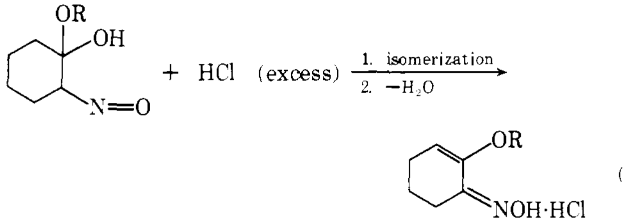
good solvating properties on the other, sulfur dioxide plays a dual role. It allows a sufficiently high concentration of nitrosonium ion and at the same time "stabilizes" the intermediate 1-hydroxy-2-nitrosocarbonium ion *without reacting with the positive charge*, thus making the reaction with the alcohol possible. Other polar but nonbasic solvents like nitromethane and sulfolane behave similarly, and thus the nitrosolysis reaction can also be carried out in these solvents. The successful outcome of this reaction must be due to at least in part to the fact that during the reaction cycle only a small amount of free hydrochloric acid is present.[7] Presumably, the hydrochloric acid generated in the reaction between nitrosyl chloride and the alcohol serves as the catalyst for the enolization of the ketone and the cleavage of the α-nitrosohemiketal and then becomes "neutralized" by the oxime produced.

When, however, the nitrosation of cyclohexanone was carried out in the presence of an additional equivalent of hydrogen chloride, the competing reaction, the acid catalyzed isomerization of the secondary nitroso group,[8] followed by water elimination to afford the 2-alkoxy-3-oximinocyclohexene, becomes more important and the carbon-carbon bond cleavage is suppressed (eq 5).



(5)

Clearly, the nitrosolysis reaction is a remarkably simple procedure for the carbon-carbon bond cleavage of a variety of ketones[10] providing products with valuable functional groups. In effect, the nitrosolysis reaction represents an advantageous supplement to a Beckmann fragmentation of the α-oximino ketones. The reaction is carried out under much milder conditions and eliminates the need for the prior preparation of the α-oximino ketones. It should be particularly useful for the transformation of cyclopentanone, cyclohexanone, and cyclohexanone derivatives where α-oximino ketones are extremely difficult to prepare.[3,11] Furthermore, similar reaction of cyclohexanone, but in the presence of an excess of added acid, provides for the first time a direct and convenient access to 2-alkoxy-3-oximinocyclohexene, a novel derivative of mononitrosated cyclohexanone.

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(4) The oximino enol ether hydrochloride is a fairly unstable material that decomposes at room temperature overnight, but could be stored over an extended period of time in a refrigerator. The free oximino enol ether is stable at room temperature and does not undergo appreciable decomposition over a period of several months. The chemistry of this interesting intermediate will be described elsewhere.
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(7) In this regard the commonly used technique for in situ generation of nitrosyl chloride, by the reaction of an alkyl nitrite and hydrogen chloride (e.g., ref 2), suffers from the disadvantage that the rate of addition of hydrogen chloride usually appears to be too fast, resulting in concomitant formation of the oximino enol ethers.
(8) It is of interest that the isomerization (eq 5) occurred most readily in the presence of hydrogen chloride or boron trifluoride etherate, and in the presence of other acids like sulfuric and methanesulfonic acid the isomerization apparently was not extensive. This fact is probably responsible for the successful nitrosolysis of cyclohexanone to ω-oximinocaproic acid with nitrosylsulfuric acid in concentrated sulfuric acid.[9]
(9) P. Lafont and M. Thiers, U.S. Patent 3,356,698 (1967).
(10) No attempts were made to optimize the reaction conditions for each individual ketone.
(11) After the completion of this work, Ohno and Kataoka[3] reported unsuccessful attempts to fragment α-oximinocyclohexanone.

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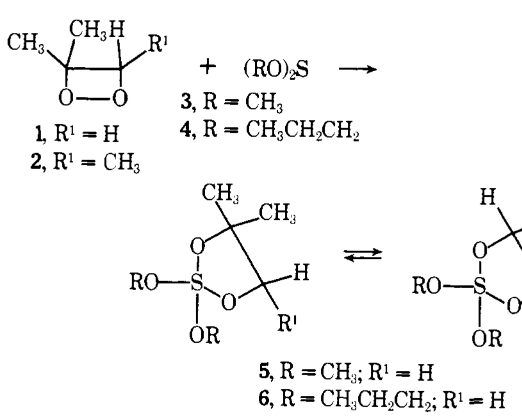
Reactions of Dioxetanes with Sulfoxylates and Sulfides. Preparation of Novel Tetraalkoxysulfuranes

Sir:

Sulfuranes, i.e., tetrasubstituted sulfur compounds, are a little known class of substances.[1] Recently various energy rich substances such as organic hypochlorites[2] and perfluorohypofluorites[3] have been allowed to react with divalent sulfur compounds to prepare sulfuranes and persulfuranes. Attempts to prepare sulfuranes by reaction of diethyl peroxide with divalent sulfur compounds have been fruitless.[4] It did seem, however, that the more reactive four-membered ring peroxides, dioxetanes,[5] might react with divalent sulfur compounds to give sulfuranes. In particular it seemed that sulfur compounds with electronegative ligands might lead to relatively stable sulfuranes. After the completion of this work Wasserman and Saito[6] reported that diphenyl sulfide does indeed react with several dioxetanes to give diphenyl sulfoxide. No evidence for the intervention of sulfuranes was obtained.

The dioxetanes, **1** and **2**, have been used in this study.[7] When **1** was allowed to react with **3** at −78° in methylene chloride a reaction mixture was obtained whose 100-MHz ^{1}H NMR spectrum at −60° showed singlet absorptions at δ 1.32, 1.47, 3.26, 3.66, each three hydrogens, and absorptions at δ 3.73 and 3.78, two hydrogens. The 20-MHz ^{13}C NMR spectra, decoupled and off-resonance decoupled, showed four methyl group carbons at δ 24.55, 26.00, 48.50, and 54.55. A methylene carbon was found at δ 70.32 and a quaternary carbon appeared at δ 83.69. When these reaction mixtures were allowed to warm to room temperature dimethyl sulfite and a nonvolatile, presumably polymeric, material were formed. These results are in concordance with the production of a tetraalkoxysulfurane, **5**, where the upfield ^{1}H and ^{13}C NMR chemical shifts are due to the appropriate absorptions of the elements of the methyl groups on the ring. The downfield absorptions are those of methyl group hydrogens and carbons. These are nonequivalent and environmentally quite different methoxy groups. These data cannot be used to exclude various conformers for **5**. For example the structure illustrated, a trigonal bipyramid, is in agreement with the data; however, a square pyramid also fits the data. Pseudorotations between various conformers which do not render the groups equivalent cannot be eliminated. It should be noted though that the methoxy groups experience a considerably different environment. This observation suggests a structure(s) where this is achieved.

Reaction of **1** with **4** at −78° gave reaction mixtures whose ^{1}H and ^{13}C NMR spectra at low temperatures are in agreement with the production of a sulfurane, **6**; i.e., aside from the complications introduced by the *n*-propyl groups the spectra were very similar to that of **5**. On warming reaction mixtures of **6** a smooth decomposition occurred with the production of *n*-propyl sulfite and isobutyraldehyde. The latter can be formed from **6** by heterolysis of the O-$C(CH_3)_2$ bond with hydride migration and S-O bond cleav-



age. The reason for the difference in modes of decomposition of **5** and **6** is not clear. It appears that **5** decomposes by some sort of chain reaction whereas **6** decomposes by an intramolecular path. It does not seem reasonable that electronic effects can account for this difference, and steric interactions may be responsible for the change in reaction course.

Reactions of diphenyl sulfide, **7**, with **1** at low temperature led to the production of diphenyl sulfoxide and isobutylene oxide. These products could arise from a sulfurane or a zwitterion(s). Reaction of **7** with **2** yielded trimethylethylene oxide, diphenyl sulfoxide, and diphenyl sulfone. In a separate experiment it was shown that diphenyl sulfoxide reacts with **2** to give diphenyl sulfone and trimethylethylene oxide. The dioxetane **2**, is considerably more stable than **1** and thus it survives long enough under the reaction conditions to react with diphenyl sulfoxide.

When dimethyl sulfide, tetrahydrothiophene, and trimethylene sulfide were allowed to react with **1** at −78°, exothermic reactions occurred which led to the destruction of **1** and with the production of nonvolatile residues. Virtually none of the sulfides were consumed in this process.

Dimethyl sulfide and tetrahydrothiophene reacted with **2** to give 3-hydroxy-3-methyl-2-butanone. This process is similar to that observed by Kornblum[8] for the base catalyzed decomposition of peroxides and hydroperoxides bearing α-hydrogens. Wasserman and Saito[6] have investigated the decomposition of dioxetanes by diphenyl sulfide.

The results of this study show that there is a multiplicity of reaction paths for the reactions of divalent sulfur compounds with dioxetanes. The inherent instability of **5** and **6** suggests that more electronegative groups will have to be introduced to achieve greater stabilization.

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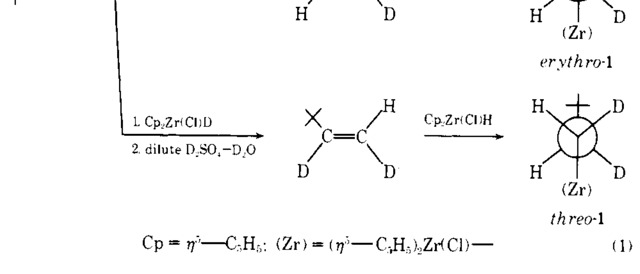
Electrophilic Cleavage of the Carbon–Zirconium(IV) Bond. Comparison and Contrast with Other Transition Metal Alkyl Systems

Sir:

Mechanisms for electrophilic cleavage of the carbon–metal bond in transition metal alkyls can be elucidated by observing the stereochemical consequences, at carbon, of the cleavage process.[1] A point of recurrent interest in this area deals with the mechanism that leads to *inversion* of configuration at carbon in the electrophilic cleavage by halogen of alkyliron[1] and -cobalt[2] complexes. In these cases, there is evidence that oxidation of the complex followed by backside nucleophilic attack by halide ion[3,4] occurs, rather than backside electrophilic attack by the halogen molecule (S_E2 (open) mechanism). We have previously observed that bromination of di(η^5-cyclopentadienyl)(chloro)alkylzirconium(IV) complexes yields alkyl bromides.[5] It appeared worthwhile to examine the stereochemistry, at carbon, of certain electrophilic cleavage reactions, since, for these d^0 species, routes involving oxidation are unlikely. Indeed, we find that the stereochemical course at carbon for cleavage reactions involving Zr(IV) alkyls differs from that observed for other transition metal alkyls in several key instances.

The alkyl group which has proved to be most useful for the study of cleavage reactions of metal alkyls is (*erythro*- or *threo*-)$(CH_3)_3CCHDCHD$, since the stereochemistry at carbon of the process can be monitored directly by NMR.[1] The Zr(IV) complexes of this moiety can be easily prepared by addition of a suitably deuterated olefin to the hydride (or deuteride) $(\eta^5\text{-}C_5H_5)_2Zr(Cl)X$ (X = H or D).[5,6] Interestingly, the deuterated olefin is also prepared using the same hydride (reaction 1). This route to diastereomeric transition metal alkyls is much faster and more convenient than those previously employed.[1] The ^{1}H NMR spectral parameters[7] of **1** are shown in Table I.[8]



Cp = η^5—C_5H_5; (Zr) = $(\eta^5\text{—}C_5H_5)_2Zr(Cl)$— (1)