ion to three symmetry-related copper(I) ions and to the central copper(II) ion. Figure 1 gives a view of the complex down a $\bar{4}$ axis (parallel to the *z* axis of the unit cell). The labeling scheme and selected interatomic distances and angles are given in Figure 2.

There are two complexes in the unit cell with the central Cu2 ions in special positions (0, 0, 0) and ($^1/_2$, $^1/_2$, $^1/_2$) with $\bar{4}$ symmetry. Each Cu2 ion is octahedrally coordinated to four equatorial and two axial BTA ligands. The four equatorial BTA ligands illustrated in Figure 1 occupy general positions in the unit cell; their central nitrogen atoms (N1 positions) lie 0.005 (13) Å from the $z = {}^1/_2$ plane ($z = 0$ plane for the complex at the origin) and are coplanar with Cu2. Because N4 lies on a crystallographic $\bar{4}$ axis, a twofold axis relates the two halves of the axial BTA ligands. The central Cu2 ion is also surrounded by four Cu1 ions which lie 2.02 Å alternately above and below the Cu2 basal plane (i.e., the plane defined by Cu2 and the four N1 atoms). The four equatorial BTA ligands define planes (average deviation = 0.008 Å; maximum deviation = 0.017 Å for C4) which make acute angles of 41.7° with the Cu2 basal plane. Because of symmetry considerations, the two planes defined by the axial BTA ligands (average deviation = 0.006 Å; maximum deviation = 0.014 Å for C9) are normal to the Cu2 basal plane.

The stereochemistry about Cu2 is unusual in that it is an undistorted octahedron of a compressed form. Cu2 is coordinated to four equatorial and two axial BTA ligands at the N1 and N4 positions, respectively (Figure 2). While the two Cu2-N4 bond distances are typical, the four Cu2-N1 distances are longer than those usually found for nitrogen coordinated to copper(II).[8,9] Similar copper(II)-nitrogen distances have been observed in Cu(dien)$_2$(NO$_3$)$_2$[10] and Cu(V)$_2$(MEEN),[11] compounds in which the copper(II) ion has distorted, compressed octahedral geometry.

The coordination geometry about Cu1 is approximately tetrahedral but, as shown in Figure 2, there are significant deviations from the ideal angles. Cu1 is coordinated to one *tert*-butyl isocyanide ligand and to three different BTA ligands (two equatorial, one axial) at the N2, N3, and N5 positions. The Cu1-C10 distance of 1.882 (17) Å and Cu1-C10-N6 angle of 175.8 (1.6)° are in general agreement with the respective values of 1.81 (15) Å and 180 (2)° found for CuI(CNCH$_3$).[12] The coordination distances to Cu1 are close to those reported for copper(I)-cyanide complexes in which Cu-N distances are typically 2.0 Å and Cu-C distances are approximately 1.9 Å with a nearly linear Cu-C-N angle.[13,14]

As a tridentate ligand, BTA is involved in two types of copper-nitrogen-copper bridges. Bridging between Cu2 and Cu1 is accomplished via the central and an adjacent nitrogen atom of a BTA ligand. The four symmetry-related Cu1 ions are bridged by the two nitrogen atoms adjacent to the central nitrogen of a BTA ligand in a manner analogous to the imidazolate bridge in [Cu$_2$(bpim)(im)]$_2$(NO$_3$)$_4$·4H$_2$O.[15] The axial BTA ligands bridge two Cu1 ions situated on the same side of the Cu2 basal plane, while the equatorial BTA ligands bridge Cu1 ions on opposite sides of the Cu2 basal plane.

Reference to Figure 1 shows that Cu$_5$(BTA)$_6$(*t*-C$_4$H$_9$NC)$_4$ contains a Cu$_4$N$_{12}$ ring, which we refer to as an azametallocyclic ring. The view of the complex presented in Figure 1 suggests a striking resemblance to a phthalocyanine; however, Cu$_5$(BTA)$_6$(*t*-C$_4$H$_9$NC)$_4$ is far more complex and fundamentally different. There are two additional Cu$_4$N$_{12}$ rings,[16] as well as many larger and smaller azametallocyclic rings, which may be defined in this three-dimensional complex. Unlike the C$_8$N$_8$ macrocycle in phthalocyanine, each Cu$_4$N$_{12}$ ring is nonplanar, with the four copper(I) ions in a ruffled arrangement. Thus, conjugation between the BTA anions and their coordinated copper(I) is probably severely inhibited because of the tetrahedral geometry about copper(I). In this regard, the established architecture for Cu$_5$(BTA)$_6$(*t*-C$_4$H$_9$NC)$_4$ is similar to the nonplanar macrocycle proposed to be present in the pentacopper(II) compound Cu$_5$(BTA)$_6$(acac)$_4$.[17] By replacing tetrahedral copper(I) with planar silver(I) or gold(I), it may be possible to synthesize compounds with planar, conjugated azametallocyclic rings similar to the C$_8$N$_8$ macrocycle in phthalocyanine. In addition, the use of divalent metal ions other than copper(II) in a template synthesis analogous to that described for this compound may lead to a broad class of new metal-nitrogen clusters.

The reaction of benzotriazole with metallic copper leads initially to copper(I) benzotriazolate[18,19] which subsequently oxidizes in air. The structure described herein shows how the benzotriazolate anion, acting as a tridentate ligand, can bridge multiple sites containing both copper(I) and copper(II). It is possible that similar bonding is involved in the corrosion-resistant surface phase produced on the bulk metal.

Acknowledgment. We thank Drs. C. R. Hubbard and R. M. Doherty for assistance and helpful comments. We are grateful for support from the National Bureau of Standards Graduate Cooperative Education Program.

Supplementary Material Available: Tables of atomic positional and thermal parameters and a listing of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

---

(8) Hämäläinen, R.; Turpeinen, U.; Ahlgrén, M. *Acta Crystallogr., Sect. B* **1979**, *35*, 2408-10.

(9) van Niekerk, J. C.; Nassimbeni, L. R. *Acta Crystallogr., Sect. B* **1979**, *35*, 1221-3.

(10) dien = diethylenetriamine. Stephens, F. S. *J. Chem. Soc. A* **1969**, 883-90.

(11) V = 4-formyl-2-methoxyphenolato, MEEN = tetramethylethylenediamine. Greenhough, T. J.; Ladd, M. F. C. *Acta Crystallogr., Sect. B* **1978**, *34*, 2744-52.

(12) Fisher, P. J.; Taylor, N. E.; Harding, M. M. *J. Chem. Soc.* **1960**, 2303-9.

(13) Vrabel, V.; Garaj, J.; Kutschabsky, L. *Acta Crystallogr., Sect. B* **1979**, *35*, 357-60.

(14) Williams, R. J.; Cromer, D. T.; Larson, A. C. *Acta Crystallogr., Sect. B* **1971**, *27*, 1701-6.

(15) bpim = 4,5-bis[[[2-(2-pyridyl)ethyl]imino]methyl]imidazolate, im = imidazolate. Kolks, G.; Frihart, C. R.; Rabinowitz, H. N.; Lippard, S. J. *J. Am. Chem. Soc.* **1976**, *98*, 5720-1.

(16) The two additional Cu$_4$N$_{12}$ rings are easily seen when the complex is viewed down the *x* and *y* axes of the unit cell. In Figure 1, these two Cu$_4$N$_{12}$ rings form horizontal and vertical "figure eights".

(17) acac = 2,4-pentanedionato(1−). Marshall, J. H. *Inorg. Chem.* **1978**, *17*, 3711-3.

(18) Siedle, A. R.; Velapoldi, R. A.; Erickson, N. *Inorg. Nucl. Chem. Lett.* **1978**, *15*, 33.

(19) Siedle, A. R.; Velapoldi, R. A.; Erickson, N. *Appl. Surf. Sci.* **1979**, *3*, 229-35.

(20) Johnson, C. K. ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

Evidence for a Novel Carbene-Carbene Rearrangement of a New Foiled Methylene[1]

Udo H. Brinker* and Lothar König

Abteilung für Chemie der Ruhr-Universität
4630 Bochum, West Germany

Received August 5, 1980

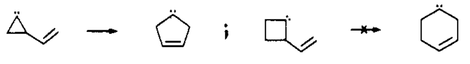
While cyclopropylidene (**1**) undergoes a carbene-carbene rearrangement with a 1,3-carbon shift, **1** → **2**,[2] 2-vinylcyclobutylidene (**3**) surprisingly does not.[3] Different methods of

---

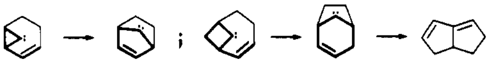
(1) Carbene Rearrangements, part 6. Part 5: Brinker, U. H.; Streu, J. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 631-632.

(2) (a) Skattebøl, L. *Chem. Ind. (London)* **1962**, 2146-2147. (b) *Tetrahedron* **1967**, *23*, 1107-1117. (c) Holm, K. H.; Skattebøl, L. *Tetrahedron Lett.* **1977**, 2347-2350. (d) Jones, W. M.; Brinker, U. H. In "Pericyclic Reactions"; Marchand, A. P., Lehr, R. E., Eds.; Academic Press: New York, 1977; pp 159-165. (e) Schoeller, W. W.; Brinker, U. H. *J. Am. Chem. Soc.* **1978**, *100*, 6012-6017. Concerning the participation of carbenes or carbenoids in rearrangement **1** → **2**, see: Warner, P.; Chang, S.-C. *Tetrahedron Lett.* **1978**, 3981-3984 and ref 3, footnote 4.

0002-7863/81/1503-212$01.00/0 © 1980 American Chemical Society


1 2 3

generation, conformational effects, and less embodied strain in **3** have been suggested to account for the divergent behavior of **1** and **3**.[3] Skattebøl found that 7-norcar-2-enylidene (**4**) containing **1** as a structural subunit rearranges to 7-norbornenylidene (**5**).[2b,4]


4 5 6 7 8

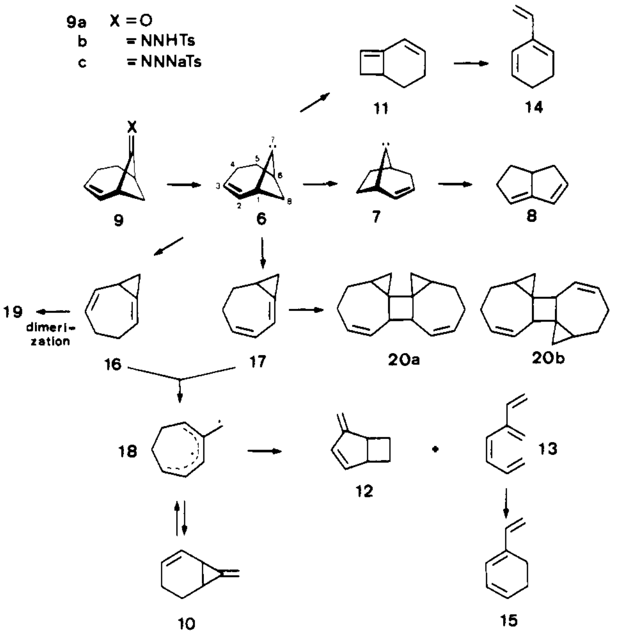
We suspected that the propensity of the divalent carbon in a 2-vinylcyclobutylidene to undergo rearrangement with participation of the double bond should be enhanced if it is incorporated into a strained bicyclic system. Bicyclo[4.1.1]oct-2-en-7-ylidene (**6**), therefore, was expected to be the appropriate carbene for initiating the potential carbene–carbene rearrangement **6** → **7**. Rearranged carbene **7**[5] is known to give nearly exclusively bicyclo[3.3.0]oct-1,7-diene (**8**). Furthermore, **6** is believed to represent a new foiled methylene[6] and is expected to provide access to highly strained hydrocarbons such as bridgehead alkenes.[7]

We report on the rearrangements of carbene **6** generated by decomposition of the dry sodium salt of bicyclo[4.1.1]oct-2-en-7-one tosylhydrazone (**9c**) in a flash vacuum pyrolysis system at 200 (±5) °C. The formation of **8** provides evidence for the novel type of carbene–carbene rearrangement **6** → **7**.

Ketone **9a** was synthesized by using a procedure outlined in the literature.[8] Transformation of **9a** (99.5% pure) to the corresponding tosylhydrazone **9b**[9] proceeded with 85–90% yield. **9b** was converted quantitatively to the sodium salt **9c** by treatment with sodium hydride. Pyrolysis of **9c** in a flash vacuum device produced both monomeric and dimeric hydrocarbons,[9] as indicated in Table I. Under the different pyrolysis conditions used, the product distribution varied only slightly, with **8**, **10**, and **11** being the main isomers produced (Scheme I). Structure **11** can be regarded as the only primary product of **6**, while compounds **12**–**15** are formed as secondary products of **10** and **11**, respectively (vide infra).

The thermolysis of 7-methylenebicyclo[4.1.0]hept-2-ene (**10**), which makes up as much as 43% of the monomers, has recently been studied by Billups et al.[10] in the temperature range between 126.1 and 186.2 °C in a stirred flow system. **10** is reported to rearrange to **12** and **15**[11] at nearly the same rate. Their formation was rationalized via a common diradical **18**, affording **12** and **13**; the latter, however, being unstable under the reaction conditions, undergoes ring closure to **15**. Independent pyrolysis of **10** in our flash vacuum system at 200 (±5) °C under conditions[12] mimicking those of the pyrolysis of **9c**, however, allows isolation of *cis*-2-vinylhexa-1,3,5-triene (**13**)[9] in addition to **12** and **15** (Table I). As expected, pyrolysis of pure **13**[12] produced only **15** and recovered starting material. When hydrogenated (Pd/C, ether), **13** yields 3-methylheptane. Finally, **12** remained unchanged under our pyrolysis conditions.

Scheme I



The reaction pathway leading from carbene **6** to **10** can be thought to involve, as the primary step, two competitive cyclobutylidene–methylenecyclopropane rearrangements[6a] to form bridgehead alkenes[7] **16** and **17** (Scheme I). These ring-contraction reactions by rupture of either bond C_1–C_8 or C_6–C_8 in **6**, affording **17** and **16**, respectively, bear close analogy with the rearrangement of the parent 2-vinylcyclobutylidene (**3**).[3,13] Cleavage of the bond opposite to the quaternary carbon atom in **16** and **17**, under the conditions applied, forms the same resonance-stabilized diradical **18** that can close to **10**. The fact that **10** is by far the main product formed out of diradical **18** suggests a lower activation barrier to **10** than to **12** or **13**.[10b]

Although we have not as yet been able to isolate **16** or **17**,[16] evidence for the intermediacy of **17** is provided by the isolation of the main dimer, a waxy solid (mp 29–30 °C), which could be separated by VPC from the four dimers formed (ratio 72:13:11:4).[17a,b] The ^{13}C NMR spectrum provides only eight

---

(3) Brinker, U. H.; König, L. *J. Am. Chem. Soc.* **1979**, *101*, 4738–4739.

(4) Holm, K. H.; Skattebøl, L. *J. Am. Chem. Soc.* **1977**, *99*, 5480–5481. Kirmse, W.; Jendralla, H. *Chem. Ber.* **1978**, *111*, 1873–1882.

(5) Fickes, G. N.; Rose, C. B. *J. Org. Chem.* **1972**, *37*, 2898–2899. **8** and a compound not identified are formed from **7** in a 97:3 ratio (80–90% isolated yield). **7** was generated at 150 °C in diglyme (NaOMe) by decomposition of the corresponding tosylhydrazone.

(6) (a) Kirmse, W. "Carbene Chemistry"; Academic Press: New York, 1971. (b) Baron, W. J.; DeCamp, M. R.; Hendrick, M. E.; Jones, M., Jr.; Levin, R. H.; Sohn, M. B. "Carbenes"; Wiley: New York, 1973; Vol. 1, pp 50–51. (c) Jones, W. M. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980.

(7) Köbrich, G. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 464–473. Keese, R. *Ibid.* **1975**, *14*, 528–538. Buchanan, G. L. *Chem. Soc. Rev.* **1974**, *3*, 41–63. Lenoir, D. *Nachr. Chem. Tech. Lab.* **1979**, *27*, 762–765.

(8) LeBel, N. A.; Spurlock, L. A. *Tetrahedron* **1964**, *20*, 215–229. Foote, C. S.; Woodward, R. B. *Ibid.* **1964**, *20*, 687–715. Erman, W. F.; Kretschmar, H. C. *J. Am. Chem. Soc.* **1967**, *89*, 3842–3846.

(9) Satisfactory combustion analyses were obtained for all new compounds. Selected spectral data are as follows. **9b**: mp 159–161 °C ($MeOH/H_2O$); ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.2–2.7 (m, 6 H), 2.45 (s, 3 H), 3.2–3.8 (m, 2 H), 5.4–6.2 (m, 2 H), 7.2–8.1 (m, 4 H, AA′BB′), N–H varies; IR (KBr) 3400, 2920, 1335, 1160 cm^{-1}. **11**: ^{1}H NMR (250 MHz, $CCl_4/CDCl_3$) δ 1.3–1.55 (m, 1 H), 1.95–2.35 (m, 4 H), 2.5–2.7 (m, 2 H), 5.53 (s, 1 H), 5.75–5.85 (m, 1 H), 6.0–6.15 ("d", 1 H); IR (CCl_4) 3025, 2910 cm^{-1}; UV (*n*-hexane) 240 nm, 271.5 (sh). **13**: ^{1}H NMR (60 MHz, CCl_4) δ 4.95–5.45 (m, 6 H), 5.85–7.05 (m, 4 H); IR (film) 3090, 3010, 1580 cm^{-1}; UV (*n*-hexane) 219 nm (ϵ 36000), 226 (33000), 241 (sh, 10500), 258 (sh, 8500). **20a** or **20b**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.35–0.55 (m, 6 H), 1.10–1.25 (m, 2 H), 1.95–2.25 (m, 6 H), 2.90 ("s", 2 H), 5.58 ("s", 4 H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 17.2 (t), 17.8 (d), 28.3 (t), 30.2 (s), 30.4 (t), 49.0 (d), 128.9 (d), 132.9 (d).

(10) (a) Billups, W. E.; Baker, B. A.; Chow, W. Y.; Leavell, K. H.; Lewis, E. S. *J. Org. Chem.* **1975**, *40*, 1702–1704. (b) Billups, W. E.; Leavell, K. H.; Chow, W. Y.; Lewis, E. S. *J. Am. Chem. Soc.* **1972**, *94*, 1770–1771.

(11) Doering, W. von E.; Roth, W. R. *Tetrahedron* **1963**, *19*, 715–737. Roth, W. R.; Peltzer, B. *Liebigs Ann. Chem.* **1965**, *685*, 56–74. Ziegenbein, W. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 70. Japenga, J.; Klumpp, G. W.; Schakel, M. *Tetrahedron Lett.* **1978**, 1869–1872.

(12) The results obtained from the pyrolysis of hydrocarbons **10**, **11**, **12**, **13**, the mixture of the dimers, and the sodium salt **9c** are not directly comparable because different pyrolysis methods were applied. The sodium salt **9c** was introduced into the reaction vessel as a dry solid to promote its decomposition on the hot glass surface. On the other hand, the liquids **10**, **11**, **12**, and **13** had to pass through a 30-cm (1-cm i.d.) quartz tube filled with glass turnings held at 200 °C.

(13) The ratio of allylidenecyclopropane to vinylmethylenecyclopropane observed in the reaction of **3** was strongly in favor of allylidenecyclopropane.[3] By analogy, **17** is expected to be the main product in the cyclobutylidene–methylenecyclopropane rearrangement of **6**.

(14) Tarakanova, A. V.; Grishin, Y. K.; Vashakidze, A. G.; Mil'vitskaya, E. M.; Platé, A. F. *J. Org. Chem. USSR (Engl. Transl.)* **1972**, *8*, 1655–1658.

(15) Baumann, M.; Köbrich, G. *Tetrahedron Lett.* **1974**, 1217–1220.

(16) **16**, when generated under basic conditions, is reported to rearrange to **10** at 15–25 °C.[10b,14] On the other hand, a tetramethyl-substituted **16** can be distilled in vacuo at 90 °C without decomposition.[15]

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.

---

[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 **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

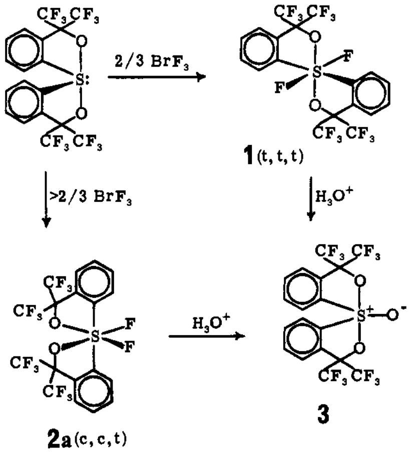
Ronald S. Michalak and J. C. Martin*

Roger Adams Laboratory, University of Illinois
Urbana, Illinois 61801

Received October 14, 1980

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**.



---

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

0002-7863/81/1503-214$01.00/0