type of delocalization in the two systems is quite different, the cyclopropylcarbinyl cations are the best model and cmr shifts would be expected in the same region of the carbon-13 scale. The chemical shift of the methylene carbons is not consistent with open chain equilibrating primary carbenium ions or with a system of high degree of ethylenic character.[8] (4) Charge distribution and chemical shifts have the expected relationship with regard to substituent effects. The methylene carbon shifts are quite consistent with substituent effects based on what has been observed for other arylonium ion systems studied. The most deshielded cyclopropyl carbon absorption is that of **2**-H; the most shielded is that of **2**-OCH_3, as would be expected from the ability of the aryl ring to bear positive charge. Interestingly, at the temperature studied (−78°), there is no observed rotational barrier to the C_{arom}–O bond of the *p*-methoxy substituent. This is also the case in the *p*-methoxycumyl cation,[16] and in the *p*-methoxystyryl cation.[3] However, nonequivalence of the ortho protons and carbons, indicating a sizable rotational barrier, is observed for the *p*-methoxybenzyl[17] cation as well as for C-protonated anisole (*p*-methoxybenzenonium ion).

In summary, the direct observation of the ethylene-phenonium and ethylene-*p*-toluonium ions and their ^1H and ^{13}C nmr spectroscopic study fully substantiate their bridged spirocyclopropylbenzenonium ion type structure and eliminate the possibility of open chain rapidly equilibrating β-phenylethyl cations. We feel that the data obtained give direct structural evidence for these long controversial ions, and also indicate the charge distribution into the aryl ring and spirocyclopropyl system.

Acknowledgment. Partial support of our work by the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

(16) G. A. Olah, M. B. Comisarow, and C. J. Kim, *J. Amer. Chem. Soc.*, **91**, 1458 (1969).

(17) G. A. Olah, R. D. Porter, and C. L. Jevell, to be published.

* Address correspondence to this author.

G. A. Olah,* R. D. Porter
Department of Chemistry, Case Western Reserve University
Cleveland, Ohio 44106

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A New Pathway to Unsymmetrical Disulfides. The Thiol-Induced Fragmentation of Sulfenyl Thiocarbonates[1]

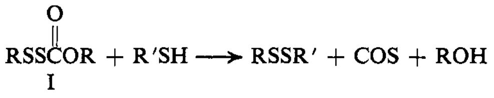
Sir:

The literature abounds with reports on synthetic options to unsymmetrical disulfides. Prominent among the more attractive routes to *homogeneous* unsymmetrical disulfides are the nucleophilic displacement reactions of sulfenyl[2] derivatives with thiols as depicted in eq 1.

$$RS^{\delta+}\text{—}X^{\delta-} + R'S^- \longrightarrow RSSR' + X^- \qquad (1)$$

The most notable sulfenyl reagents presently available for constructing mixed disulfides according to eq 1 are the sulfenyl halides,[4] sulfenyl thiocyanates,[5] sulfenyl hydrazides,[6] thiosulfates,[7] sulfenyl thioureas,[8] thiolsulfonates,[9] and sulfenimides.[10] Unfortunately, the synthetic entanglements created by the instability and unreactivity of the sulfenyl reagents and functional group interactions in the sulfenyl moiety have substantially reduced the scope and utility of the known procedures. More seriously, disulfide interchange (disproportionation) engendered by reaction conditions and side products, among other causative factors, constitutes a major obstacle to the design of homogeneous unsymmetrical disulfides *via* these electrophilic substrates.

In the present communication, we wish to report a unique and extremely facile heterolytic fragmentation route to unsymmetrical disulfides. We have discovered that the thiol-mediated fragmentation of sulfenyl thiocarbonates (I) at room temperature gives unsymmetrical disulfides cleanly and quantitatively in accord with eq 2.



$$\underset{\text{I}}{RSS\overset{\overset{\large O}{\|}}{C}OR} + R'SH \longrightarrow RSSR' + COS + ROH \qquad (2)$$

We believe that the heterolytic fragmentation route offers decided advantages over the presently known S_N2 pathways to mixed disulfides. The key synthetic merits, which will be touched upon briefly here, comprise the facile preparation of the sulfenyl reagents, the lack of functional group interactions, the remarkable stability and high reactivity of the sulfenyl electrophiles, and the absence of side products in the mixed disulfide.

The sulfenyl thiocarbonate reactants (Table I) are easily prepared in excellent yields *via* the reaction of

Table I. Sulfenyl Thiocarbonates[a]

Entry	Structure	Bp [mp], °C (*P*, mm)	% yield
Ia	$EtSSC(=O)OMe$	53–54 (1)	95
Ib	$EtSSC(=O)OEt$[b]	74–75 (0.5)	94
Ic	$HOCH_2CH_2SSC(=O)OMe$	112 (0.35)	98
Id	$HCl\text{-}NH_2CH_2CH_2SSC(=O)OMe$	[107–108]	99
Ie	$HCl\text{-}NH_2CH_2CH_2SSCO(CH_2)_{11}CH_3$	[92–93]	92

[a] The analytical and spectral data for all compounds were fully consonant with the structures shown. [b] Reference 11 reports bp 69° (0.12 mm).

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(1) Part I in the series: New Synthetic Concepts in Organosulfur Chemistry.

(2) From a mechanistic standpoint, Foss[3] proposed that a wide spectrum of sulfur analogs could be fitted into the family of compounds which exhibited "sulfenyl behavior" in the sense of eq 1. The classification suggested by Foss has proved valuable since it accommodates new examples as they are encountered, and emphasizes the broad scope of this area of study.

(3) (a) O. Foss, *Acta Chem. Scand.*, **1**, 307 (1947); (b) M. Kharasch, Z. S. Ariyan, and A. J. Havlik, *Quart. Rep. Sulfur Chem.*, **1**, 97 (1966).

(4) E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. 3, Chemical Publishing Co., New York, N. Y., 1960, p 368.

(5) R. G. Hiskey and B. F. Ward, Jr., *J. Org. Chem.*, **35**, 1118 (1970), and earlier references.

(6) T. Mukaiyama and K. Takahashi, *Tetrahedron Lett.*, 5907 (1968); V. Bockelheide and J. L. Mondt, *ibid.*, 1203 (1970); S. J. Brois, unpublished results.

(7) D. L. Klayman and R. J. Shine, *Quart. Rep. Sulfur Chem.*, **3**, 231 (1968).

(8) K. Sirakawa, O. Aki, T. Tsujikawa, and T. Tsuda, *Chem. Pharm. Bull.* (*Tokyo*), **18**, 235 (1970); S. J. Brois and H. W. Barnum, unpublished results.

(9) L. Field and J. D. Buckman, *J. Org. Chem.*, **33**, 3865 (1968), and earlier references.

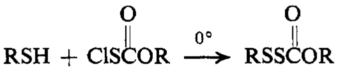
(10) K. S. Boustany and A. B. Sullivan, *Tetrahedron Lett.*, 3547 (1970); D. N. Harpp, D. K. Ash, T. G. Back, J. G. Gleason, B. A. Orwig, W. F. Van Horn, and J. P. Snyder, *ibid.*, 3551 (1970).

Table II. Disulfides *via* Fragmentation[a]

Reagents	Product	Bp [mp], °C (P, mm)	% yield
Ia,[b] $PhCH_2SH$	$PhCH_2SSEt$	75–76 (0.07)	99
Ia, PhSH	PhSSEt	89–90 (1.2)	95
Ia, PrSH	PrSSEt	104–106 (80)	94
Id, MeC(=O)SH	$MeC(=O)SSCH_2CH_2NH_2$–HCl[c]	[101–103]	99
Id, PhC(=O)SH	$PhC(=O)SSCH_2CH_2NH_2$–HCl	[102–103]	98
Id, $HSSO_3H$[d]	$NH_2CH_2CH_2SSSO_3H$	[175–176]	93

[a] All reactions conducted in methanol at 25° unless indicated otherwise. The analytical and spectral data for all compounds were consistent with the proposed structures. [b] Fragmentation of Ia was catalyzed by Et_3N. [c] Fragmentation reaction conducted at 0°. The structure was confirmed by an alternate synthesis involving displacement on acetylsulfenyl chloride by 2-mercaptoethylamine hydrochloride in methanol. [d] Fragmentation conducted at −40°. The thiosulfuric acid was prepared according to S. J. Brois (U. S. Patent 3,468,925 (1969)).

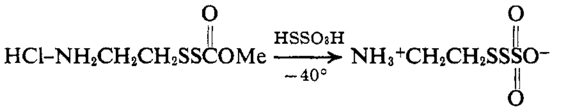
thiols with carboalkoxysulfenyl chlorides[11] at low temperatures in methanol solution.



$$RSH + ClS\overset{\overset{O}{\|}}{C}OR \xrightarrow{0^\circ} RSS\overset{\overset{O}{\|}}{C}OR$$

Preliminary study suggests that most of the common functional groups are compatible with the sulfenyl thiocarbonate moiety. Especially gratifying was the successful design of thiocarbonates which incorporated *amine salt* functions as typified by structure Id (Table I). Surprisingly, these salts exhibit *excellent stability* and could be conveniently recrystallized. The ready availability of such versatile electrophilic reagents has provided us access to a wide spectrum of exotic, mixed disulfides of cysteamine.

Undoubtedly, the most prominent feature of the present process is the *highly facile* and *selective* manner in which the sulfenyl thiocarbonates are fragmented by thiols. While most reactions of I are effected at room temperature for convenience, the use of much milder temperatures[13] has been found to be entirely realistic. Thus, the fragmentation of Id with thiosulfuric acid at −*40*° in methanol afforded the first insolable[14] sulfenyl thiosulfate (II).



$$HCl\text{–}NH_2CH_2CH_2SS\overset{\overset{O}{\|}}{C}OMe \xrightarrow[-40^\circ]{HSSO_3H} NH_3{}^+CH_2CH_2SS\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}O^- \quad (3)$$

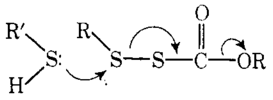
Id II

By analogy with its lower sulfur homolog, 2-aminoethyl thiosulfate, the infrared spectrum of II discloses two prominent bands at about 8.3 and 9.8 μ; these absorption bands appear to be characteristic of such internal Bunte salts. The proton spectrum of II in D_2O exhibits the expected A_2B_2 multiplet (methylene protons) centered at δ 3.31.

Special significance may be attached to the successful design of acetyl 2-aminoethyl disulfide hydrochloride using the fragmentation route at 0° since previous attempts by Field and Buckman[16] to construct this disulfide *via* the thiolsulfonate route gave only the disproportionation product, cystamine dihydrochloride. We are confident that a wide spectrum of previously inaccessible mixed disulfides may be preparable from I. Moreover, the prospect of readily designing complex cystine peptides[5] *via* the fragmentation route appears promising.

In a typical experiment, 12.4 g (0.1 mol) of benzyl mercaptan was added dropwise to a stirred solution of 0.1 mol of Ia in 50 ml of methanol at *ca.* 25°. The fragmentation of Ia was markedly accelerated by adding catalytic amounts (2 drops) of triethylamine. After thiol addition, the reaction mixture is concentrated by evaporation, leaving 18.2 g (99% yield) of analytically and spectrally homogeneous benzyl ethyl disulfide. The reaction of Id with thiols or thio acids appeared to be instantaneous even below 0° and no amine catalyst was required (see Table II).

In addition to its broad synthetic potential, the thiol-induced reaction of sulfenyl thiocarbonates is mechanistically intriguing. In accord with the reaction pathway postulated by Grob[17] for fragmentable systems, the experimental evidence clearly indicates that alkylsulfenyl thiocarbonates (I) undergo a thiol-mediated fragmentation (eq 4) wherein RS– denotes the



(4)

electrofugal group, COS is the unsaturated fragment, and RO– is the nucleofugal group.[18] At present, we favor a cyclic transition state (III) as a more precise description of the disulfide-forming fragmentation

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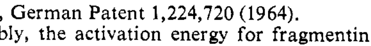
[11] G. Zumach and E. Kühle, *Angew. Chem., Int. Ed. Engl.*, **9**, 54 (1970). These authors report that the reaction of equimolar quantities of chlorocarbonylsulfenyl chloride[12] and alcohol at 30–60° affords very good yields of carboalkoxysulfenyl chlorides.



$$ROH + Cl\overset{\overset{O}{\|}}{C}SCl \xrightarrow{30\text{–}60^\circ} RO\overset{\overset{O}{\|}}{C}SCl + HCl$$

[12] W. Weiss, German Patent 1,224,720 (1964).

[13] Conceivably, the activation energy for fragmenting I by thiols may be diminished appreciably as a consequence of the highly favorable free energy of formation of COS (−40.45 kcal/mol).

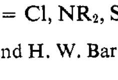
[14] The existence of sulfenyl thiosulfates has been proposed by Foss[3a] as well as Scandurra and DeMarco,[15] but an authentic sulfenyl Bunte salt has never been isolated and characterized.

[15] R. Scandurra and C. DeMarco, *Ric. Sci., Parte 2, Sez. B*, **32**, 119 (1962); *Chem. Abstr.*, **58**, 13782*b* (1963).

[16] L. Field and J. D. Buckman, *J. Org. Chem.*, **32**, 3467 (1967).

[17] C. A. Grob, *Angew. Chem., Int. Ed. Engl.*, **8**, 535 (1969), and previous papers.

[18] The dramatic effect of other electro- and nucleofugal groups on the reactivity of i toward thiols will be described elsewhere.[19] Most recently, we discovered that the thiol-induced fragmentation of i (X = Cl, SR) *in the presence of trialkylamines* is also an exceptionally attractive pathway to mixed disulfides. The fascinating role that amines play in accelerating disulfide-forming fragmentations awaits elucidation.

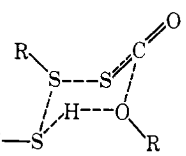


$$RSS\overset{\overset{O}{\|}}{C}X$$

i, X = Cl, NR_2, SR

[19] S. J. Brois, J. F. Pilot, and H. W. Barnum, submitted for publication.

event. In our mechanistic proposal, we envision the *synchronous* fragmentation of III to be rapid with the loss of carbonyl sulfide acting as a potent driving force.



III

Complete details of the synthetic and mechanistic aspects of this work will be elaborated in the full paper.

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* Address correspondence to this author.

Stanley J. Brois,* John F. Pilot, Harry W. Barnum
Esso Research and Engineering Company
Linden, New Jersey 07036

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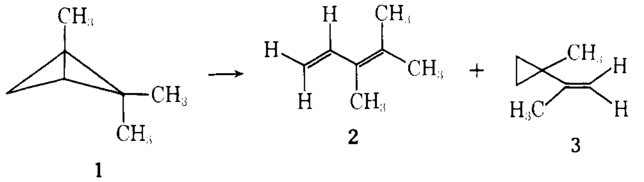
A Formal Retrocarbene Addition. The Reaction of 1,2,2-Trimethylbicyclo[1.1.0]butane with Transition Metal Catalysts[1]

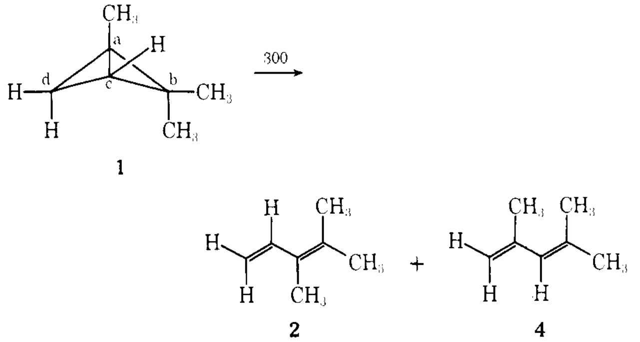
Sir:

The thermal isomerization of derivatives of bicyclo[1.1.0]butane to derivatives of 1,3-butadiene has been investigated by numerous workers[2] and the mechanism of this interesting thermal rearrangement has been discussed in detail.[2m,2o,3,4] Although the bicyclo[1.1.0]butane nucleus has a strain energy of *ca.* 66 kcal/mol,[5] temperatures of 150–300° and activation energies in excess of 40 kcal/mol[2d,2g] appear necessary for a reasonable rate of isomerization. We now wish to report that 1,2,2-trimethylbicyclo[1.1.0]butane[6] (**1**) is rapidly isomerized to a mixture of 3,4-dimethyl-1,3-pentadiene (**2**) and the vinylcyclopropane **3** at room temperature by specific transition metal catalysts. We also wish to record that these facile exothermic reactions differ dramatically from the well-established thermal rearrangements in that different carbon–carbon bonds are cleaved in the two processes.



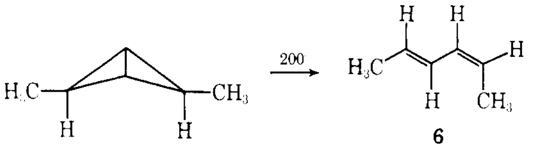
1 **2** **3**

Skattebøl and Moore and coworkers have shown[6] that **1** was readily isomerized to a 53:47 mixture of **2** and **4**

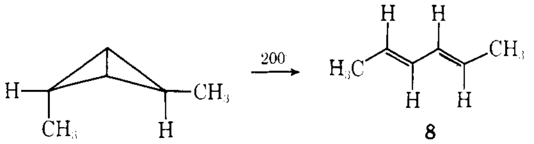


1 **2** **4**

in the vicinity of 300°. These thermolysis products are readily rationalized in terms of a molecular orbital allowed concerted process[4] as discussed for the 2,4-dimethylbicyclo[1.1.0]butanes by Closs and Pfeffer,[3c] who found that **5** gave 93% of **6** while **7** yielded 95% of **8**. The rearrangements of **5** and **7** required that one



5 **6**



7 **8**

cyclopropyl ring be cleaved in a disrotatory manner while the other be opened predominantly in a conrotatory manner. Although the same stereochemical aspects are not present, it can be seen that similar pyrolysis of **1** would give **2** *via* cleavage of the a–d and b–c bonds and **4** *via* cleavage of the a–b and c–d bonds. The results of Closs and Pfeffer[3c] leave no doubt concerning the lack of cleavage of the a–c bond in such thermal reactions.

When **1** was treated with 3 mol % of rhodium dicarbonyl chloride dimer in chloroform at room temperature an immediate exothermic reaction occurred to yield, after 5 min, 58% **2** and 30% **3**.[7] In contrast to the pyrolysis of **1**, no trace of **4** could be detected. In principle the formation of **2** in the transition metal catalyzed reaction could occur either *via* cleavage of the

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[1] Paper XIV of a series on The Chemistry of Bent σ Bonds. For the preceding paper in this series see P. G. Gassman and G. D. Richmond, *J. Amer. Chem. Soc.*, **92**, 2090 (1970).

[2] (a) W. Mahler, *J. Amer. Chem. Soc.*, **84**, 4600 (1962); (b) D. M. Lemal, F. Menger, and G. W. Clark, *ibid.*, **85**, 2529 (1963); (c) K. B. Wiberg and G. M. Lampman, *Tetrahedron Lett.*, 2173 (1963); (d) J. P. Chesick, *J. Phys. Chem.*, **68**, 2033 (1964); (e) R. Srinivasan, A. A. Levi, and I. Haller, *ibid.*, **69**, 1775 (1965); (f) H. M. Frey and I. D. R. Stevens, *Proc. Chem. Soc.*, 144 (1964); (g) H. M. Frey and I. D. R. Stevens, *Trans. Faraday Soc.*, **61**, 90 (1965); (h) A. Small, *J. Amer. Chem. Soc.*, **86**, 2091 (1964); *J. Org. Chem.*, **33**, 1441 (1968); (i) W. von E. Doering and J. F. Coburn, Jr., *Tetrahedron Lett.*, 991 (1965); (j) S. Masamune, *ibid.*, 945 (1965); (k) E. P. Blanchard, Jr., and A. Cairncross, *J. Amer. Chem. Soc.*, **88**, 487, 496 (1966); (l) J. Pusset and R. Beugelmans, *Tetrahedron Lett.*, 3249 (1967); (m) K. B. Wiberg and R. A. Fenoglio, *J. Amer. Chem. Soc.*, **90**, 3395 (1968); (n) D. P. G. Hamon, *ibid.*, **90**, 4513 (1968); (o) K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968); K. B. Wiberg, *Advan. Alicyclic Chem.*, **2**, 185 (1968); (p) R. B. Woodward and D. L. Dalrymple, *J. Amer. Chem. Soc.*, **91**, 4612 (1969); I. A. D'yakonov, V. V. Razen, and M. I. Komendantov, *Tetrahedron Lett.*, 1127, 1135 (1966).

[3] (a) K. B. Wiberg and J. M. Lavanish, *J. Amer. Chem. Soc.*, **88**, 5272 (1966); (b) K. B. Wiberg and G. Szeimies, *Tetrahedron Lett.*, 1235 (1968); (c) G. L. Closs and P. E. Pfeffer, *J. Amer. Chem. Soc.*, **90**, 2452 (1968).

[4] R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969). In particular see pp 810–814.

[5] For recent discussions of strain in polycyclic molecules see R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, Jr., and M. Pomerantz, *J. Amer. Chem. Soc.*, **90**, 4315 (1968); N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.*, **50**, 1262 (1969); P. Schleyer, J. E. Williams, and K. R. Blanchard, *J. Amer. Chem. Soc.*, **92**, 2377 (1970); S. Chang, D. McNally, S. Shary-Tehrany, M. J. Hickey, and R. H. Boyd, *ibid.*, **92**, 3109 (1970); N. C. Baird, *Tetrahedron*, **26**, 2185 (1970).

[6] L. Skattebøl, *Tetrahedron Lett.*, 2361 (1970); W. R. Moore, K. G. Taylor, P. Müller, S. S. Hall, and Z. L. F. Gaibel, *ibid.*, 2365 (1970).

[7] The structures of the products were established by a combination of infrared, ultraviolet, and nmr spectroscopy. In addition **2** was reduced to 2,3-dimethylpentane which was identical in all respects with an authentic sample and **3** was compared with an authentic sample[6] of **3**.