Table I. Product Distribution from Decomposition of 9c and 10

	no.	$T \pm 5$, °C	torr[a]	N_2, mL min^{-1}	10	11	8	12	13	14	15	ΣC_8H_{10}, %	isolated yield, % ΣC_8H_{10}	isolated yield, % $\Sigma C_{16}H_{20}$	total isolated, yield, %
9c	1	200	2×10^{-2}		34.3	21.0	10.0	5.0	7.9	7.1	7.0	92.3[c]	69	11	80
9c	2	200	1×10^{-2} [b]	50	43.2	18.1	9.6	8.3	10.9	5.2	1.6	96.9	48	10	58
9c	3	300	1×10^{-4}		42.5	19.2	10.2	5.2	6.5	7.9	4.0	95.5[c]	56	17	73
10		200	2×10^{-3}		28.8			34.9	17.8		17.1	98.6	86		86

[a] Pressure at the beginning of pyrolysis. [b] 0.9–1 torr during pyrolysis. [c] In addition, cycloocta-1,3,5-triene and its valence isomers are formed in 1.1–1.8% yield.

signals, reflecting molecular symmetry, thus ruling out crossover dimers of **16** and **17** and structures other than dimers **19** and **20** which result from formal [2 + 2] cycloadditions[18] of the distorted double bond of the two molecules **16** and **17**, respectively. A decision in favor of dimers **20** deriving from **17** can be made with the aid of the ^1H NMR spectrum.[19] The broadened singlet at $\delta = 2.9$ is of diagnostic value representing allylic bridgehead protons only present in dimers **20**. The combined spectra data, however, do not allow further differentiation between the head–head or the head–tail arrangement **20a** and **20b**, respectively. Likewise, the sites of the three-membered rings remain unknown. The isolation of **20a** or **20b**, however, bears testimony to the intermediacy of **17**.

Bicyclo[4.2.0]oct-1(8),2-diene (**11**),[9] an air-sensitive and readily polymerizing compound, comprises conjugated double bonds arranged in bicyclo[4.2.0]octadienes[20] in a hitherto unknown fashion. The formation of **11**[17c] from **6** can be rationalized by migration of the C_1–C_2 bond to the divalent carbon, the predominant reaction of thermally generated foiled methylenes.[6,21] When pyrolyzed at the temperature of its generation, **11** exclusively undergoes ring opening to 2-vinylcyclohexa-1,3-diene (**14**).[22] On hydrogenation (Pd/C, ether) of **11**, bicyclo[4.2.0]octane is obtained.

Bicyclo[3.3.0]oct-1,7-diene (**8**), the product expected from the novel carbene–carbene rearrangement (**6** → **7**) and subsequent vinyl migration, is found among the monomers in 10% yield. No evidence for the formation of **8** is provided from a series of flash pyrolysis of all hydrocarbons (C_8H_{10}) isolated from the reaction of **6** at the temperature of their generation.[12] **7** was generated independently by flash pyrolysis of the sodium salt of bicyclo[3.2.1]oct-2-en-8-one tosylhydrazone (**21**) under the conditions employed for the decomposition of **9c**. Almost exclusively **8** and a minor unidentified compound were obtained in the ratio 98:2 with an isolated yield (85–90%) virtually identical with those reported.[5] The present findings suggest that 2-vinylcyclobutylidenes can undergo the same type of carbene–carbene rearrangements as vinylcyclopropylidenes, i.e., ring enlargement with participation of the double bond. However, the amount of **8**[23] formed out of **6** reveals that rearrangement to carbene **7** with subsequent stabilization is outweighed by competing reactions, i.e., cyclobutylidene–methylenecyclopropane rearrangement and vinyl migration.

Acknowledgment. Financial support of this work from the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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(17) (a) The ratio of the dimers formed (VPC/MS) does not change on further pyrolysis under the reaction conditions employed. (b) By comparison of VPC retention times, three of these dimers are identical with those obtained from cyclobutylidene–methylenecyclopropane rearrangement of bicyclo[4.2.0]oct-2-en-8-ylidene generated by thermal decomposition of the corresponding tosylhydrazone salt. (c) Likewise, this carbene produces **11** in low yield. Brinker, U. H.; König, L., manuscript in preparation.

(18) In principle, **17** can dimerize by formal [4 + 4] cycloaddition which leads to a third symmetrical dimer, containing a central cycloocta-1,5-diene ring. Such a structure, however, is not compatible with the ^1H NMR spectrum.

(19) We thank Dr. W. Dietrich and L. Hermsdorf for recording the 250-MHz spectra of **11**, **20a**, and **20b**, respectively.

(20) Very recently the synthesis of bicyclo[4.2.0]oct-1(8)-ene has been reported: Levashova, T. V.; Semeikin, O. V.; Balenkova, E. S. *J. Org. Chem. USSR* (*Engl. Transl.*) **1980**, *16*, 53–56.

(21) Migration of bond C_5–C_6 to the divalent carbon would lead to bicyclo[4.2.0]octa-1(8),4-diene which under the reaction conditions could rearrange to **15**. The activation barrier for this transformation is estimated to be lower than the one expected for the conversion **11** → **14**. Thus part of the amount of **15** formed could derive from such a process. Table I indicates, however, that pyrolysis of **9c** with nitrogen as carrier gas affords only 1.6% of **15**—while the percentage of the identified monomers produced is highest—thus suggesting that **15** almost exclusively stems from **13**.

(22) Spangler, C. W. *Tetrahedron* **1976**, *32*, 2681–2684.

(23) Photolysis of bicyclo[3.2.1]oct-2-en-8-one tosylhydrazone (MeOH, NaOMe) and subsequent hydrogenation (Pt/C) of the products obtained gave 2-methoxybicyclo[3.3.0]octanes in ca. 15% yield. However, upon deamination of **9b** followed by hydrogenation under identical conditions, *no* significant formation of these products was detected. Thus, formation of **8** is not likely to be the result of any reaction sequence involving a bicyclo[4.1.1]oct-2-en-7-yl–bicyclo[3.2.1]oct-2-en-8-yl cation rearrangement. Brinker, U. H.; König, L., unpublished results.

Cis–Trans Isomers of 12-S-6 Species—Dissociative Permutational Isomerization of a Persulfurane

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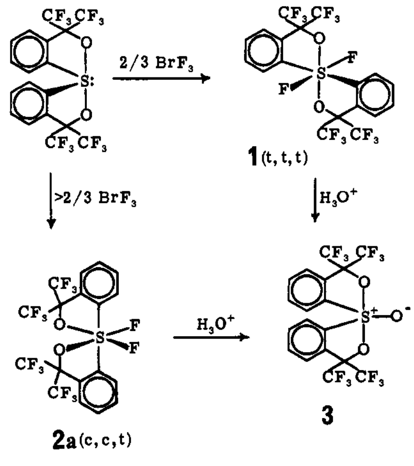
We have reported[1] the synthesis of a persulfonium ion by the reaction of more than 1 equiv of a Lewis acid with difluoropersulfurane **1**. We now report the isomerization of **1** to the geometrical isomer **2a**, in a process catalyzed by traces of Lewis acids.

When more than 1 equiv of BrF_3 ($^2/_3$ mol/mol) is used in attempts to prepare *all-trans*-**1** [**1**(t,t,t)] from the sulfurane precursor, a different product is isolated. This product (**2a**) has an elemental analysis identical with that of **1**, shows a very similar fragmentation pattern in its mass spectrum, and gives the same sulfurane oxide (**3**) as does **1** upon acid-catalyzed hydrolysis but has different ^{19}F and ^1H NMR spectra and a melting point 20 °C higher than that of **1**.



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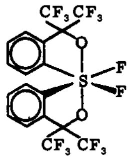
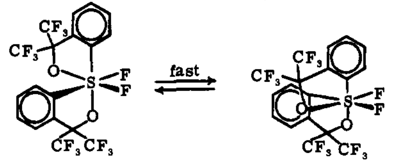
(1) Michalak, R. S.; Martin, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 5921.

The ^{19}F NMR for **2a** shows two unresolved six-fluorine (CF_3) multiplets at −74.3 and −74.7 ppm and an unresolved multiplet at 77.0 ppm (**2**, S–F).[2] Structures **2a** and **2b** are compatible with the NMR data. If permutational isomerization of the all-cis structure **2c** [**2c**(c,c,c)], interconverting the enantiomers as shown, is fast on the NMR time scale, this could also be a possible structure. The choice of **2a** is based on a complete X-ray crystallographic structure to be reported later.

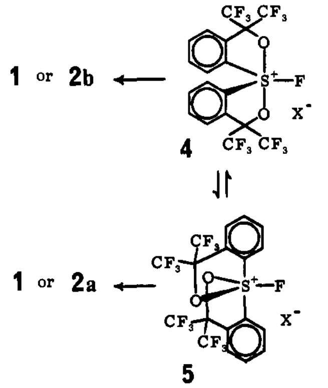


2b(c,c,t)



2c(c,c,c)

A reasonable route for the formation of **1** and **2** involves a common intermediate, trigonal-bipyramidal (TBP) persulfonium salt **4** (X = F). Attack of fluoride at the sulfur opposite fluorine leads to the kinetically preferred all-trans isomer (**1**), while attack at either of the other two positions in the equatorial plane gives the unobserved cis isomer (**2b**). Formation of the observed cis isomer (**2a**) could occur by pseudorotation of **4** to give the higher energy TBP conformer **5**, with equatorial oxygen and apical carbon, followed by attack of fluoride in the equatorial plane of **5** to provide either **1** or **2a**. We have reported the formation of **1** in the reaction of **4** (X = PF_6) with amines,[1] evidence for kinetically favored attack on **4** or **5** to give **1**.



Most, but not all, known compounds of hexacoordinate chalcogens (S, Se, Te) have all-trans geometries. Denney has reported[3] the low-temperature syntheses of some thermally unstable tetrafluoropersulfuranes, R_2SF_4, including a few which were constrained to a cis geometry by a ring system.[5] Cady reported[4] the only previous example of a *cis*-persulfurane, $SF_4(OSF_5)_2$, which was not thus constrained. There are no reported examples of the isolation of both cis and trans isomers of the same persulfurane. The only other chalcogen for which the isolation of cis and trans isomers of the same composition has been reported is tellurium.[5]

The permutational isomerization of **1** to **2** could be imagined to occur by a nondissociative mechanism. A twist mechanism[6] such as the Bailar twist[7] (a process maintaining C_3 symmetry) or the Ray and Dutt twist[8] (C_2 symmetry) involves no bond rupture. The lower limit for the activation energy for isomerization of **1** to **2** by such a twist process is >45 kcal/mol. This was determined by heating a solution of **1** in quinoline at 235 °C for 18 h, with no detectable formation of the more stable isomer **2a**.

Addition of a catalytic amount of SbF_5 to a CH_2Cl_2 solution of **1** results in rapid isomerization of **1** to **2**. None of the trans isomer has been detected by ^{19}F NMR.[9] Since SbF_5 is known to convert **1** or **2a** to persulfonium salt **4** (X = SbF_6), it is reasonable to assume that this rapid acid-catalyzed isomerization of **1** to **2** occurs by a dissociative mechanism. Persulfonium ion intermediate **4** (X = SbF_6) is detectable in the ^{19}F NMR of the isomerization mixture. The formation of **2a**, rather than **1**, in the oxidation of the sulfurane with excess BrF_3 is attributed to the Lewis acidity of BrF_3.

The greater thermodynamic stability of **2a** relative to **1** was further confirmed by calorimetry.[10] The difference in the heat of hydrolysis of the cis and trans isomers to the same sulfurane oxide (**3**) was found to be 2.0 ± 0.5 kcal/mol at 28 °C.[11]

The recently reported isomerizations of a series of hexacoordinated phosphorus anions (12-P-6 species) showed the cis isomers to predominate in equilibrium at room temperature.[12] A related thermodynamic preference for unsymmetrically apically substituted sulfurane (10-S-4) species has been noted.[13]

The greater stability of **2a** relative to **1** may reflect the ionic resonance energy in a unsymmetrically substituted three-center four-electron bond, an effect parallel to that long known to be important in two-center two-electron bonds.[13] The structure **2a** has two O–S–F three-center bonds, while **1** has one O–S–O and one F–S–F three-center bond. The present work leaves unanswered the question of the relative stabilities of the unobserved isomers **2b** and **2c**.

Acknowledgment. This research was supported in part by a grant from the National Science Foundation (Grant 7905692). We thank Michael R. Ross for the construction of the calorimeter which we used.

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(2) Fluorine chemical shifts are expressed in ppm downfield from $CFCl_3$.

(3) Denney, D. B.; Denney, D. Z.; Hsu, Y. F. *J. Am. Chem. Soc.* **1973**, *95*, 8191.

(4) Merrill, C. I.; Cady, G. H. *J. Am. Chem. Soc.* **1963**, *85*, 909.

(5) Lentz, D.; Pritzkow, H.; Seppelt, K. *Inorg. Chem.* **1978**, *17*, 1926.

(6) For reviews of twist mechanisms involving metal species, see: (a) Fortman, J. J.; Sievers, R. E. *Coord. Chem. Rev.* **1971**, *6*, 331. (b) Serpone, N.; Bickley, D. G. *Prog. Inorg. Chem.* **1972**, *17*, 391.

(7) Bailar, J. C., Jr. *Inorg. Nucl. Chem.* **1958**, *8*, 165.

(8) Ray, P. C.; Dutt, N. K. *J. Indian Chem. Soc.* **1943**, *20*, 81.

(9) Because of interference by overlapping peaks in ^{1}H and ^{19}F NMR spectra, it is difficult to identify unambiguously or to quantify the small amount of **1** in equilibrium with **2a**.

(10) We used a calorimeter built by Michael R. Ross in an adaptation of plans by Arnett et al. and Beak et al. [Arnett, E. M.; Bentrude, W. G.; Burke, J. J.; Duggleby, P. M. *J. Am. Chem. Soc.* **1965**, *87*, 1541. Beak, P.; Bonham, J.; Lee, J. T. *Ibid.* **1968**, *90*, 1569.]

(11) The value of ΔH for the hydrolysis of **1** in a solution of $PhCH_3/CF_3CO_2H$ (2:1 v/v) containing 1% H_2O was −12.4 kcal/mol and for the hydrolysis of **2a**, −10.4 kcal/mol.

(12) Font Freide, J. J. H. M.; Trippett, S. *J. Chem. Soc., Chem. Commun.* **1980**, 157.

(13) Lam, W. Y.; Martin, J. C. *J. Org. Chem.*, submitted for publication.

(14) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 81.

Synthesis, Structure, and Stability of (i,o)-Bicyclo[6.2.2]dodeca-9,11-dienes. Generation of Unusually Expanded Carbon–Carbon–Carbon Bond Angles

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The last two decades have witnessed extensive progress in our accumulation of knowledge of highly strained carbon–carbon bonds.[1] The vast majority of the studies which exist deal with

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(1) For a recent review, see A. Greenberg and J. F. Liebman, "Strained Organic Molecules", Academic Press, New York, 1978.