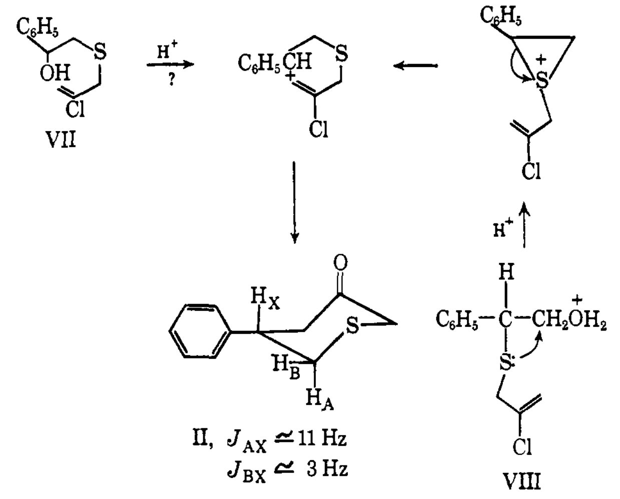
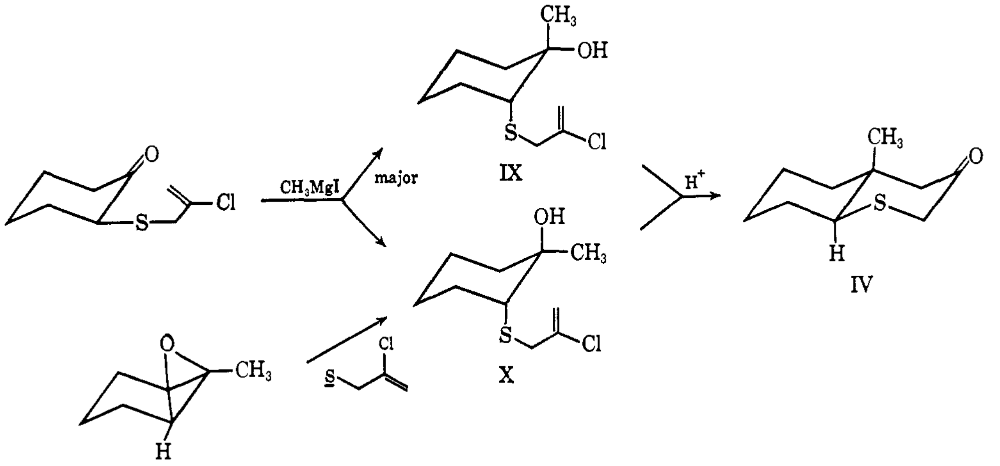
Chart I



of II from precursors VII *and* VIII (Chart I). On the other hand, ionization without sulfur participation[8] might be expected with the epimeric derivatives IX and X (as well as with VII) which stereoselectively produce a single 4-thia-9-methyl-2-decalone (IV). Regardless of whether or not episulfonium ions intervene, a relatively stable carbonium ion must be generated for closure to occur.[7]

Chart II



5-Phenyl-3-thianone (II) was rigorously characterized[2] by hydrogen peroxide oxidation to the sulfone[9] and Raney nickel hydrogenolysis to 2-phenylpentane. Similarly III (2,4-DNPH mp 129–131°) was hydrogenolyzed to 2,2-dimethylpentane and showed the expected simple nmr spectrum (six-proton singlet at 1.13 ppm and three two-proton singlets at 2.17 ($CH_2C(=O)-$), 2.60, and 3.03 ppm ($SCH_2C(=O)-$) with no evidence for hindered ring inversion at $-60°$). Thiadecalone IV[2] (semicarbazone mp 215–216°), obtained from two precursors (Chart II) and hydrogenolyzed to 1-methyl-1-cyclohexylacetone, is assumed to have a *trans* ring fusion on the basis of two AB quartets attributable to diastereomeric methylene groups at C_1 (centered at 2.23 ppm, $\Delta\nu_{AB} = 0.82$ ppm, $J_{AB} = 14$ Hz) and C_3 (centered at 3.07 ppm, $\Delta\nu_{AB} = 0.48$ ppm, $J_{AB} = 13$ Hz) which show no coalescence on heating as expected.[10]

The piperidone VI (2,4-dinitrophenylhydrazone[11] mp 186–188°) displayed the expected nmr spectrum (six-proton singlet at 0.99 ppm, three two-proton singlets at 2.01, 2.85, and 3.30 ppm, plus *p*-toluenesulfonyl group signals). Likewise, N-*p*-toluenesulfonyl-5-phenyl-3-piperidone[2] (V) showed consistent spectral properties, but the conformation of the phenyl group is not yet known (as in the case of II) because attempted deuteration at C_2 and C_6 (to allow analysis of the ABX system at C_4 and C_5) led to decomposition.

Further studies on the scope and limitations of the "heterocyclohexanone" synthesis are in progress, as well as investigations of the chemistry of these interesting ketones.[3]

Acknowledgment. We are grateful to the U. S. Army Research Office (Durham) for partial financial support and to Dr. Raymon P. Elliott for initial studies on V.

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[7] If the episulfonium salts (or protonated carbinols) are not capable of SN1-type ionization to open carbonium ions cycloalkanone formation seems to be prevented, since front-side attack by β-chloroallyl groups cannot occur. Thus, 3-thianone itself is not formed from 2-(2-chloroallylthio)ethanol under conditions suitable for II–IV.

[8] The question of sulfur participation is being further studied by means of isotopic labeling, stereochemistry, etc. It is pertinent to note that thioalkyl groups participate *only partially* in silver ion assisted acetolysis of *trans*-7-chloro-8-thioalkoxydibenzobicyclo[2.2.2]octadiene (S. J. Cristol, R. Caple, R. M. Sequeira, and L. O. Smith, Jr., *J. Am. Chem. Soc.*, 87, 5679 (1965)).

[9] We thank Dr. G. A. Pagani, University of Milan, for an authentic sample of 5-phenyl-3-thianone 3,3-dioxide, which was identical by melting point and infrared and nmr spectra with our material.

[10] E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 280.

[11] Lit. mp 190°: Brown, *et al.*, Table II, footnote *a*.

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Singlet Oxygen Sources in Ozone Chemistry

Sir:

It has been known for some time that a number of materials react with ozone in a manner which results in one oxygen atom of the ozone being incorporated in the oxidized product with the concomitant production of molecular oxygen. Examples include the oxidation of tertiary amines to amine oxides, phosphines to phosphine oxides, sulfides to sulfoxides, and sulfoxides to sulfones.[1] In addition, some olefins which have special structural features give epoxides upon ozonolysis, and these products have been explained by postulating an intermediate π or σ complex[2-4] which subsequently loses molecular oxygen and gives the epoxide. The observation that olefin stereochemistry is preserved in the epoxide so produced perhaps lends support to these explanations.[3]

We have been convinced for some time that the oxygen evolved in some or all of these reactions probably has singlet multiplicity. Corey and Taylor have made a similar suggestion.[5]

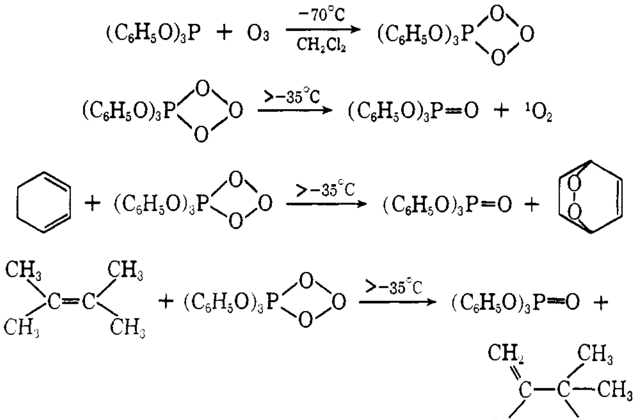
We wish to report that one such oxidation evolves oxygen which undergoes typical singlet oxygen reactions. This observation strongly suggests that the oxygen involved in a wide range of such oxidations probably has singlet multiplicity. The case examined in detail is based on the report by Thompson[6] that triaryl and trialkyl phosphites are oxidized rapidly and quantitatively to phosphates by ozone. In particular, Thompson found that some triaryl phosphites formed 1 : 1 adducts with ozone at low temperature; these adducts could be used to oxidize other added materials. We have observed that the oxygen formed during the decomposition of this adduct will undergo singlet oxygen reactions.

A number of recent reports have provided strong evidence for the involvement of singlet oxygen in photochemical oxidation and provided useful techniques for diagnosing the presence of singlet oxygen.[5,7-12] We have taken advantage of these techniques to test for the presence of singlet oxygen in the ozone oxidations of triaryl phosphites to phosphates.

We have shown that the adduct between triphenyl phosphite and ozone prepared at −70° can be used to convert 1,3-cyclohexadiene (1.5:1; adduct:diene ratio) into 5,6-dioxabicyclo[2.2.2]octene-2 (norascaridol) in 67% yield, mp (on samples recrystallized from pentane) 90–91°, some gas evolution (lit.[13] mp 88.5°). The material obtained is identical (nmr and infrared spectra) with that formed by photochemical oxidation.

The triphenyl phosphite–ozone adduct also converts an equimolar amount of 2,3-dimethylbutene-2 to 2,3-dimethyl-3-hydroperoxy-butene-1 (53% yield, bp 52–54° (9 mm); lit.[7] bp 55° (12 mm)); the product had infrared and nmr spectra identical with those of the product of photosensitized oxidation. In both reactions a quantitative yield of triphenyl phosphate was obtained. These reactions are typical of those which have been ascribed[5,7-12] to the presence of singlet oxygen generated by chemical or photochemical techniques.

Chart I. Reaction Scheme for Oxidation of Singlet Oxygen Acceptors by Phosphite–Ozone Adduct



A summary of the reaction scheme is given in Chart I. The exact nature of the phosphite–ozone adduct is still in doubt, but Thompson[6] has suggested the structure shown on the basis of ^{31}P nmr data. In the reactions described, the phosphite–ozone adduct was formed at −70° in methylene chloride by passing in an oxygen–ozone stream until the blue color of ozone persisted. Excess ozone was then removed by nitrogen purge. A cold solution of the cyclohexadiene or tetramethylethylene in methylene chloride was then added, and the reaction mixture was allowed to warm slowly to $\sim -30°$. This temperature was maintained for several hours and then continued warming to room temperature was permitted. Control experiments in the absence of singlet oxygen acceptors showed rapid oxygen evolution at −10°.

An orange solution of rubrene was bleached when treated with a nitrogen-purged solution containing the triphenyl phosphite–ozone adduct beginning at $\sim -35°$. No bleaching occurred at −70° in this same solution. If a nonpurged solution was used, bleaching did occur at −70°, indicating that the nitrogen purge successfully removes ozone and that the bleaching which occurs beginning at $\sim -35°$ in the purged solution is due not to ozone but most likely to the evolved oxygen.

The phosphite–ozone adduct is a convenient source of singlet oxygen in which the oxygen can be liberated in a controlled rate to accomplish the desired oxidation in high yield. We are continuing similar investigations to determine whether singlet oxygen can be detected in the other ozone oxidations referred to above.

Acknowledgment. We wish to acknowledge helpful discussions with Dr. A. M. Trozzolo and to thank Mrs. S. R. Fahrenholtz for authentic samples of the *endo*-peroxide and hydroperoxide.

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(5) E. J. Corey and W. C. Taylor, *ibid.*, **86**, 3882 (1964).

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The Mercury(II)-Catalyzed Isomerization of the Sulfur-Bonded Monothiocyanate Complex of Chromium(III)[1]

Sir:

It was reported earlier that the reaction of mercury(II) with the sulfur-bonded monothiocyanate complex

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(1) Research performed under the auspices of the U. S. Atomic Energy Commission.