mide ions in this system. More striking is the observation that benzyl trifluoromethyl sulfone (PhCH$_2$-SO$_2$CF$_3$) does *not* react at all[10] with tetraethylammonium bromide under these conditions. A similar lack of reaction[10] was also observed with dibenzyl sulfone (PhCH$_2$SO$_2$CH$_2$Ph), benzyl phenacyl sulfone (PhCH$_2$-SO$_2$CH$_2$COPh), and phenyl phenylmethanesulfonate (PhCH$_2$SO$_2$OPh), the last being also unaffected by sodium phenoxide. To account for these observations in terms of a reaction proceeding *via* I would require that one explain why a BrSO$_2^-$ group is a better leaving group than either CF$_3$SO$_2^-$, PhCOCH$_2$SO$_2^-$, PhOSO$_2^-$, or PhCH$_2$SO$_2^-$ by more than five orders of magnitude in each case. We find it much simpler to interpret these observations on the basis of the concerted fragmentation process (*i.e.*, *via* II), the observed rate order then reflecting the normal order of Br, Cl, CF$_3$, etc., as leaving anions ("nucleofugal" groups[11]).

In the light of this conclusion it is pertinent to inquire into the possibility of other concerted fragmentation processes that involve S$_N$2 reaction on carbon. A case for such a mechanism, based on $\Delta S^\ddagger$ values, has been made by Buncel and Millington[12] for the solvolysis of alkyl chlorosulfates. Two other reactions, the chloride ion catalyzed decomposition of alkyl chloroformates[13] and the analogous cleavage of alkyl chlorosulfites,[14] are sufficiently similar as to strongly suggest that they too may be fragmentation reactions, though direct evidence on the point is lacking at present. The twofold problem of elucidating the mechanism of the known processes and of devising and testing possible new members of this class of reactions is now under active study.

(10) Control experiments show that a reaction with $k_2 > 10^{-7}$ l. mole^{-1} sec^{-1} would have been readily detected. Lack of reaction in these cases therefore corresponds to a rate at least 2×10^5 times slower than reaction 1.

(11) J. Mathieu, A. Allais, and J. Valls, *Angew. Chem.*, 72, 71 (1960); see also C. A. Grob and P. W. Schiess, *ibid.*, 79, 1 (1967).

(12) E. Buncel and J. P. Millington, *Can. J. Chem.*, 43, 556 (1965).

(13) J. Kenyon, A. G. Lipscomb, and H. Phillips, *J. Chem. Soc.* 2275 (1931); D. N. Kevill, G. H. Johnson, and W. A. Neubert, *Tetrahedron Letters*, 3727 (1966).

(14) E. S. Lewis and G. M. Coppinger, *J. Am. Chem. Soc.*, 74, 308 (1952).

(15) Alfred P. Sloan Research Fellow.

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Bicyclo[6.2.0]deca-2,4,6,9-tetraene

Sir:

Numerous recent publications describe thermally and photolytically induced rearrangements of unsaturated hydrocarbons.[1] The behavior of the title compound (**1**) is of particular interest because several modes of

(1) For the bond isomerization of several C$_{10}$H$_{10}$ hydrocarbons, for instance, see (a) W. von E. Doering and J. W. Rosenthal, *J. Am. Chem. Soc.*, 88, 2078 (1966); (b) *Tetrahedron Letters*, 349 (1967); (c) M. Jones, Jr., and L. T. Scott, *J. Am. Chem. Soc.*, 89, 150 (1967); (d) E. E. van Tamelen and T. L. Burkoth, *ibid.*, 89, 151 (1967); (f) J. A. Elix, M. V. Sargent, and F. Sondheimer, *ibid.*, 89, 180 (1967).

isomerization are conceivable for this compound,[2] *e.g.* (i) ring opening to give *trans*(*cis*)[4]-1,3,5,7,9-cyclodecapentaene (**2**); (ii) subsequent rearrangement of **2** to *trans*-9,10-dihydronaphthalene (**3**); (iii) sigmatropic rearrangement to bicyclo[4.2.2]deca-2,4,7,9-tetraene (**4**);[1b,c] (iv) degenerate bond isomerization to give the same compound; (v) ring opening to afford (*cis*)[5] cyclodecapentaene (**5**)[1d] followed by secondary reactions; and (vi) ring closure leading to the tricyclo compound **6** (stereochemistry unspecified). We describe herein the synthesis of this intriguing molecule and further present a preliminary account of its chemistry.[3]

A solution of bicyclo[6.1.0]nona-2,4,6-triene-*trans*-9-carboxaldehyde tosylhydrazone (**7**)[1c,4] in dry tetrahydrofuran containing an equivalent amount of sodium methoxide was irradiated at 0 or −30° with a Hanovia mercury lamp using a Pyrex filter. Evolution of the theoretical amount of nitrogen usually required 5–6 hr. Gas chromatography (10% silicone rubber, 90°) of the distillable product mixture provided **3**, naphthalene (the combined yield of **3** and naphthalene was 45%), cyclooctatetraene (27%), **4** (7%), and a new compound (**6'**) (21%) (*vide infra*). This product distribution is similar to that of the thermolysis of **7** (dry salt)[1c] except that no trace of *cis*-9,10-dihydronaphthalene (**8**) was found in the photolysis products. When the products were kept below 0° throughout the entire work-up process[5] we obtained another new compound (**1**) at the expense of **3** and naphthalene.

Compound **1** (calcd mol wt for C$_{10}$H$_{10}$, 130.0783 and for C$_9$^{13}CH$_9$, 130.0738; found, *m/e* 130.0758 (intensity, 20% of M − 1 base peak); calcd for C$_{10}$H$_9$, 129.0704; found, *m/e* 129.0704)[6] showed a maximum at λ_{max}^{EtOH} 258 mμ ($\epsilon \sim 1300$).[7] The nmr spectrum showed a sharp singlet at τ 3.98 (2 H) characteristic of the olefinic signal of symmetrically (σ) substituted cyclobutenes,[8] a broad singlet at τ 6.32 ascribed to two allylic protons, and other olefinic signals (6 H) at τ 4.1 to ~4.3, similar to those of the bicyclo[6.1.0]nona-2,4,6-triene system. These spectral data are consistent with the formulation of structure **1**.

(2) R. B. Woodward and R. Hoffmann, *ibid.*, 87, 395 (1965); H. C. Longuet-Higgins and E.W. Abrahamson, *ibid.*, 87, 2045 (1965); R. B. Woodward and R. Hoffmann, *ibid.*, 87, 2511 (1965).

(3) Our original aim was to prepare the carbocyclic analog of 4-azabicyclo[5.2.0]nonatriene and compare the properties of the two series of compounds: see S. Masamune and N. T. Castellucci, *Angew. Chem. Intern. Ed. Engl.*, 3, 582 (1964).

(4) The reaction product of ethyl diazoacetate and cyclooctatetraene consisted of an approximately 19:1 mixture of *trans* and all-*cis* (with respect to the substituents of the cyclopropane ring) esters. Because of the necessity of confirming the earlier stereochemical assignments [K. F. Bangert and V. Boekelheide, *J. Am. Chem. Soc.*, 86, 905, 1159 (1964)], the known acid derived from the major component was converted to cyclopropane-*trans*-1,2,3-tricarboxylic acid with permanganate-periodate. The minor acid, mp 146–147°, was isolated in pure form and the three cyclopropane ring protons showed the same chemical shift (τ 7.95): S. Masamune, unpublished.

(5) The final purification involved alumina chromatography (Woelm, neutral grade 1, pentane) followed by distillation at 0°, 0.1 mm.

(6) Taken with a direct insertion probe (MS-9) by first freezing a sample with liquid nitrogen.

(7) Compound i exhibited a maximum, λ_{max}^{hexane} 258 mμ (ϵ 1300): G. Schröder and W. Martin, *Angew. Chem. Intern. Ed. Engl.*, 5, 130 (1966).

i
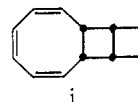
(8) For instance, see ref 3. For a revised set of coupling constants of cyclobutene itself, see E. A. Hill and J. D. Roberts, *J. Am. Chem. Soc.*, 89, 2047 (1967).

Catalytic hydrogenation of **1** with palladium on carbon or platinum provided quantitatively a saturated hydrocarbon (**9**), $C_{10}H_{18}$ (calcd mol wt, 138.1409; found, m/e 138.1409), which was found to be identical (mass, glpc, nmr, infrared) with those obtained by two alternative routes. The bis(dibromocarbene) adduct (mp 93–94°) of cycloocta-1,3-diene was treated with methyllithium at −30°[9] to afford through thermally unstable cyclodeca-1,2,4,5-tetraene a good yield of bicyclo[6.2.0]deca-1,7,9-triene (**10**). The latter compound was characterized by its nmr spectrum: τ 3.40 (sharp singlet, 2 H), 4.75–4.95 (triplet, 2 H), 7.7–7.95 (multiplet, allylic 4 H), 8.15–8.55 (multiplet, 4 H). Compound **10** was converted into **9** upon catalytic hydrogenation. Alternatively, pyrolysis of the sodium salt of bicyclo-[6.1.0]nonane-9-carboxaldehyde tosylhydrazone[10] at [160°[11] provided, in addition to cyclooctene, bicyclo-[6.2.0]dec-9-ene (calcd mol wt, 136.1252; found, m/e 136.1250); nmr, τ 4.06 (sharp singlet, 2 H), 7.1–7.4 (broad doublet, 2 H), 8.2–8.7 (multiplet, 12 H). The latter compound was subsequently converted into **9**.[12]

Compound **1** readily and *quantitatively* isomerized to *trans*-9,10-dihydronaphthalene. The rate of isomerization was measured with an approximately 0.15 M solution of **1** in deuteriochloroform and the intensity of the nmr signals at τ 6.32 of **1** and at τ 7.13 of **3** was compared at intervals, using a small sample of methylene bromide as an intensity standard. The isomerization was first order and provided the following kinetic data: $k_{42°} = (6.9 \pm 0.2) \times 10^{-5}$ sec⁻¹, $k_{70°} = (1.72 \pm 0.05) \times 10^{-3}$ sec⁻¹. In this temperature range the product **3** was essentially stable and began to change into naphthalene at a measurable rate only above 120°. An obvious proposal for this stereospecific reaction is that the C_1–C_8 bond opens in a conrotatory process to produce an unstable intermediate **2** (presumably being situated close to the transition state in the energy profile) which cyclizes in a disrotatory process at C_1 and C_6 to form **3**.[13]

Compound **6′** (calcd mol wt, 130.0783; found, m/e 130.0783) showed an nmr spectrum consisting of five complex and equally intense multiplets centered around τ 3.32, 4.08, 4.40, 6.85, and 7.53. Upon irradiation (triple) at the last two signals, the absorption at τ 3.32 and 4.40 showed an AX pattern and that at τ 4.08 collapsed to a singlet. Irradiation (triple) at the first and fourth signals produced an almost symmetrical pattern for the second and the last signals, suggesting an AA′XX′ system for the latter two sets of protons. These data lead to the proposal of a tentative structure **6** for this compound. The appearance of the diallylic protons at such a high field (τ 7.53) can be rationalized by assigning the *cis,anti,cis* stereochemistry to **6′**, as indicated in **6a**. However, structure **6a** should by no means be taken as established, because other possibili-

ties such as tricyclo[5.3.0.0⁴,⁸]deca-2,5,9-triene have not been rigorously excluded.

Photolysis of **1** under similar conditions to those described above[14] produced **4** in addition to other compounds. It is probable that **4** is a secondary reaction product derived from **1**. The photochemical reaction of **1** is highly complex, and we will elaborate on this subject in a separate report.
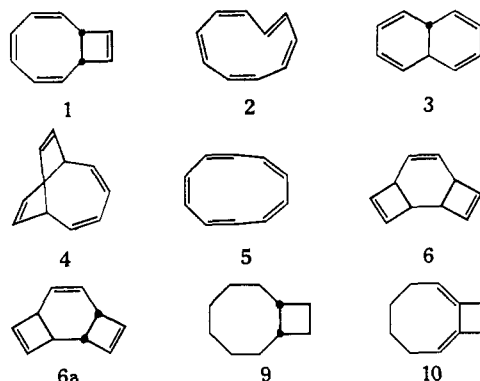
(14) Survival of **1** in the photolysis of **7** is due to the formation of insoluble sodium tosylsulfinate, which reduced greatly the transparency of the reaction medium, during the photolysis.

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The Reactions of Sulfur Atoms. X. Addition to Carbon–Carbon Triple Bonds and the Formation of Thiirenes

Sir:

Addition of divalent radicals such as CH_2,[1,2] O atom,[3,4] and NH[1] to acetylene results in extensive cracking and/or isomerization of the primary adduct even in low-temperature matrices. With dimethylacetylene the primary methylene addition product, dimethylcyclopropene, has been observed,[5] but the expected primary products of oxygen atom additions, the corresponding oxirenes, have never been obtained. As it appears to date, in spite of the deliberate efforts, the synthesis of the oxirene structure has not been achieved.[6] For the analogous sulfur compounds, the thiirenes, no reference can be found in the literature.[7]

We have recently examined the reactions of sulfur atoms with acetylenes utilizing a novel technique of

(9) L. Skattebøl and S. Solomon, *J. Am. Chem. Soc.*, **87**, 4506 (1965).
(10) Prepared from the corresponding carboxylic acid. This acid, prepared from cyclooctene and reported as melting at 113.5–114.8° [S. Akiyoshi and T. Matsuda, *ibid.*, **77**, 2476 (1955)], was found to contain some of the stereoisomer. The pure sample melted at 123.0–123.5°.
(11) W. Kirmse and K.-H. Pook, *Chem. Ber.*, **98**, 4022 (1965).
(12) **9** is presumably the same compound as that reported in ref 1f.
(13) Because of lack of molecular symmetry of **1**, **2**, and **3** necessary for the symmetry arguments pertaining to the above modes of isomerization, we cannot apply in a rigid sense the Woodward and Hoffmann rule² to these cases. However, provided that the simple MO calculation gives the correct order for the energy levels of the molecular orbitals of **5** (planar), it is predicted that **1** photolytically opens to give **5** (disrotatory) which closes thermally to *trans*-fused bicyclo[6.2.0]deca-2,4,6,9-tetraene (conrotatory) or *cis*-9,10-dihydronaphthalene (disrotatory).

(1) M. E. Jacox and D. E. Milligan, *J. Am. Chem. Soc.*, **84**, 4080 (1962).
(2) T. Terao, N. Sakai, and S. Shida, *ibid.*, **85**, 3919 (1963).
(3) C. A. Arrington, W. Brennen, G. P. Glass, J. V. Michael, and H. Niki, *J. Chem. Phys.*, **43**, 525 (1965).
(4) I. Haller and G. C. Pimentel, *J. Am. Chem. Soc.*, **84**, 2855 (1962).
(5) W. von E. Doering and T. Mole, *Tetrahedron*, **10**, 65 (1960).
(6) M. Berthelot, *Bull. Soc. Chim. France*, **14**, 113 (1879); R. N. McDonald and P. A. Schwab, *J. Am. Chem. Soc.*, **86**, 4866 (1964); W. Madelung and M. E. Oberwegner, *Ann.*, **490**, 201 (1931); W. G. Dauben, C. F. Hiskey, and M. A. Muhs, *J. Am. Chem. Soc.*, **74**, 2082 (1952); H. Schlubach and V. Franzen, *Ann.*, **577**, 60 (1952); V. Franzen, *Ber.*, **87**, 1479 (1954); J. K. Stille and D. D. Whitehurst, *J. Am. Chem. Soc.*, **86**, 4871 (1964).
(7) A. Hückel MO calculation by Zahradnik suggests a very low stability for thiirene (R. Zahradnik, *Advan. Heterocyclic Chem.*, **5**, 14 (1965).