

further experimental details, will be presented in a full paper.

(15) National Science Foundation Undergraduate Research Participant, 1964-1965.

Edgar F. Kiefer, Melvin Y. Okamura¹⁶
 Department of Chemistry, University of Hawaii
 Honolulu, Hawaii 96822
 Received May 20, 1968

Free-Radical Intermediates in Chromic Acid Oxidation

Sir:

A previous report from this laboratory¹ noted a small amount of polymerization of acrylonitrile added to a chromic acid oxidation of phenyl-*t*-butylcarbinol (2,2-dimethyl-1-phenyl-1-propanol). The polymerization occurred under conditions which lead to the formation of relatively large (~50%) amounts of the "cleavage" products, benzaldehyde and *t*-butyl alcohol. It was noted that the conversion to polymer was low (approximately 0.020 g for 20 ml of 0.025 *M* CrO₃ solution) and the product ratios were unchanged from oxidations under the same conditions but without acrylonitrile. The source and nature of the radicals initiating the polymerization could not be identified. We have now found that these radicals result from the oxidation of benzaldehyde by an intermediate Cr(IV) [most probable] or Cr(V) species.

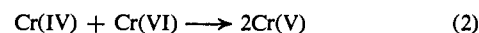
No polymer could be detected in the oxidation of 2-propanol under the same conditions. However, the dropwise addition of 10 ml of a solution of CrO₃ (0.05 *M* in 85% aqueous acetic acid) to a solution containing 1 ml of 2-propanol, 1 ml of benzaldehyde, 5 ml of acrylonitrile, and 15 ml of the 85% aqueous acetic acid led to precipitation of the polymer within 15 min. The precipitation continued as long as the addition was continued (about 6 hr). Two grams of film-forming polymer was isolated. In the absence of the 2-propanol, polymer precipitation was delayed for several hours and only poor conversions were obtained over 48 hr (0.050 g). Omission of the benzaldehyde under the above conditions led to no polymer formation. These data suggest that the intermediate Cr(IV) or Cr(V) species formed in the oxidation of the alcohol² was responsible for the radical products and that the oxidation of benzaldehyde was involved in the initiation. These Cr(IV) and Cr(V) species are formed much more slowly in the oxidation of benzaldehyde than in the oxidation of a secondary alcohol.

When extra benzaldehyde was added to the oxidation of phenyl-*t*-butylcarbinol, the benzaldehyde was oxidized at a much greater rate than was observed for Cr(VI) alone. The extent of this secondary oxidation was dependent on the amount of benzaldehyde added. This is characteristic of previously observed "induced oxidations" by Cr(IV) and Cr(V).²⁻⁴ As would be expected for this interpretation, the polymerization reaction was completely eliminated by the addition of Ce(III) to the oxidation. The Ce(III) removes the

lower oxidation states of chromium from the reaction.^{2,5}

In view of the above, it should be noted that Wiberg and Richardson³ reported that ~30% yields of carbon monoxide could be obtained by the Cr(VI) oxidation of triphenylacetaldehyde, probably by decarbonylation of the radical formed by attack of Cr(IV) on the triphenylacetaldehyde.

In a full publication which is in preparation, we will relate these observations to the mechanisms of chromic acid oxidations of alcohols and aldehydes. The one-electron reagent is identified as Cr(IV) in the above cases. If Cr(V) acted as a one-electron reagent (reaction 1), the reaction would be an autocatalytic chain reaction due to reaction 2. Since these aldehyde oxidations are not autocatalytic,^{3,6,7} this process cannot occur to any appreciable extent.



(5) The quenching of Cr(IV) and Cr(V) reactions by Ce(III) is more complicated than previously indicated. This subject will be included in a future publication.

(6) K. B. Wiberg and T. Mill, *J. Am. Chem. Soc.*, **80**, 3022 (1958).

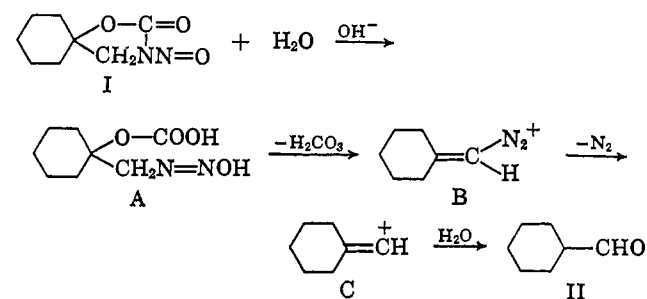
(7) G. T. E. Graham and F. H. Westheimer, *ibid.*, **80**, 3030 (1958).

William A. Mosher, G. L. Driscoll
 Department of Chemistry, University of Delaware
 Newark, Delaware 19711
 Received March 29, 1968

Unsaturated Carbenes Formed by Reaction of Nitrosooxazolidones with Bases

Sir:

Some time ago a mechanism was proposed to account for the products produced in the alkaline decomposition of nitrosooxazolidones in which an unsaturated carbonium ion was the key intermediate.¹ This mechanism is illustrated below in the reaction of 3-nitroso-1-oxa-3-azaspiro[4.5]decan-2-one (I) with hydroxide ion to yield formylcyclohexane (II). The hypothetical species involved were A, B, and C.



All of the products isolated in this and other cases^{2,3} could be satisfactorily accounted for by assuming that unsaturated carbonium ions similar to C were involved. In his book,⁴ Hine suggested that by a different mechanism A could decompose *via* an unsaturated diazo compound (E) to yield an unsaturated carbene (F) which could then give rise to products.

(1) M. S. Newman and A. Kutner, *J. Am. Chem. Soc.*, **73**, 4199 (1951). As in the present paper, the timing of proton movements was ignored.

(2) M. S. Newman and W. M. Edwards, *ibid.*, **76**, 1840 (1954).

(3) M. S. Newman and A. E. Weinberg, *ibid.*, **78**, 4654 (1956).

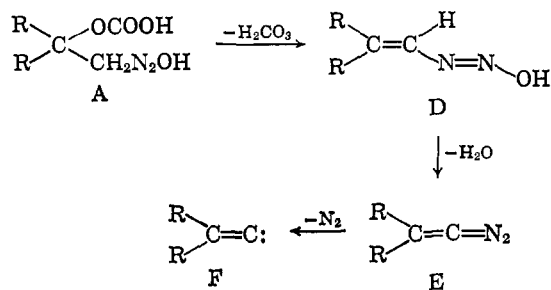
(4) J. Hine, "Divalent Carbon," The Ronald Press Co., New York, N. Y., 1964, pp 89-90.

(1) W. A. Mosher, W. H. Clement, and R. L. Hilliard, "Selective Oxidation Processes," Advances in Chemistry Series, No. 51, American Chemical Society, Washington, D. C., 1965, pp 81-88.

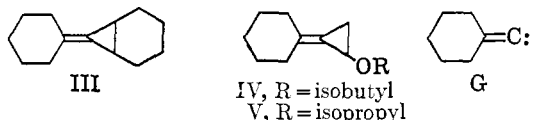
(2) J. Hampton, A. Leo, and F. H. Westheimer, *J. Am. Chem. Soc.*, **78**, 306 (1956).

(3) K. B. Wiberg and W. H. Richardson, *ibid.*, **84**, 2800 (1962).

(4) J. Rocek and A. Riehl, *Tetrahedron Letters*, 1437 (1966).



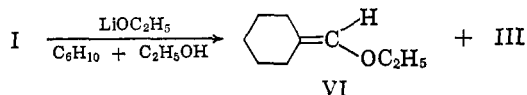
Herein we report that good yields (65–85%) of III, IV, and V are formed in the reaction of I with cyclohexene, isobutyl vinyl ether, and isopropyl vinyl ether,⁵ respectively, in the presence of lithium ethoxide at 20–45° in 1,2-dimethoxyethane.⁶



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 Hine⁴ 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 acetylenes¹ 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.



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 cyclopropanes by reaction with cyclohexene, the above results cannot be quantitatively evaluated.⁷ Experiments to clarify the picture are under way.

Furthermore, the formation of acetylenes can be explained at present either by the rearrangement of un-

(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).

saturated carbonium ions³ 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.

(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).

Melvin S. Newman, Abraham O. M. Okorodudu
Evans Chemistry Laboratory, The Ohio State University
Columbus, Ohio 43210
Received May 15, 1968

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 bromination² of 5,6-dibenzoylacene³ with *N*-bromosuccinimide 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 $\lambda_{\text{max}}^{\text{cyclohexane}}$ ($m\mu$ (ϵ)) 245 (20,600), 250 (21,400), 322 (10,800), 403 (54,000), 548 (3040), 612 (2980), and 652 (2140), with tailing to 725 $m\mu$. This

(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 CDCl₃. Compound IV gave singlet resonance for the protons α to the sulfoxide group at δ 5.75 while the protons α to the sulfide 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.