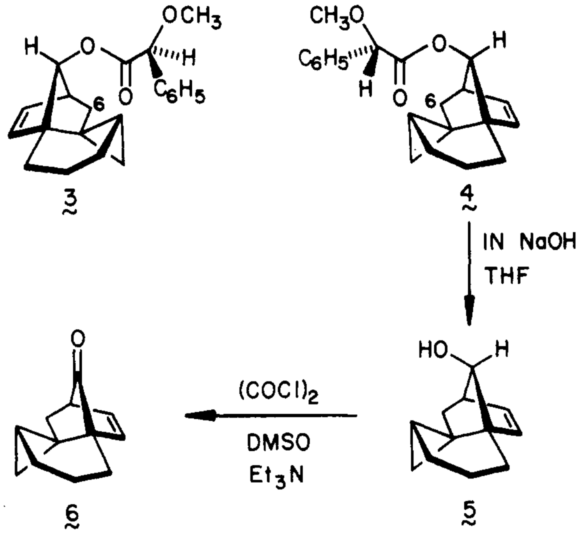
Because the individual needles were clustered and never very large, it became necessary to remove several crystals together for the optical rotation measurements. This need to deal with part-clusters was unfortunate, for it did result in the physical admixing of enantiomorphically related crystal fragments. The sublimed crystals of **2** do not exhibit hemihedrism. Typical data from three experiments have been compiled in Table I. Significantly, the nonsublimed solid in each instance exhibited no meaningful optical rotation.[7a]

In order to define absolute configurational assignments to the enantiomers of **2**, the racemic alcohol was condensed with the acyl chloride of (*S*)-(+)-*O*-methylmandelic acid.[8] The absolute configurations of the diastereomers **3**, $[\alpha]_D^{20}$ +34.4° (*c* 2.58, C_2H_5OH), and **4**, $[\alpha]_D^{20}$ +21.5° (*c* 3.03, C_2H_5OH), whose complete separation was achieved by MPLC on silica gel, were deduced in the following manner. As the Mosher[9] and Trost[10] NMR correlations would suggest, the downfield position of $H\text{-}6_{exo}$ in **3** (δ 1.79) relative to **4** (δ 1.15) implicates the latter as experiencing an upfield shift because of long-range eclipsing by the phenyl ring. Independent support for this analysis was derived by independent saponification of **3** and **4** to enantiomerically pure samples of (–)-**2** [mp 98 °C, $[\alpha]_D^{20}$ –89.8° (*c* 1.95, C_2H_5OH)] and (+)-**5** [mp 94–95 °C, $[\alpha]_D^{20}$ +81.0° (*c* 2.16, C_2H_5OH)], respectively. Swern oxidation of (+)-**5** afforded **6**, $[\alpha]_D^{20}$ +94.5° (*c* 0.97, C_2H_5OH). In line with expectations based on the octant rule,[11] the CD spectrum of this ketone showed two positive Cotton effects at 212.5 and 280 nm.[12]



The FT-IR spectra of solid (–)-**2**, (+)-**5**, and (±)-**2** determined at high resolution were superimposable, thereby providing further indication that the racemate is a conglomerate.[7b] Differential scanning calorimetry studies[7c] were uniquely consistent with the same conclusion.

To sum up, spontaneous resolution by sublimation of a chiral compound exhibiting conglomerate behavior has not been described previously. In the case of **2**, enantiomorphic crystals have been obtained by this technique that happen to be large enough to pick apart mechanically. Our studies have dismissed the operation of a rare racemic compound $\rightleftharpoons$ conglomerate transformation.[2,13] We emphasize that the present observations are significant only because no prior report of this phenomenon has been recorded.[14] In actuality, comparable findings should begin to surface with increasing frequency as X-ray analyses become simpler to perform.

Acknowledgment. We thank Professors Ernest L. Eliel and Samuel H. Wilen for helpful exchanges of information. The financial support of this research by the National Science Foundation is gratefully acknowledged.

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(13) In the absence of such a transformation, recrystallization of the crude racemic norbornenol to yield reasonably sized and nontwinned crystals should lead to results similar to those in Table I but without sublimation. However, we have been uniformly unsuccessful in crystallizing **2** satisfactorily from a variety of solvents.

(14) The sublimation of a racemate with attendant conversion of a racemic compound to a conglomerate has, in fact, been reported.[2] However, these investigators failed to measure the rotations of the sublimed crystals.

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Intramolecular Arene-Alkyne Photocycloadditions

Summary: The intramolecular photocycloaddition of substituted 5-aryl-1-pentynes has been studied. A variety of bicyclo[6.3.0]undecane systems (cyclopentane-annulated cyclooctatetraenes) involving both carbocyclic and heterocyclic rings has been prepared by using this method.

Sir: The photochemistry of benzene and its derivatives has been studied for some 120 years.[1] Renewed interest in this area derives from some of the recent synthetic applications of benzene photochemistry[2] involving the meta-photoaddition, as well as a deeper theoretical understanding of benzene excited-state reactivity.[3] A useful mnemonic device to come from this work is that close matching of the ionization potentials (<0.4 eV) of the arene and alkene is required in order for meta-photoaddition to occur.[4] Otherwise ortho (as in the addition of benzene to acetylenes) or para adducts are found. Almost all acetylenes that participate in the ortho-photoaddition bear strongly electron-withdrawing groups, and the reaction has provided a direct if low-yielding entry into substituted cyclooctatetraenes.[5] The only exception to this generalization is the photoaddition of cyclooctyne to benzene,[6] clearly a special case. Morrison's important contributions to the study of bichromophoric molecules have included the intramolecular reaction of 6-phenyl-2-hexyne,[7] but the

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(1) Bryce-Smith, D.; Gilbert, A. *Tetrahedron* **1976**, *32*, 1309–1326. Bryce-Smith, D.; Gilbert, A. *Tetrahedron* **1977**, *33*, 2459–2490.

(2) Wender, P. A.; von Geldern, T. *Photochemistry in Organic Synthesis*; Coyle, J., Ed.; 1986; p 226.

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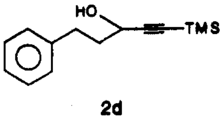
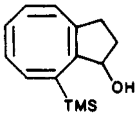
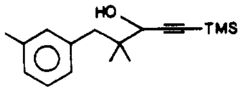
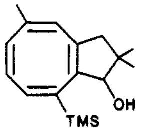
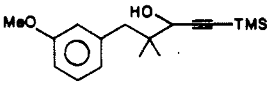
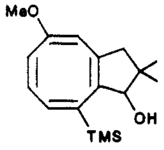
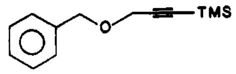
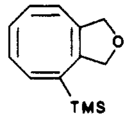
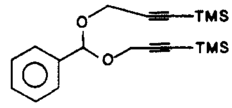
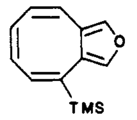
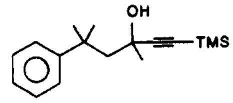
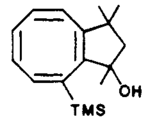
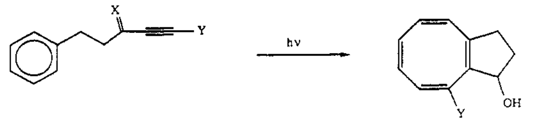
Table I

substrate[a]	product[b]	yield (%)[c]	time (h)	[mM]
 **2d**	 **3d**	46	4	2.3
 **4**	 **9**	38	4	1.7
 **5**	 **10**	31	5	1.3
 **6**	 **11**	42	2	2.7
 **7**	 **12**	55	2	0.9
 **8**	 **13**	50[d]	5	2.1

[a] For short experimental descriptions of methods used to prepare these substrates, see supplementary material. [b] A solution of 0.28 mmol of substrate was prepared in 100 mL of hexane in a quartz tube. After nitrogen was bubbled through the solution for 10 min, the tube was sealed with a serum cap and irradiated in a Rayonet photochemical reactor equipped with 254-nm lamps. The reaction was followed by TLC (ether/hexanes; product has a lower R_f) or capillary GC (product has shorter retention time). [c] Yields are for product purified by flash chromatography. [d] Includes minor amount of elimination product. [e] All new compounds reported in this paper demonstrate spectroscopic and analytical properties in accord with the assigned structure.

isolated yield (<5%) did not suggest broad synthetic utility for this transformation. Both triplet[6] and singlet[8] reactive states have been implicated in these reactions. Described here are the first intramolecular reactions involving alkynylsilanes that provide a concise entry into cyclooctane-containing ring systems.

A variety of substrates 1 and 2 was selected for initial study of the potential of the intramolecular arene–alkyne photocycloaddition in generating cyclooctane derivatives. At high concentration (50 mM in hexane) only **2d** provides a cyclooctatetraene product on irradiation, but the reaction is difficult to push to completion. Similar to Miller's findings,[6] product inhibition was implicated by a concentration study. After irradiation of **2d** for 1 h, conversions are as follows: 50 mM, 3%; 5 mM, 18%; 0.5 mM, 60%. A negligible solvent effect (hexane, acetonitrile, methanol) is observed in the photocyclization, and the reaction has thus far not been sensitizeable (acetone, Pyrex). At low concentration, **2a** and **2c** also cyclize, albeit in low yield (**3a**, 21%; **3c**, 16%) with considerable production of polymer. A partial explanation for this behavior was discovered by examination of UV spectra of the cyclooctatetraenes. A typical cyclooctatetraene spectrum is displayed by **3a**, with a weak transition at 246 nm and a shoulder at 286 nm. Neither **3c** nor **3d** exhibits these bands. Silicon substitution may thus act both in promoting cycloaddition and in preventing degradation of the products.



1 X = O
2 X = H, OH

3 Y = a. H
b. CO_2Me
c. $CH_2CH_2CH_3$
d. $SiMe_3$
e. OCH_2CH_3

These results prompted an investigation of the scope of the arene–alkynylsilane photoaddition. While intermolecular additions of (ethynyl)trimethylsilane, bis(trimethylsilyl)ethyne, and cyanotrimethylsilane to benzene have thus far been unsuccesful, the results collected in Table I demonstrate the generality of the intramolecular version. Substituted aromatics not only participate in the reaction but do so with remarkable regioselectivity. The lower isolated yield of **10** is attributed to its hydrolysis on

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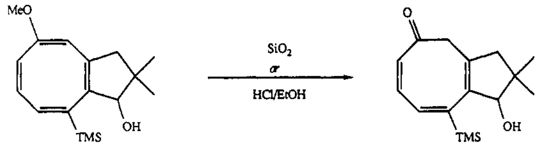
silica gel to ketone **14**, a transformation that is also accomplished in ethanolic HCl. The photoproduct derived from **7** undergoes elimination on concentration and warming, giving the interesting furan derivative **12** (UV λ_{max} 232, log ϵ 2.98; λ_{max} 276, log ϵ 2.34). Optically active products are also easily obtained. Alpine-borane reduction[9] of **1d** provides **2d** in 86% yield (α^{20}_{D} −22.3°, *c* 0.60, hexane), and photocyclization gives **3d** (α^{20}_{D} −170.3°, *c* 0.40, hexane). It should also be emphasized that seemingly trivial extensions of Morrison's work fail. For example, an attempt to prepare the asteriscane skeleton[10] by using an analogue of **9** (Me_3Si replaced by CH_2OSiR_3 or CO_2Me) provides no cyclooctatetraene product.



10 14

While silyl substitution is known to lower the ionization potential of acetylene,[11] the effect is not great enough to satisfy the mnemonic mentioned above, so the 1,2-photoaddition is predicted. In order to compare these results to the intermolecular reactions where energy transfer from the aromatic to the electron-poor acetylene is observed, the fluorescence lifetime of **2d** was measured. It is 4 ns, compared to 37 ns for toluene. This lifetime is consistent with that obtained from the quenching data above. To provide an alternate, nonaromatic trap for any excited acetylene, the allyl ether of **2d** was prepared. On irradiation, it provides only the allyl ether of **3d**. This suggests that if energy transfer occurs, no free excited acetylene is produced. These results challenge current theories of aromatic photoaddition, since ortho additions with S_1 benzene are thought to be disfavored. The intramolecular arene/alkynylsilane photoaddition has obvious potential in synthesis of bicyclo[6.3.0]undecane natural products, an area of considerable recent interest.[12] The transformations available to vinylsilanes should also make these photoproducts versatile intermediates in synthesis.[13]

Acknowledgment. Mass spectra were obtained through the Mass Spectrometry Facility, University of California, San Francisco (NIH Division of Research Resources, Grant RR 01614). The NSF (CHE 8215712) provided financial support. NMR spectra were obtained on an instrument provided by NSF equipment grant CHE 8109064. M.C.P. is a Presidential Young Investigator (NSF CHE 8451324) and a Research Fellow of the Alfred P. Sloan Foundation. The assistance of Prof. C. Frank's group in obtaining the fluorescence data is appreciated.

Supplementary Material Available: Short experimental descriptions and spectra for new compounds (2 pages). Ordering information is given on any current masthead page.

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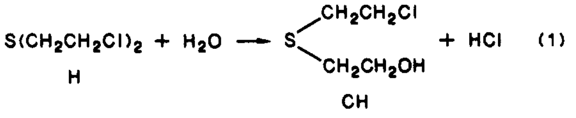
Direct NMR Measurements of Sulfonium Chlorides Produced from the Hydrolyses of 2-Chloroethyl Sulfides

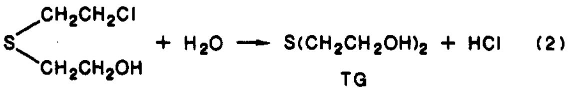
Summary: Sulfonium chlorides have been directly identified for the first time with NMR as additional products in the hydrolysis of 2-chloroethyl sulfides.

Sir: In our previous kinetic studies[1,2] on the hydrolyses of 2-chloroethyl sulfide derivatives (10^{-4} to 10^{-3} M) we occasionally measured lower HCl concentrations in the final reaction mixtures than predicted from stoichiometry, particularly when insufficient organic solvent was used to dissolve the sulfide before mixing with water. (These results were obviously discarded for rate coefficient determinations.) The same problem was also reported by Blandamer and his co-workers during the hydrolysis of 10^{-3} M 2-chloroethyl methyl sulfide (CEMS).[3] These authors noted that the proton concentration was lower than the chloride ion concentration in the final reaction mixture, but offered no explanation.

We suspected that this might be caused by the formation of dimeric sulfonium chlorides and that the 2-hydroxyethyl sulfides and HCl (as shown in eq 1 and 2 for



$$\underset{\text{H}}{S(CH_2CH_2Cl)_2} + H_2O \longrightarrow \underset{\text{CH}}{S\begin{matrix}\diagup CH_2CH_2Cl \\ \diagdown CH_2CH_2OH\end{matrix}} + HCl \qquad (1)$$



$$S\begin{matrix}\diagup CH_2CH_2Cl \\ \diagdown CH_2CH_2OH\end{matrix} + H_2O \longrightarrow \underset{\text{TG}}{S(CH_2CH_2OH)_2} + HCl \qquad (2)$$

2,2′-dichlorodiethyl sulfide (H)) were not the only hydrolysis products. However, according to Bergman and his co-workers,[4] these salts should have been negligible in solutions of less than 10^{-3} M sulfide. The authors, though, could only identify and measure these salts indirectly. We have attempted to use NMR to detect the presence of these salts in both the H–water and 2-chloroethyl ethyl sulfide (CEES)–water systems and to follow their formation as a function of time and initial concentration with CEES, since only one sulfonium chloride is expected to form. A Varian XL-200 Superconducting FT-NMR system was used for ^1H analyses at 200 MHz and for ^{13}C at 50 MHz. The ^1H spectra were obtained by using a D_2O lock and referenced to internal TSP (sodium 3-(trimethylsilyl)propionate-*2,2,3,3-d*$_4$), while the ^{13}C spectra were referenced to external TSP in D_2O. All samples were

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[1] Yang, Y.-C.; Ward, J. R.; Wilson, R. B.; Burrows, W.; Winterle, J. S. *Thermochim. Acta*, in press.

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