strongly supports the *cis*-fused structures for VIII and IX.

Acknowledgment. We are grateful to Professor A. L. Wilds for generous samples of X and XI and to the U. S. Army Research Office (Durham) for partial financial support.

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A Facile Entry into 3-Thianone and 3-Piperidone Ring Systems

Sir:

We have noted previously¹ the presence of electrophilic and nucleophilic sites in 2,3-dichloropropene (I) which can be used to advantage in compact re-

Table I

In this communication we extend our cycloalkanone synthesis in novel fashion to heterosubstituted cyclohexanones² containing sulfur and nitrogen in place of C_3 , compounds of substantial theoretical³ and synthetic⁴ interest, but not readily accessible.

In one variation, I can first be nucleophilically attacked by a species bearing the heteroatom to be incorporated at position 3 and the resultant derivative used to open an epoxide, which provides an alcohol for intramolecular cyclization.¹ This is illustrated in the preferred preparation of several 3-thianones⁵ (Table I). Alternatively, I can be attacked by the nucleophilic derivative formed *after* epoxide cleavage, which appears to be the method of choice for constructing 3-piperidones. (Table II).

In the 3-thianone synthesis, the sodium salt of β chloroallyl mercaptan⁶ attacks the less substituted carbon of unsymmetrical epoxides predominantly (only one isomer was detected with isobutylene oxide and 1-methylcyclohexene oxide, whereas styrene oxide gave a 60:40 ratio of isomers VII and VIII). The acid-induced cyclization can proceed via episulfonium intermediates⁷ as suggested by the exclusive generation



^a For reactions using \sim 1 g of carbinol precursor in 25–30 ml of solvent.

Table II



^a Lit. mp 110° (R. F. C. Brown, V. M. Clark, and Lord Todd, J. Chem. Soc., 2105 (1959)).

action sequences with suitable bifunctional compounds (containing nucleophilic and potential electrophilic centers) to produce cycloalkanone rings, *e.g.*



(1) P. T. Lansbury and E. J. Nienhouse, J. Am. Chem. Soc., 88, 4290 (1966).

(2) All new compounds gave satisfactory elemental analyses and were further characterized by infrared and nmr spectroscopy.

(3) For example, possible transannular interactions of the heteroatom with the carbonyl group and the heteroatom effect on kinetic and equilibrium acidities at $C_2 vs$. C_5 are being explored by us.

(4) Lengthy sequences leading to substituted 5-methyl-3-piperidones for use in total syntheses of jervine, veratramine, and related Veratrum alkaloids have recently been reported by T. Masamune and W. S. Johnson and their coworkers (J. Am. Chem. Soc., 89, 4521, 4523 (1967)).

(5) The alternative epoxide opening by bisulfide ion followed by displacement upon I is poor because of substantial sulfonium salt formation in the S-alkylation step.

(6) Bp 56-57° (70 mm); 2,4-dinitrophenyl thioether derivative mp 67-68.5°; nmr SH at 2.02 ppm (triplet, J = 8 Hz), CH₂S at 3.5 ppm (doublet, J = 8 Hz), vinyl protons at 5.30 and 5.49 ppm (doublets, J = 2 Hz).

Chart I



of II from precursors VII and VIII (Chart I). On the other hand, ionization without sulfur participation⁸ Chart II

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tained 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 C1 (centered at 2.23 ppm, $\Delta v_{AB} = 0.82$ ppm, $J_{AB} = 14$ Hz) and C₃ (centered at 3.07 ppm, $\Delta v_{AB} = 0.48$ ppm, $J_{AB} = 13$ Hz) which show no coalescence on heating as expected.¹⁰

The piperidone VI (2,4-dinitrophenylhydrazone¹¹ 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-piperidone² (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



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

5-Phenyl-3-thianone (II) was rigorously characterized² by hydrogen peroxide oxidation to the sulfone⁹ 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 (CH₂C(=O)-), 2.60, and 3.03 ppm (SCH₂C(=O)-) with no evidence for hindered ring inversion at -60°). Thiadecalone IV² (semicarbazone mp 215-216°), ob-

(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.

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.

(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.

(12) Alfred P. Sloan Foundation Fellow, 1963-1967.(13) Graduate school predoctoral fellow, 1967-1968.

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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