

Acknowledgment. The authors gratefully acknowledge helpful discussions with G. D. Mendenhall (National Research Council of Canada) and A. Frimer (Bar-Ilan University, Israel). Financial assistance by Kansas State University is greatly appreciated.

References and Notes

- (1) Presented in part at the 174th National Meeting of the American Chemical Society, Chicago, Ill., Aug 28–Sept 2, 1977, Abstracts ORGN 112.
- (2) (a) C. S. Foote in "Free Radicals in Biology", W. A. Pryor, editor, Academic Press, New York, N.Y., 1975, Chapter 3, p 85, and references therein; (b) H. J. Guiraud and C. S. Foote, *J. Am. Chem. Soc.*, **98**, 1984 (1976); (c) A. U. Khan, *ibid.*, **99**, 370 (1977), and references therein; (d) A. Mayeda and A. J. Bard, *ibid.*, **96**, 4023 (1974); (e) J. Ericksen, C. S. Foote, and T. L. Parker, *ibid.*, **99**, 6455 (1977); (f) D. T. Sawyer, M. J. Gibian, M. M. Morrison, and E. T. Seo, *ibid.*, **100**, 627 (1978).
- (3) The reaction of KO_2 with acyl chlorides to yield the corresponding diacyl peroxides has been reported.⁴ However, no explanation was offered for the formation of varying amounts of carboxylic acids that were isolated in all the trials.
- (4) R. A. Johnson, *Tetrahedron Lett.*, 331 (1976).
- (5) C. S. Foote, *Acc. Chem. Res.*, **1**, 104 (1968).
- (6) J. A. Howard and G. D. Mendenhall, *Can. J. Chem.*, **53**, 2199 (1975).
- (7) See abstracts, International Symposium on Singlet Oxygen and Related Species in Chemistry and Biology, Pinawa, Manitoba, Canada, Aug 1977.
- (8) P. B. Merkel and D. R. Kearns, *J. Am. Chem. Soc.*, **94**, 7244 (1972).
- (9) From scavenging studies with **1**, we have found that 0.5 mmol (0.05 M) of benzoyl peroxide in 10 mL of benzene added to a slurry of 1.2–1.8 mmol of KO_2 , 0.5 mmol (0.033 M) of 18-crown-6, and 1.2 mmol (0.08 M) of **1** in 15 mL of benzene gave high yields of **2**.
- (10) C. S. Foote and R. W. Denny, *J. Am. Chem. Soc.*, **90**, 6233 (1968).
- (11) Unlike the photosensitized oxygenations of alkenes and sulfides via a non-singlet-oxygen mechanism involving a superoxide-cation-radical adduct,^{2e} we find no reaction of *trans*-stilbene under our conditions.

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$\text{S}_{\text{N}}2'$ Reactions of *cis*-3,4-Dichlorocyclobutene

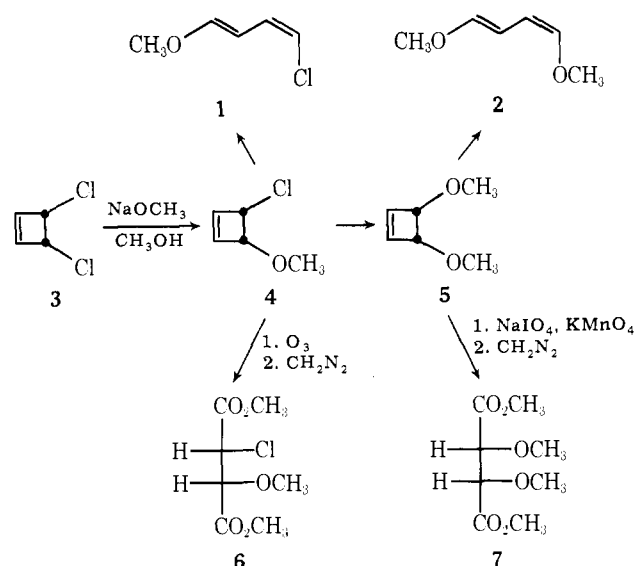
Sir:

The $\text{S}_{\text{N}}2'$ reaction (bimolecular nucleophilic substitution with allylic rearrangement) has been the subject of considerable interest as well as substantial controversy.¹ Most of the reported examples involve bulky nucleophiles and/or hindered substrates which minimize $\text{S}_{\text{N}}2$ displacement. Syn attack (in which the nucleophile and leaving group are on the same face of the allylic system) has been demonstrated with secondary amines and, in some cases, with thiolates.^{2,3} Whether this is due to hydrogen bonding or to an inherent stereoelectronic preference in $\text{S}_{\text{N}}2'$ reactions remains to be settled. Some cases of predominant anti attack by other nucleophiles are known.^{4,5} Theoretical calculations supporting both syn and anti pathways are available.⁶

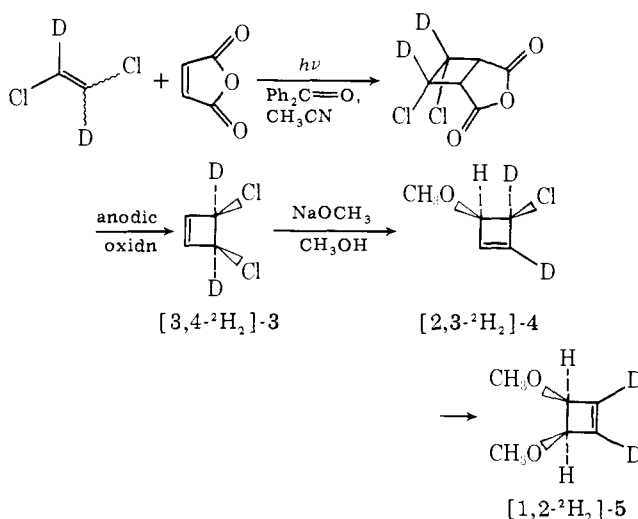
We should like to report that the reactions of *cis*-3,4-dichlorocyclobutene (**3**) with methoxide proceed exclusively with syn stereochemistry and with allylic rearrangement (see Scheme I). Treatment of **3** with 1 equiv of NaOCH_3 (4 M in methanol, 1.5 h, 80 °C) afforded a mixture containing ~25% *cis*-3-chloro-4-methoxycyclobutene (**4**), ~25% *cis*-3,4-dimethoxycyclobutene (**5**), and ~50% **3**.⁷ An excess of methoxide produced **5** quantitatively. No reaction occurred without added methoxide. When **3** reacted in $\text{CH}_3\text{OD}/\text{NaOCH}_3$, no deuterium was incorporated into **4** and **5**.

The configuration of **4** was established by ozonolysis, followed by treatment with diazomethane, to give dimethyl *erythro*-2-chloro-3-methoxysuccinate (**6**).⁸ GLC of the crude product revealed the absence of any threo isomer. Similarly, Lemieux oxidation⁹ of **5** afforded exclusively *meso*-2,3-dimethoxysuccinate (**7**).¹⁰ The thermal rearrangement of **4** and **5** to give *Z,E* dienes is also consistent with their *cis* configuration. Two products may arise from the conrotatory reaction

Scheme I



Scheme II



of **4**, but only one was actually found which we assign as (1*Z*,3*E*)-1-chloro-4-methoxybutadiene (**1**) on the basis of $J_{1,2} = 6$, $J_{3,4} = 12$ Hz. The remarkable effects of alkoxy groups on the rates and selectivities of cyclobutene rearrangements will be subject of a forthcoming paper.

The $\text{S}_{\text{N}}2'$ mechanism of the **3** → **4** + **5** transformation was established with the aid of [3,4-²H₂]-**3**, synthesized as shown in Scheme II.^{11,12} In the NMR spectrum of **4**, 3-H (δ 5.0) and 4-H (4.4) are clearly resolved. The spectrum of labeled **4**, obtained from [3,4-²H₂]-**3**, displayed the signals of 4-H and of one vinylic proton. No resonances due to vinylic protons were found in the NMR spectrum of labeled **5**. Obviously, the nucleophilic displacements at **3** and **4** involve allylic rearrangement.

Theoretical analyses have led to the prediction that $\text{S}_{\text{N}}2$ reactions of strained cyclic systems should proceed with retention of configuration.¹³ This postulate has not yet received experimental support. Cyclobutyl tosylates prefer the inversion pathway.¹⁴ The present work shows that the cyclobutenyl chloride **3** avoids $\text{S}_{\text{N}}2$ displacement in favor of an exceptionally clean $\text{S}_{\text{N}}2'$ reaction.

References and Notes

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- (2) G. Stork and W. N. White, *J. Am. Chem. Soc.*, **78**, 4609 (1956); G. Stork and A. F. Kreft, III, *ibid.*, **99**, 3850 (1977).
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 (7) The components were readily separated by GLC (1.5 m polypropylene-glycol, 80 °C). Heating above 80 °C led to thermal rearrangement of **4** and **5**.
 (8) Obtained from the corresponding 2-chloro-3-hydroxysuccinic acid with $\text{CH}_2\text{N}_2/\text{BF}_3$. For the preparation and configuration of *erythro*- and *threo*-2-chloro-3-hydroxysuccinic acid, see R. Kuhn and F. Ebel, *Ber. Dtsch. Chem. Ges.*, **58**, 919 (1925); O. Gawron, A. J. Glaid, A. Lo Monte, and S. Gary, *J. Am. Chem. Soc.*, **80**, 5856 (1958).
 (9) Following the procedure of S. W. Pelletier, K. N. Iyer, and C. W. J. Chang, *J. Org. Chem.*, **35**, 3535 (1970).
 (10) W. N. Haworth and E. L. Hirst, *J. Chem. Soc.*, 1858 (1926).
 (11) The photosensitized addition of 1,2-dichloroethylene to maleic anhydride has been reported by R. Steinmetz, W. Hartmann, and G. O. Schenck, *Chem. Ber.*, **98**, 3854 (1965). The anodic decarboxylation was carried out according to R. Radlick, R. Klem, S. Spurlock, J. J. Sims, E. E. van Tamelein, and T. Whitesides, *Tetrahedron Lett.*, 5117 (1968).
 (12) We thank Dr. E. K. G. Schmidt for a generous gift of [1,2- $^2\text{H}_2$]-1,2-dichloroethylene.
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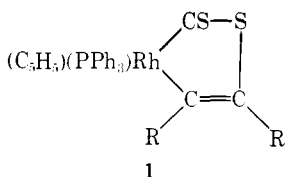
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 Received February 10, 1978

Novel Route to Iron-Carbene Complexes via η^2 -CS₂ Derivatives. 1,3-Dithiolium Species as Precursors for Dithiolene-Iron Complexes and Tetrathiafulvalenes

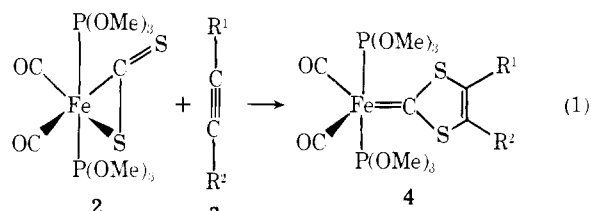
Sir:

Although several routes to carbene-metal complexes have been described which involve modification of a coordinated ligand,¹ none of these methods utilize the cycloaddition of alkynes to a ligand with 1,3-dipolar character. We wish to report here the first examples of carbene complex generation via the addition of activated alkynes to η^2 -CS₂-iron derivatives as well as the use of these intermediate carbenes for the synthesis of dithiolene iron compounds and tetrathiafulvalenes.

Dimethylacetylene dicarboxylate is known to add to a η^2 -CS₂-rhodium complex $\text{Rh}(\text{CS}_2)(\text{PPh}_3)(\text{C}_5\text{H}_5)$ giving the heterocyclic five-membered metalloring derivative **1**.²



By contrast we have found that η^2 -CS₂-iron complexes of type **2**,³ for which a 1,3-dipolar structure has been suggested,⁴ readily react with activated alkynes **3** in benzene at room temperature following a different route: alkynes **3a**, **3b**, or **3c** with complex **2** give air-sensitive adducts **4a**, **4b**, or **4c** which were isolated in 85–95% yields using inert atmosphere column chromatography⁵ (eq 1). The spectroscopic characteristics of complexes **4a–c** were not consistent with what we would have expected for heterometallic compounds, but instead support the carbene structure. The infrared showed two car-



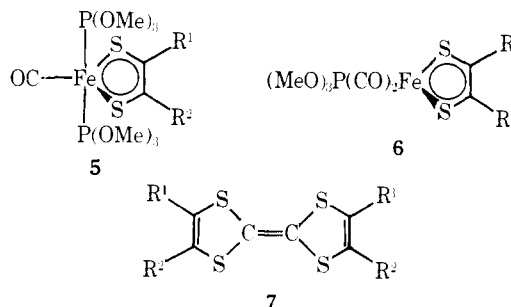
R¹, R²: a (H, CO₂Et); b (*p*-ClC₆H₄, CHO); c (CO₂Me, CO₂Me); d (*p*-O₂NC₆H₄, COCH₃); e (C₆H₅, CHO)

bonyl absorption bands for **4a** (1930, 1870 cm⁻¹), **4b** (1925, 1880 cm⁻¹), and **4c** (1928, 1880 cm⁻¹) at lower frequencies than those of the η^2 -CS₂-iron precursor **2** (2020, 1964 cm⁻¹).⁴ Such a shift is in agreement with the strong electron-donating effect expected for a carbene ligand containing heteroatoms bonded to the carbene carbon atom.⁶ Moreover, ¹³C NMR spectra showed two signals at low field. One triplet corresponds to two equivalent carbonyl ¹³C nuclei coupled with two identical *cis* ³¹P nuclei: **4a**, δ (C₆D₆) 219.6 ($2J = 36.0$ Hz); **4b**, δ 222.8 ($2J = 35.9$ Hz); **4c**, δ 220.7 ($2J = 38.1$ Hz). A singlet at lower field⁷ (250.7 (**4a**), 239.6 (**4b**), and 239.4 ppm (**4c**)) corresponds to the range of ¹³C NMR chemical shifts already reported for deshielded, coordinated carbene carbon nuclei.^{1a,8}

¹H and ¹³C NMR data for derivative **4c** rule out the metalloring formulation. Thus the ¹H NMR spectrum presents only one line for the CO₂Me groups (δ 2.65 ppm). Moreover, only three types of ¹³C nuclei originating from alkyne unit were observed in the ¹³C NMR spectrum: δ 52.4 (OCH₃), 145.1 (–C=), 158.8 ppm (–C=O). Equivalence of ¹³C nuclei by pairs indicating the incorporation of the alkyne **3c** in a symmetrical ligand is again in agreement with the 1,3-dithiolium carbene structure.

The trapping of the carbene moiety in complexes **4** under mild conditions is significant since it lends direct support to the suggestion of Hartzler⁹ that cyclic 1,3-dithiolium carbenes are the initial, unstable intermediates in the reactions of free carbon disulfide with activated alkynes. The activation toward cycloaddition afforded by η^2 coordination of carbon disulfide results from the enhancement of nucleophilic character at the uncoordinated sulfur atom and electrophilic character at the coordinated sulfur atom in complexes of type **2**.¹⁰ In contrast, for the rhodium complex $\text{Rh}(\eta^2\text{-CS}_2)(\text{PPh}_3)(\text{C}_5\text{H}_5)$ the metal atom appears to be more electrophilic than the ligated sulfur atom of carbon disulfide.²

Two significant aspects of the behavior of the air-sensitive carbene species **4** are emphasized by their transformation into 1,2-dithiolene-iron complexes and tetrathiafulvalenes. Air-stable, violet compounds **5** were formed when solutions of the corresponding derivatives **4** were allowed to stand in air at room temperature and complexes **5a** (23%), **5b** (22%), or **5c** (35%) could be isolated using Kieselgel thick layer chromatography.¹¹ In addition to complex **5a** a small amount of unstable dithiolene iron derivative **6a** was isolated and characterized.¹²



Dithiolene complexes **5** were more readily obtained without isolation of the carbene intermediate. Thus compounds **5d**