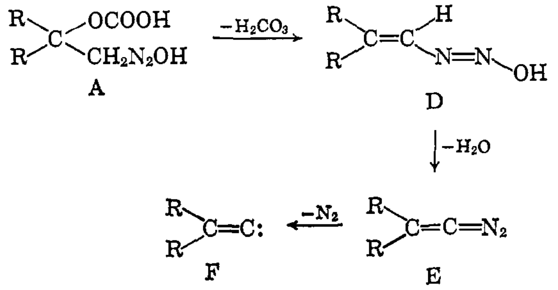
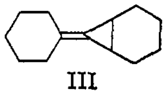
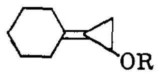


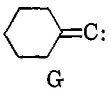
Herein we report that good yields (65-85%) of III, IV, and V are formed in the reaction of I with cyclohexene, isobutyl vinyl ether, and isopropyl vinyl ether,[5] respectively, in the presence of lithium ethoxide at 20-45° in 1,2-dimethoxyethane.[6]



III



IV, R = isobutyl
V, R = isopropyl

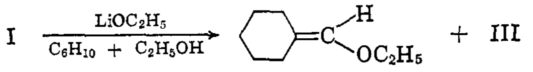


G

These products provide evidence that an unsaturated carbene, cyclohexylidenemethylene (G), is involved and that Hine was correct in his hypothesis that an unsaturated carbene is formed.[4]

The formation of unsaturated carbene (F) was postulated by Hine[4] to proceed *via* the unsaturated diazo compound E. Alternately, the unsaturated diazonium ion B might lose nitrogen to yield the unsaturated carbonium ion C which then could lose a proton to yield an unsaturated carbene. Further studies to try to distinguish between these mechanisms are under way.

In the earlier work the formation of vinyl ethers[1,3] and acetylenes[1] on treatment of nitrosooxazolidones (type I) with base were described.[2] Their formation was presumed to occur *via* unsaturated carbonium ions (type C). Possibly, however, each of these products could arise *via* a carbene intermediate (type F). Accordingly, we treated I with lithium ethoxide in the presence of excess cyclohexene and absolute ethanol in equimolar ratio at two temperature ranges (3-30° and 60-65°). The ratio of vinyl ether (ethoxymethylenecyclohexene) (VI) to III formed was about 4.7:1 and 6.8:1, respectively.



VI

Since we do not know the relative tendencies of unsaturated carbonium ions to react with alcohols to form vinyl ethers, as compared to the reaction of unsaturated carbenes to form either vinyl ethers by insertion into the OH bond of an alcohol or cyclopropenes by reaction with cyclohexene, the above results cannot be quantitatively evaluated.[7] Experiments to clarify the picture are under way.

Furthermore, the formation of actylenes can be explained at present either by the rearrangement of unsaturated carbonium ions[3] or by the formation of unsaturated carbenes followed by rearrangement.[8-10] In two cases,[9,10] free unsaturated carbenes cannot be involved because of the stereospecificity of the reaction involved.

Acknowledgment. This work was supported by the National Science Foundation, Grant 5552.

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[5] H. D. Hartzler, *J. Am. Chem. Soc.*, **86**, 526 (1964), used vinyl ethers to trap unsaturated carbenes.

[6] The structures of all new compounds were established by elemental analyses and ir and nmr spectra.

[7] In a communication on the generation of an alkylidenecarbene by treatment of a vinyl chloride with potassium *t*-butoxide, the formation of a vinyl *t*-butyl ether was noted. However, the authors did not account for this by assuming that the carbene inserted into *t*-butyl alcohol. See M. Tanabe and R. A. Walsh, *J. Am. Chem. Soc.*, **85**, 3522 (1963).

(8) D. Y. Curtin, J. A. Kampmeier, and B. R. O'Connor, *J. Am. Chem. Soc.*, **87**, 863 (1965).

(9) A. A. Bothner-By, *ibid.*, **77**, 3293 (1955).

(10) D. Y. Curtin, E. W. Flynn, and R. F. Nystrom, *ibid.*, **80**, 4599 (1958).

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A Stable Tetravalent Sulfur Heterocycle

Sir:

A new class of tetravalent sulfur heterocycles has been described recently.[1] Examination of these novel systems has been restricted because of their extreme reactivity. A detailed study of the sulfur bonding found in these compounds clearly required the preparation of a stable example. We now wish to report the synthesis of a crystalline deep blue tetravalent sulfur compound, 6,7-dibromo-1,3-diphenylacenaphtho[5,6-*cd*]thiopyran (I).

Exhaustive bromination[2] of 5,6-dibenzoylacenaphthene[3] with N-bromosuccimide gave the orange dibromo diketone II in 92% yield, mp 305°. Sodium borohydride reduction of II gave rise to diol III, mp 161°, in 70% yield. Treatment of III with phosphorus pentasulfide in pyridine gave a mixture of the *cis* and *trans* sulfides IV and V.[4] The mixture of sulfides was oxidized with *m*-chloroperbenzoic acid to give, after thick layer chromatography, the corresponding *cis* sulfoxide VI, mp 215° dec, 45% yield, and the *trans* sulfoxide VII, mp 226° dec, 5% yield.[5]

Prolonged heating of sulfoxide VI in a degassed solution of acetic anhydride at 120° gave in 75% yield heterocycle I as dark blue crystals which slowly decomposed above 130°. Compound I formed instantaneously when VI was treated with phenyllithium in benzene solution at room temperature.[6]

Freshly prepared solutions of I showed absorption maxima at $\lambda_{max}^{cyclohexane}$ (mμ (ϵ)) 245 (20,600), 250 (21,400), 322 (10,800), 403 (54,000), 548 (3040), 612 (2980), and 652 (2140), with tailing to 725 mμ. This

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(1) (a) R. H. Schlessinger and I. S. Ponticello, *J. Am. Chem. Soc.*, **89**, 3641 (1967); (b) R. H. Schlessinger and I. S. Ponticello, *Tetrahedron Letters*, 4057 (1967); (c) M. P. Cava and N. M. Pollack, *J. Am. Chem. Soc.*, **89**, 3639 (1967); (d) M. P. Cava, N. M. Pollack, and D. A. Repella, *ibid.*, **89**, 3640 (1967); (e) R. H. Schlessinger and A. G. Schultz, *ibid.*, **90**, 1676 (1968).

(2) For examples of this reaction, see B. M. Trost and D. R. Brittelli, *J. Org. Chem.*, **32**, 2620 (1967).

(3) H. J. Richter and F. B. Stocker, *ibid.*, **24**, 366 (1959).

(4) All melting points are uncorrected. Satisfactory analyses were obtained for all new compounds except IV and V.

(5) Nmr spectra were determined in $CDCl_3$. Compound IV gave singlet resonance for the protons α to the sulfoxide group at δ 5.75 while the protons α to the sulfoxide group in VI came at δ 5.51. For a more detailed discussion of the structural assignment of similar sulfide and sulfoxide pairs, see ref 1e.

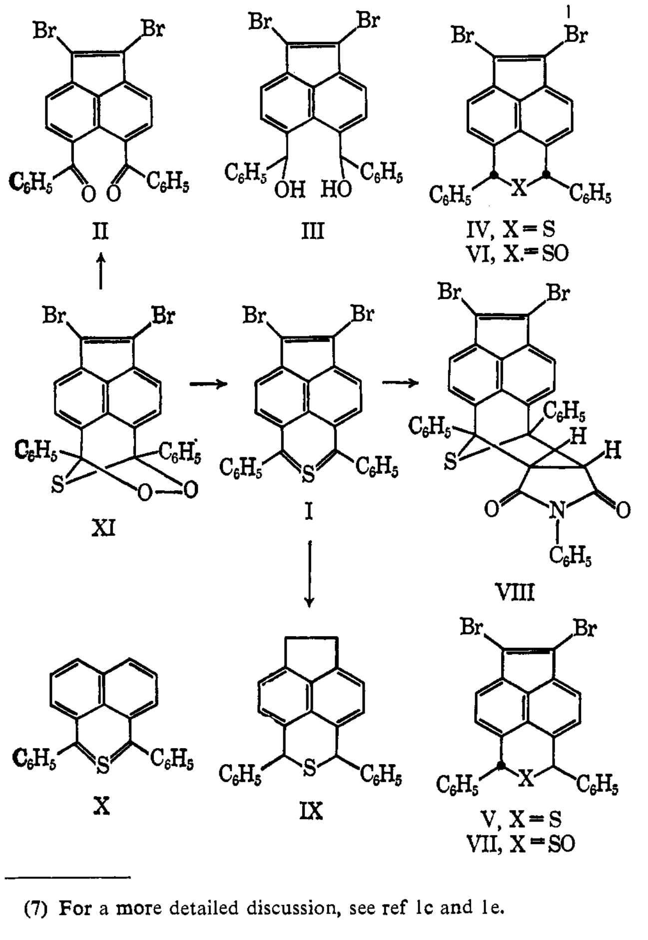
(6) This reaction has been found to be general for cyclic and acyclic benzylic sulfoxides. Detailed comments on the mechanism and scope of this reaction will appear shortly.

spectrum changed very little in methanol or dioxane. The nmr spectrum of I showed resonance for the phenyl protons centered at δ 7.62 and a well-defined quartet for the naphthalene protons centered at δ 7.95 and 8.35 with a coupling constant of 9 cps. The mass spectrum gave peaks at *m/e* 517.9185 (heterocycle I, 517.9164 based on $C_{26}H_{14}Br_2S$) and 485.9467 (1,2-dibromo-5,6-diphenylpyracylene, 485.9443 based on $C_{26}H_{14}Br_2$).

Reaction of I with N-phenylmaleimide in degassed benzene solution at 80° gave rise to the *exo* Diels–Alder adduct VIII as yellow needles, mp >340°, in high yield. The same adduct was obtained from the decomposition of sulfoxide VI in acetic anhydride at 120°. Adduct VIII exhibited an ultraviolet spectrum similar to the other dibromoacenaphthylene derivatives in this series. The mass spectrum of VIII showed a retro-Diels–Alder fragmentation pattern with peaks at *m/e* 517.9183 (heterocycle I) and 173 (N-phenylmaleimide) as well as the parent ion at 690.9636 (calculated 690.9671). The nmr spectrum of the adduct gave resonance for the two protons α to the imide carbonyls at δ 5.25, a position compatible with *exo* geometry.[7]

Heterocycle I did not undergo catalytic hydrogenation with palladium on carbon in methanol. Sulfide IX was obtained from I in low yield when platinum oxide was used.

The transient heterocycle 1,3-diphenyl-2-thiaphenalene (X)[1e] has been reported to undero sulfur extrusion, giving rise to 1,2-diphenylacenaphthylene. This reaction was shown to occur by ring closure of X to the corresponding episulfide. A similar conversion of I to the corresponding pyracylene has not been found thus far. Heating either melts or solutions of I above 130° results only in the formation of polymer. Degassed benzene solutions of I are completely unchanged after long irradiation with a variety of wavelengths of light.[8]



Heterocycle X was found also to undergo reaction with oxygen to give 1,8-dibenzoylnaphthalene.[1e] It was suggested that this reaction might occur by initial formation of a peroxide adduct followed by loss of sulfur to give the diketone. Dark blue benzene solutions of I saturated with oxygen rapidly faded to orange when irradiated with light of wavelengths greater than 360 mμ. Initial thin layer chromatographic examination of the reaction mixture showed the presence of two orange components, one of which was identified as the diketone II. On further irradiation or standing in the dark, the second component was observed to decompose to the diketone. Thick layer chromatography of the reaction mixture gave II in good yield. Oxygen-enriched solutions of I have been found to be stable in the dark. These results suggest that I in the excited state sensitizes the formation of singlet oxygen which then undergoes Diels–Alder reaction with ground-state heterocycle to give the peroxide adduct XI.[9] We have made no attempt to isolate XI although it seems reasonable to assume that it is the second component of the photolysis mixture. It is not possible at this time to conclude that heterocycle X reacts with oxygen in the same manner.

Heterocycle I contains $4n + 2$ peripheral π electrons which may be delocalized in a number of resonance forms. This favorable electronic configuration together with the heavy-atom influence of bromine may account for the stability of I. It is hoped that further effort, including an X-ray study of I, will make possible a more definitive description of these interesting systems.

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(7) For a more detailed discussion, see ref 1c and 1e.

(8) A Hanovia 450-W medium-pressure mercury arc lamp fitted either with interference or color filters was used.

(9) For an excellent review of the role of singlet oxygen in photosensitized oxygenations, see C. S. Foote, *Accounts Chem. Res.*, 1, 104 (1968).

(10) To whom inquires should be addressed.

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Control of Photochemical Reaction Pathways by Excited-State Multiplicity. Mechanistic and Exploratory Organic Photochemistry. XXXIV[1]

Sir:

The number of intramolecular photochemical reactions in which the pathway chosen by the triplet excited state differs from that of the singlet is exceedingly limited. We presently wish to report an especially

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(1) For paper XXXIII see H. E. Zimmerman, K. G. Hancock, and G. L. Licke, *J. Am. Chem. Soc.*, in press.