyl acetate/chloroform). Only 10d (R = CH_3) and 10d (R = C_2H_5) were solid substances (mp 238 °C and 225 °C, respectively), all others were oily substances. The formation of 11 by the reaction of 4 with the applied alkyl halide was recognized in all runs. For example, an 84% yield of benzyl vinyl sulfide (11, R = $C_6H_5CH_2$) was produced in the fragmentation-alkylation sequence by using 1a and benzyl bromide. However, the isolation of 11 was not put into practice except in this case, because of its minor importance. [b] Measured in CCl_4 at 60 MHz. All products listed in the table were characterized by elemental analysis and mass spectrum in addition to ^{1}H NMR.

of the ethanediyl *S,S*-acetal of 9-fluorenone (**1d**), dimerization of the intermediary 9-(alkylthio)-9-fluorenyl radical (**6d**) occurred in addition to its conversion to 9-(alkylthio)-9-fluorenyl anion (**8d**), presumably due to a radical-stabilizing ability of the 9-fluorenyl group in **6d**. In a series of experiments shown in Table I, a larger and more bulky group than methylthio group in **6d** will impede the formation of the dimer (**10**), and with 9-(butylthio)-9-fluorenyl radical [**6d**, R = $CH_3(CH_2)_3$], which is produced in the sequence by using **1d** and *n*-butyl bromide, it was incapable of yielding the corresponding **10d** [R = $CH_3(CH_2)_3$]. This may be understandable in view of the steric congestion expected in **6d**.

Experimental Section

All ethanediyl *S,S*-acetals **1** were prepared by the $AlCl_3$-catalyzed reaction of carbonyl compounds with ethanedithiol.[12] Tetrahydrofuran was dried over lithium aluminium hydride and then distilled. The other reagents were commercially available and were used without further purification.

The general procedure was as follows. To a stirred, cooled (−78 °C) solution of diisopropylamine (0.35 g, 3.5 mmol) in tetrahydrofuran (7 mL) was added during about 2–3 min a 1.56 M solution (2.12 mL, 3.3 mmol) of *n*-butyllithium in hexane under nitrogen, followed by stirring at the same temperature for 30 min and further stirring at −15 °C for 10 min. The solution of LDA thus prepared was cooled again to −78 °C, and a solution of **1** (1.3 mmol) in tetrahydrofuran (4 mL) was added. After an additional 1 h at −15 °C, the solution was cooled once again to −78 °C, and 3.3 mmol of an alkyl halide was added with stirring. The reaction mixture was stirred for 1 h at −5 to −10 °C, warmed to ambient temperature, and stirred an additional 24 h. The reaction mixture was quenched with 100 mL of H_2O and 20 mL of a saturated

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aqueous solution of NH_4Cl. The reaction mixture was extracted with ether (3 × 60 mL). The combined ethereal extracts were dried over $MgSO_4$, filtered, and concentrated in vacuo to give a pale yellow residue, which was subjected to column chromatography.

Registry No. **1a**, 6317-10-8; **1b**, 76312-48-6; **1c**, 84811-68-7; **1d**, 7049-31-2; **7a** [R = CH_3], 15733-08-1; **7a** [R = C_2H_5], 38793-64-5; **7a** [R = $CH_3(CH_2)_3$], 35088-70-1; **7a** [R = $C_6H_5CH_2$], 6622-09-9; **7b** [R = CH_3], 84811-69-8; **7b** [R = C_2H_5], 84811-70-1; **7b** [R = $CH_3(CH_2)_2$], 84811-71-2; **7b** [R= $(CH_3)_2CH$], 84811-72-3; **7b** [R = $CH_3(CH_2)_3$], 84811-73-4; **9c** [R = CH_3], 84811-74-5; **9c** [R = C_2H_5], 84811-75-6; **9c** [R = $CH_3(CH_2)_2$], 84811-76-7; **9c** [R = $CH_3(CH_2)_3$], 84811-77-8; **9d** [R = CH_3], 84811-78-9; **9d** [R = C_2H_5], 84811-79-0; **9d** [R = $CH_3(CH_2)_3$], 84811-80-3; **10d** [R = CH_3], 84811-81-4; **10d** [R = C_2H_5], 84811-82-5; **10d** [R = $CH_3(CH_2)_3$], 84811-83-6; **11** [R = $C_6H_5CH_2$], 1822-76-0; CH_3I, 74-88-4; C_2H_5I, 75-03-6; $CH_3(CH_2)_3I$, 542-69-8; $C_6H_5CH_2Br$, 100-39-0; $CH_3(CH_2)_2Br$, 106-94-5; $(CH_3)_2CHBr$, 75-26-3; $CH_3(CH_2)_3Br$, 109-65-9; $CH_3(CH_2)_2I$, 107-08-4.

Addition of Phthalimidonitrene to 1,4-Dihydronaphthalene 1,4-*endo*-Oxide. An Attempted Synthesis of *N*-Phthalimidonaphth[2,3-*b*]azirine

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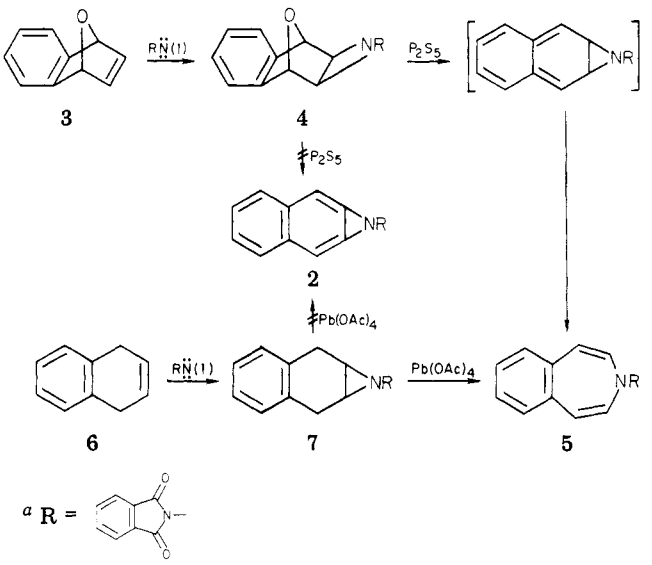
Phthalimidonitrene (1) generated by the oxidation of *N*-aminophthalimide with lead tetraacetate undergoes facile cycloaddition with a variety of substrates.[1] The reaction of 1 with acetylene has been shown to yield 2*H*-azirine which was assumed to arise by the rearrangement of the initially formed 1*H*-azirine.[2] This unique rearrangement has been attributed to the unfavorable electronic delocalization due to antiaromaticity existing in 1*H*-azirine. Such a rearrangement will be energeticaly expensive in naphth[2,3-*b*]azirine **2**. The ideal route to **2** would involve the addition of phthalimidonitrene either to 1,4-dihydronaphthalene 1,4-*endo*-oxide followed by treatment with P_2S_5 or to 1,4-dihydronaphthalene followed by oxidation with lead tetraacetate (or DDQ).

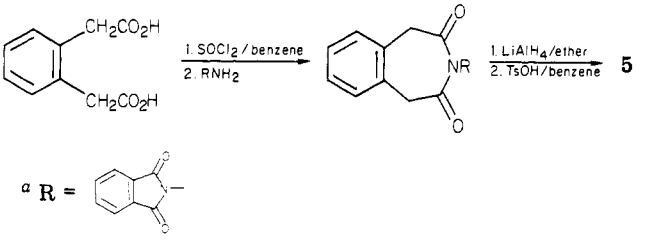
Phthalimidonitrene adds smoothly to 1,4-dihydronaphthalene 1,4-*endo*-oxide[3] (**3**) to give the adduct **4**. Its IR spectrum showed the presence of phthalimido carbonyls (1745, 1720 cm^{-1}) and C–O–C stretching (1150 cm^{-1}). The structure was further supported by the presence of a molecular ion peak at *m/e* 304 ($M^{+\cdot}$) in the mass spectrum. The exo stereochemistry is assigned on the basis of the NMR spectrum which contained singlets at δ 3.3 (H_2, H_3) and 6.7 (H_1, H_4). Dreiding models indicate a dihedral angle close to 90° for the exo adduct, while the endo adduct should show appreciable coupling. Similar exo specificity has been observed in the addition of dibromocarbene to **3**.[4]

The adduct was treated with P_2S_5[5] in anticipation of formation of naphth[2,3-*b*]azirine **2**. The reaction mixture

Scheme I[a]



Scheme II[a]



when subjected to column chromatography on neutral alumina gave a stable compound (40%) which showed no upshield shift in the NMR for the aromatic protons. The mass spectrum showed the molecular ion peak at *m/e* 288. Structure **2** could be ruled out on the basis of these data. The product was found to be different from the known *N*-phthalimido-β-naphthylamine.[6] The UV absorption at λ_{max} (EtOH) 225 nm (ϵ 24170) 290 (1036), and 340 (186.7) is characteristic of a benzazepine ring system[7] and hence enabled the assignment of the azepine structure **5** to the compound.

Another attempted approach to *N*-phthalimidonaphth[2,3-*b*]azirine involves the cycloaddition of 1 to 1,4-dihydronaphthalene (**6**), which gave an adduct in 70% yield. On the basis of the spectral data, structure **7** has been proposed for the adduct. The aziridine **7** when subjected to dehydrogenation with either lead tetraacetate or dichlorodicyano-*p*-benzoquinone (DDQ) gave *N*-phthalimido-3-benzazepine (**5**). The reaction sequence is represented in Scheme I.

N-Phthalimido-3-benzazepine was independently synthesized by the route shown in Scheme II to confirm the structure **5**. The product obtained from *o*-phenylenediacetyl chloride and *N*-aminophthalimide, without purification, was treated with $LiAlH_4$ and dehydrated to give **5** in 20% overall yield.

Experimental Section

All melting points are uncorrected. Infrared (IR) spectra were recorded on a Beckman IR-20 spectrometer, and nuclear magnetic resonance (NMR) spectra were obtained by using a Perkin-Elmer

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