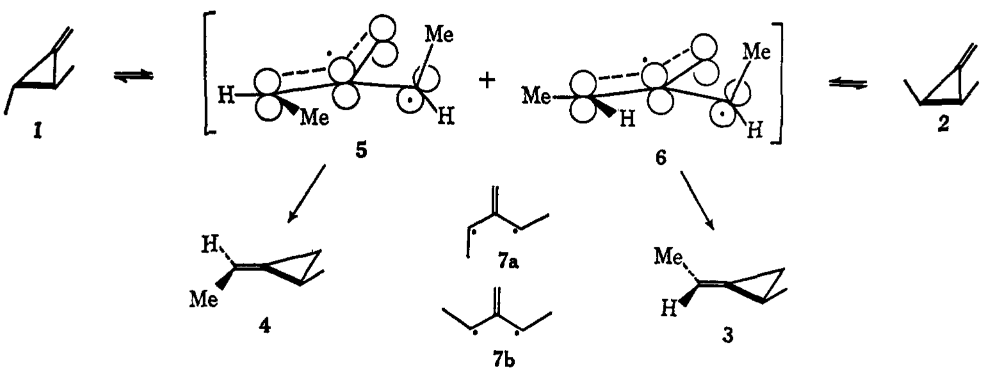

These results correspond to those obtained by Ullman in the pyrolysis of optically active Feist's ester[2a] with a number of significant additions or exceptions that allow formulation of a hypothesis for the pathways involved in the thermal self-interconversion of a relatively unperturbed methylenecyclopropane system. To the small extent that **1** racemizes *via* a direct path, k_2, and to whatever degree **3** and **4** lose optical activity when produced directly from optically active **1**, planar trimethylenemethane intermediates, **7a** and **7b**, may be envisioned. However, the simplest explanation for substantial preservation of activity of **1** and **3** and **4** and interconversion of **1** and **2** at about the same rate of rearrangement involves the postulate of two dissymmetric species, **5** and **6**, that result from allylic bond fission with a 90° rotation about only one C–C bond.[6] Inspection of the geometry of these species reveals that so long as products are formed by a single 90° rotation about an allyl bond, **5** can form **2**, inverted **4**, and retained **1**, but not **3**; **6** can form **2**, inverted **3**, and retained **1**, but not **4**. To account for similar **3**:**4** ratios from **1** and **2**, **5** and **6** must be formed in nearly the same ratio from both **1** and **2**, and they must re-form the methylenecyclopropane systems faster than bond rotation to account for the stereochemical results.

If the reasonable assumption is made that all the rate constants for formation of individual products from **5** and **6** are about the same (except that **5** gives no **3** and **6** gives no **4**) and that **7** will partition itself similarly and in accord with statistical considerations, then the **3**:**4** ratio and the optical results suggest that **6** is about 1.7 kcal/mol more stable than **5** which in turn is about as stable as **7**. These stabilities can be calculated near quantitatively on the basis of nonbonded interactions alone using Bartell's potential functions[7] and reasonable geometric parameters and making the assumption that the interaction of the half-filled p orbital in the nodal plane of the allyl radical in **5** and **6** with various atoms can be described by the same potential function used to calculate the interaction of a hydrogen with various atoms.[8,9] These steric interaction calculations also suggest that the unsubstituted planar trimethylenemethane diradical is slightly more stable than the orthogonal diradical systems corresponding to **5** and **6**, a point amenable to experimental verification. Finally, if the pathways cited for the rearrangement are appropriate, and if **6** is more stable than **5** or **7** due to steric interactions, then the stabilities of the orthogonal and planar trimethylenemethane diradical systems produced in the thermolysis of methylenecyclopropane are nearly equivalent, which implies that the two systems are stabilized by electron delocalization to roughly the same extent.

Acknowledgment. We wish to acknowledge stimulating discussions with Drs. Ullman, Doering, and Crandall and the technical assistance of Mr. L. T. Burka. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support (2754-A1,4) of this research.

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(6) (a) A variation on this mechanism which may be in accord with orbital symmetry considerations as applied to 1,3 sigmatropic shifts where the migrating orbital is antisymmetric[6b] could be responsible for **3** and **4**. Thus, the *exo*-methylene group could twist 90° simultaneous with, but in a sense opposite to, the ring bond 90° rotation. Two such pathways are required to account for formation of both **3** and **4**. Unfortunately, this mechanism does not provide for formation of **2** from **1** or **1** from **2**, nor can a planar intermediate account solely for production of **2** and **1**; therefore **5** and **6** must still be involved. (b) See J. A. Berson, *Accounts Chem. Res.*, **1**, 152 (1968).

(7) L. S. Bartell, *J. Chem. Phys.*, **32**, 827 (1960). We assume that these functions apply equally to sp^3- and sp^2-hydridized carbon. The energy was not minimized with respect to the conformation of the methyl groups; however, the methyl position chosen reflected that indicated to be the most stable by inspection of molecular models.

(8) (a) Since the lone pair of electrons on nitrogen appears to be of slightly larger "steric size" than a hydrogen,[8b] this interaction potential may not be unreasonable. Other results suggest the opposite is true.[8c,d] We only wish to point out that if no subtle electronic effect is operative, a destabilizing half-filled p-orbital–methyl interaction must be considered in order to account for preferential formation of **6** over **5**. (b) J. B. Lambert, *et al.*, *J. Am. Chem. Soc.*, **89**, 3761 (1967). (c) A. R. Katritzky, *et al.*, *J. Chem. Soc.*, *B*, 550, 554 (1968). (d) See also E. L. Eliel, M. C. Knoeber, *J. Am. Chem. Soc.*, **88**, 5347 (1966), and references contained therein.

(9) There was no evidence for chemical interaction between the half-filled p orbital and the methyl group, *i.e.*, there was no transannular hydrogen shift to produce 2-ethyl-1,3-butadiene which was found to be stable under the reaction conditions.

Benzenesulfinyl Azide and 1,3,5-Triphenyl-1,3,5,2,4,6-trithiatriazine 1,3,5-Trioxide

Sir:

Two unsuccessful attempts to prepare sulfinyl azides from *p*-toluenesulfinyl chloride and azide salts have been reported.[1] In each case, results suggested that the sulfinyl azide was a transient intermediate which disproportionates and fragments but does not undergo a Curtius-type rearrangement. Thus, considerable interest has been generated in preparing sulfinyl azides

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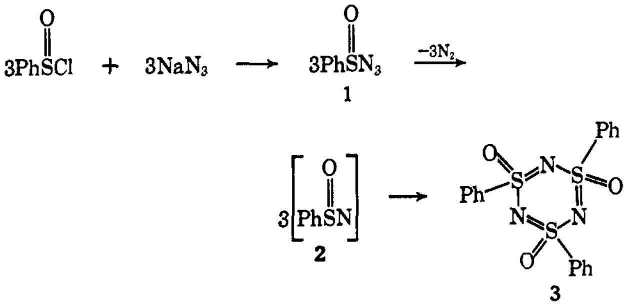
(1) (a) M. Kobayashi and A. Yamamoto, *Bull. Chem. Soc. Japan*, **39**, 2733 (1966); (b) S. T. Purrington, 12th Annual Report on Research under the Sponsorship of the Petroleum Research Fund, American Chemical Society, Washington, D. C., 1967, p 8.

and comparing their properties with carbonyl and sulfonyl azides.

We wish to report the preparation of benzenesulfinyl azide (**1**). No sulfinyl azide has previously been reported. Because of its low thermal stability, azide **1** was prepared at temperatures below −35° from benzenesulfinyl chloride[2] and sodium azide in acetonitrile under anhydrous conditions. Sodium iodide (10% molar) was added to decrease reaction times to about 3 hr. A portion of the filtered reaction mixture was distilled under vacuum (5–30 μ) at −40° to remove solvent and afford the neat azide.

Benzenesulfinyl azide is a red-orange oil that crystallizes to an orange-brown solid at about −50°. No decomposition occurred when **1** was stored overnight in Dry Ice. However, when a few drops rapidly warmed up to room temperature in a capillary, an explosive decomposition occurred. Infrared analysis (neat) of **1** at −30° showed absorption at 2100 (asym N_3), 1177 (sym N_3), and 1129 cm^{-1} (SO), plus other bands typical of monosulfur-substituted benzene. The azide bands disappeared on warming. A similar disappearance of the azide absorption was observed in chloroform solution, accompanied by gas evolution.

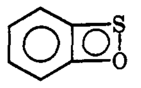
Controlled reactions of benzenesulfinyl azide in acetonitrile solution were obtained with nitrogen evolution near 0°, although very slow decomposition was observed at −20°. With solvent as substrate, nmr analysis showed no reaction with acetonitrile upon azide decomposition. It appears that only disproportionation, fragmentation, and self-condensations occurred. Partial separation of the reaction mixture afforded low yields of products. Nevertheless, benzenesulfonyl azide, phenyl disulfide, and a novel compound (**3**) with the formula $(C_6H_5NOS)_3$ were isolated. The formation of **3** might be explained by proposing an electron-deficient species, **2**, as the intermediate.



$$3\mathrm{Ph}\overset{\mathrm{O}}{\overset{\|}{\mathrm{S}}}\mathrm{Cl} + 3\mathrm{NaN_3} \longrightarrow \underset{\mathbf{1}}{3\mathrm{Ph}\overset{\mathrm{O}}{\overset{\|}{\mathrm{S}}}\mathrm{N_3}} \xrightarrow{-3\mathrm{N_2}}$$

$$\underset{\mathbf{2}}{3\left[\mathrm{Ph}\overset{\mathrm{O}}{\overset{\|}{\mathrm{S}}}\mathrm{N}\right]} \longrightarrow \mathbf{3}$$

Compound **3** is believed to be the first[3] organic derivative of the delocalized p-d π trithiatriazine ring system (1,3,5-triphenyl-1,3,5,2,4,6-trithiatriazine 1,3,5-trioxide). Such compounds are of theoretical interest and have been discussed with reference to the concept of pseudoaromaticity.[4] The structure was assigned on the basis of the following data: ir (KBr) 1468, 1441, 1255 (s), 1180, 1135 (s), 1115(s), 1084, 1021, 994, 826, 757, 746, 707, and 682 cm^{-1}. The infrared bands at 1255, 1135, and 1115 cm^{-1} are characteristic of the iminosulfonyl group.[5] *Anal.* Calcd for $C_{18}H_{15}N_3O_3S_3$: C, 51.8; H, 3.6; N, 10.1; S, 23.0. Found: C, 51.7; H, 3.6; N, 10.1; S, 22.6. High-resolution mass spectral analysis of **3** showed that the molecular ion has the empirical formula $C_{18}H_{15}N_3O_3S_3$ (error: found − calculated = 1.11 mmass units) and is quite intense, reflecting its high thermal stability.[6] Some significant fragment ions (error ≤ 1.00 mmass unit) had the empirical formulas C_6H_5NOS (of the proposed intermediate monomer **2**) and C_6H_4SO. The latter is intriguing because it was very intense and could be attributed to the radical cation of a ten π electron heteroaromatic compound, **4**.



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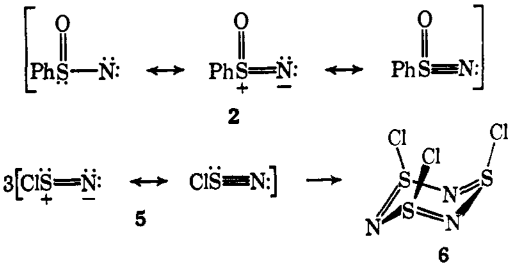
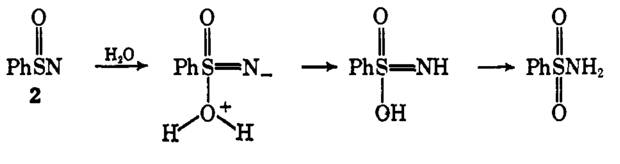
These data and other preliminary results suggest that intermediate **2** may be resonance stabilized, whereby sulfur becomes the electrophilic center instead of nitrogen. Failure to observe the Curtius rearrangement of benzenesulfinyl azide (**1**) to N-sulfinylaniline is consistent with this hypothesis, as are the failures to isolate reaction products of the azide with acetonitrile, dimethyl sulfide, and dimethyl sulfoxide. Thus, **2** might be referred to as a "nucleophilic nitrene" or a thiazile S-oxide,[7] since its reaction products are wholly unlike those of ordinary nitrenes.[8] However, there are similarities to the trimerization of thiazyl chloride (**5**) giving trithiazyl chloride (**6**).[9]



Decomposition of **1** below 25° in aqueous acetonitrile afforded benzenesulfonamide (20–29%). The product is best explained by intermediate **2**; because benzenesulfonyl azide is stable at 25°, no sulfonamide was isolated in the absence of water, and added water had no noticeable effect on the decomposition rate of **1**.



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(2) Prepared by a modification of the procedure of I. B. Douglass, B. S. Farah, and E. G. Thomas, *J. Org. Chem.*, **26**, 1996 (1961).

(3) Sulfanuric chloride (the 1,3,5-trichloro analog of **3**) is the only trithiatriazine trioxide reported in the literature: A. W. Kirsanov, *Dokl. Akad. Nauk SSSR*, 426 (1950); *Zh. Obshch. Khim.*, **22**, 88 (1952).

(4) (a) H. R. Allcock, *Chem. Eng. News*, **46** (18), 68 (1968); (b) H. R. Allcock, "Heteroatom Ring Systems and Polymers," Academic Press, New York, N. Y., 1967.

(5) (a) E. S. Levchenko, E. S. Kozlov, A. A. Kisilenko, and O. V Kirsanov, *Zh. Obshch. Khim.*, **33**, 3065 (1963); *Chem. Abstr.*, **60**, 2451*h* (1964); (b) H. Takei, I. Watanabe, and T. Mukaiyama, *Bull. Chem. Soc. Japan*, **38**, 1989 (1965); (c) R. G. Laughlin, *J. Am. Chem. Soc.*, **90**, 2651 (1968).

(6) A sample of **3** melted sharply at its original melting point (176–177°) after two heating and cooling cycles to 300°.

(7) The name thiazile (RS≡N) is derived from the elements S and N and the nitrile suffix. Thus, **2** would be called benzothiazile S-oxide.

(8) W. Lwowski, *Angew. Chem. Intern. Ed. Engl.*, **6**, 897 (1967).

(9) W. Muthmann and E. Seitter, *Ber.*, **30**, 627 (1897).

Another mode of reaction is suggested by the formation of phenyl disulfide (80%) and triphenylphosphine oxide (75%) from **1** and triphenylphospine. Thus, we are investigating further the difference between direct attack on **1** and reactions of **2**.

Acknowledgments. The author wishes to acknowledge the skillful laboratory assistance of S. C. Beckley and S. L. Suniga. V. A. Campanile and Dr. C. T. Goetschel assisted in obtaining low-temperature ir spectra and Dr. P. A. Wadsworth performed the high-resolution mass spectral study.

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[10] Work was performed at Shell Development Co., Emeryville, Calif.

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Book Reviews

Organic Syntheses via Metal Carbonyls. Volume I. Edited by IRVING WENDER, Pittsburgh Coal Research Center, Bureau of Mines, U. S. Department of the Interior, Pittsburgh, Pa., and PIERO PINO, Instituto di Chimica Organica Industriale, Universita di Pisa, Pisa, Italy. Interscience Publishers, John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1968. xi + 517 pp. 16 × 23 cm. $18.95.

This book can be strongly recommended to those interested in the chemistry of transition metal carbonyls and their derivatives or in stoichiometric or catalytic syntheses involving metal carbonyls.

The first chapter, by F. Calderazzo, R. Ercoli, and G. Natta, comprises over half the book (272 pp) and is the best account of the general chemistry of metal carbonyls yet in print. The methods of preparation, structures, and chemical properties are given, and the references are well chosen and up to date. The treatment includes many types of substituted carbonyls, hydrido carbonyls, halogeno carbonyls, phosphine carbonyls, etc.

Chapter 2, by W. Hübel, is an equally satisfying treatment of the great variety of organometallic compounds obtained from the interaction of carbonyls and acetylenes, while the next chapter by C. Hoogzand and W. Hübel is complementary in that it describes the cyclic polymerization of acetylenes by metal carbonyl compounds.

There is then an excellent account by R. F. Heck of the preparation properties and use specifically of cobalt carbonyl hydride, alkyls, and acyls and their use in organic syntheses, such as the carboxylation of epoxides or the acyldiene synthesis.

Finally a substantial chapter by A. Rosenthal and I. Wender deals with the very extensive application of the OXO or hydroformylation reaction to unsaturated compounds with carbon–nitrogen and nitrogen–nitrogen bonds in reactions such as cyclization reactions of Schiff bases, azo compounds, oximes, etc.

In all chapters much useful information on preparations, reactions, and spectra is collected in extensive tables. The indexes, both author and subject, are satisfactory.

In short "Organic Syntheses via Metal Carbonyl" is an authoritative book of interest to a wide spectrum of chemists.

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Chemistry of Dissociated Water Vapor and Related Systems. By M. VENUGOPALAN and R. A. JONES, Royal Military College of Canada, Kingston, Ontario. Interscience Publishers, John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1968. xviii 463 pp. 16 × 23.5 cm. $19.50.

This timely book fills the need for a long-awaited survey of the chemistry of dissociated water and other oxyhydrogen systems. It is the outgrowth of a lengthy article published by the authors a couple of years ago in *Chemical Reviews. A priori* one would not imagine that this topic alone could fill a book of over 450 pages; but here it is, and without too much redundance at that.

After a brief introduction outlining the historical development of the subject, some 60 pages (Chapter 2) are devoted to the various experimental methods for dissociation and excitation of gas streams, the trapping techniques, and finally the analytical methods, mostly physical: spectroscopy, diffraction, calorimetry, etc. Inevitably, a good deal of this material has already been reviewed elsewhere, in particular, in the monograph "Formation and Trapping of Free Radicals," A. M. Bass and H. P. Broida, Ed. (Academic Press, New York, N. Y., 1960). This would not be too serious were it not for the fact that the authors, as kineticists, are not familiar with most of these techniques. As a result their perspective is often distorted if not downright erroneous. For instance, on page 40, the X-ray and electron diffraction methods are related to surface structure studies, which certainly is not the case here. Then, on page 50, this reviewer is credited with the development of an isothermal ice calorimeter (in fact, it was a diphenyl ether calorimeter), and the instrument is said to have been equilibrated at −196°, a most difficult and useless task, to be sure.

Chapter 3 deals at length with the dissociation in electrical discharges at low pressures of various oxyhydrogen systems: water and hydrogen peroxide vapor, atomic hydrogen reacted with molecular oxygen or ozone. It also contains a section on the condensed products from these systems (about which, more later), and another one on reaction mechanisms. The other methods of dissociation, namely thermal, photochemical, electron impact, and radiolysis, are dealt with adequately in Chapter 4. In this, as in other chapters, attention has been focused mainly on gas-phase reactions so as to keep the size of the survey within reasonable limits.

Chapter 5 is concerned with the reactions between the two elements in question, whether it be in explosions, flames, photochemical (sensitized or not), radiochemical, and electrical discharges, both at low and ordinary pressures. Over 200 individual references are quoted in this chapter alone (well over 1000 in the whole book), and 100 basic reactions are discussed. The sixth and penultimate chapter covers, with some repetition, the properties of individual atoms and free radicals as well as their chemical reactions. The kinetics of some 15 systems, either binary or with third bodies, are summarized.

Last, and least in size, Chapter 7 is a review of the still very controversial question of the superoxides of hydrogen, H_2O_3 and H_2O_4. At that stage the authors depart from their stated policy of presenting the facts and conflicting views objectively. On reading this chapter, and previous sections on the same topic, one would think that they hold a brief to defend the cause of the superoxides. All opposing evidence is disputed or minimized, whereas every favorable argument, no matter how far-fetched, is presented down to the least minutiae (*cf.* in particular pp 128–158). One is reminded here of that meticulous critic who was said to "use gold scales to weigh fly-specks." This is not the place to point out all the inaccuracies encountered in that connection. This reviewer must, however, mention at least one since his own work is at stake. On page 132 one reads: "It is known that replacing hydrogen with deuterium in H_2O_2 results in a shift of the 0–0 vibration to *shorter* wavelengths." Now, this is contrary not only to the facts (the authors should have checked their reference) but also to the theory of spectroscopy.

It is unfortunate that the authors took this attitude on what is, after all, a minor point in the whole topic. It detracts seriously from