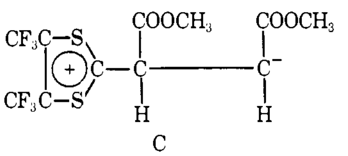
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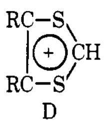
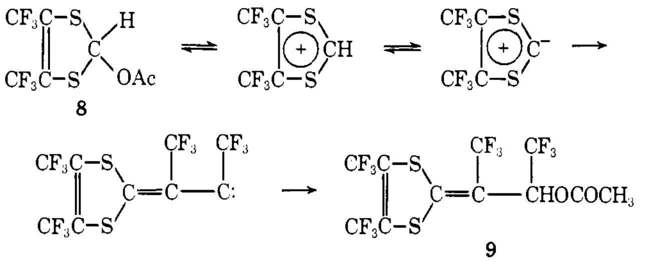

D

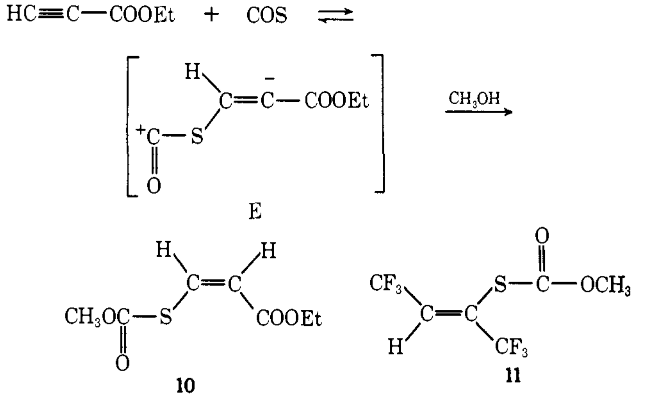
The formation of **1** in the absence of acids is believed to result from dimerization of A. The acid catalysis of the formation of **1** indicates that A is protonated to give the cation D. D would be an effective trap for the nucleophilic carbene A giving protonated **1**. The formation of **2** is probably the reaction of carbenes A and B.

If carbene B reacted with carbon disulfide analogously to the known reactions of diarylcarbenes with carbon disulfide,[7] the result would be **3**. All analytical and spectral properties of **3** are in agreement with this structural formulation.

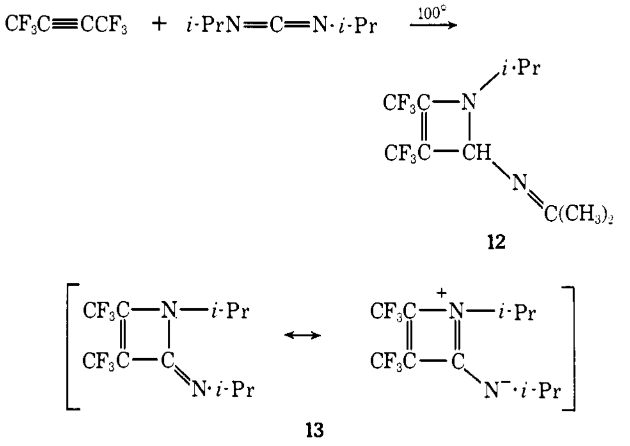
The reaction of carbon disulfide, hexafluoro-2-butyne, and acetic acid at 100° gave a 20% yield of **1** (R = CF_3) and a 70% yield of **9**. None of the expected **8** was obtained. The absence of **8** may be rationalized by its expected ease of solvolysis to give the cation, equilibration of cation and carbene, and the probably irreversible addition of carbene to acetylene. The formation of **9** suggests that carbenes B have nucleophilic as well as electrophilic character. A completely analogous result has been obtained with carbon disulfide, hexafluoro-2-butyne, and benzoic acid.



Carbonyl sulfide gave a different reaction with acetylenes. When carbonyl sulfide was heated at 100° with ethyl propiolate or hexafluoro-2-butyne starting materials were recovered unchanged. With methanol present compounds **10** and **11** were formed. The acyclic zwitterion E is believed to be an intermediate. An analogous intermediate in the carbon disulfide additions would rationalize the need for an electron-attracting substituent on the acetylene. If such a zwitterion is formed, it must cyclize at rates faster than diffusion-controlled protonations, for acyclic compounds have never been isolated in carbon disulfide additions.



Attempts were made to generate imidazolium carbenes by thermal 1,3 addition of carbodiimides to acetylenes. Hexafluoro-2-butyne and diisopropylcarbodiimide gave only **12** derived from a 1,2 addition. It is thought that the precursor of **12** is the amidine **13** which does not enjoy the normal resonance stabilization of amidines.



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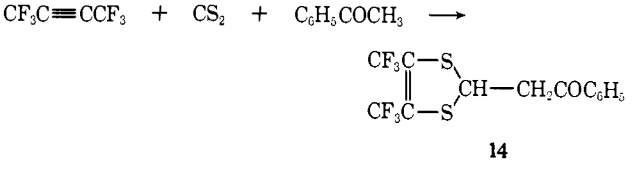
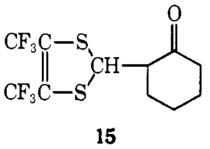
Alkylations and Acylations with 1,3-Dithiolium Carbenes

Sir:

The thermal reaction of carbon disulfide with acetylenes having at least one electron-attracting substituent has been shown[1] to generate 1,3-dithiolium carbenes which have been captured by a variety of electrophilic reagents. Another general reaction of 1,3-dithiolium carbenes has been found in the α-alkylation of aldehydes and ketones.

The reaction of hexafluoro-2-butyne, carbon disulfide, and acetophenone at 100° for 6 days gave a 79% yield of 2-(benzoylmethyl)-4,5-bis(trifluoromethyl)-1,3-dithiole (**14**). Under comparable conditions a 75% yield of 2-(2-oxocyclohexyl)-4,5-bis(trifluoromethyl)-1,3-dithiole (**15**) was obtained from cyclohexanone and a 53% yield of 2-(diacetylmethyl)-4,5-bis(trifluoromethyl)-1,3-dithiole (**16**) was obtained from 2,4-pentanedione.

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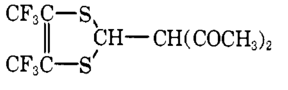
16

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(7) A. Schönberg, E. Frese, and K. Brosowski, *Chem. Ber.*, **95**, 3077 (1962).

(1) H. D. Hartzler, *J. Amer. Chem. Soc.*, **92**, 1412 (1970).

Analogous products have been obtained from acetone and from 2-butanone in slightly lower yields. In these cases products **2** and **3** (R = CF_3)[2] from the acetylene and carbon disulfide alone were also obtained. With 2-butanone, alkylation occurred exclusively at the methylene group. Aliphatic aldehydes such as propionaldehyde and isobutyraldehyde gave analogous products in 28 and 29% yield along with **2** and **3**.

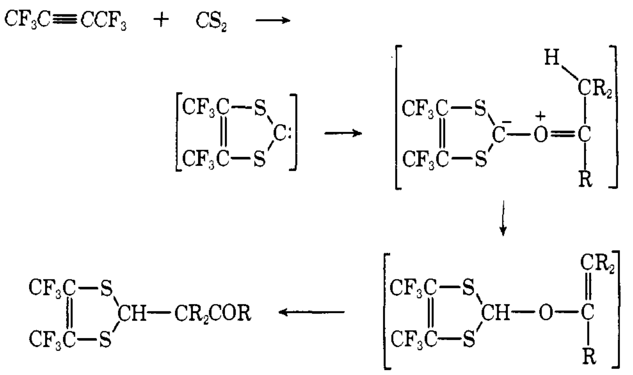
Dimethyl acetylenedicarboxylate reacted similarly with carbon disulfide and aldehydes and ketones. Slightly higher temperatures (120–140°) were needed and yields have generally been lower.

This reaction is not general for compounds with acidic hydrogen. Ethyl malonate and malononitrile were not alkylated. In these cases products **1**, **2**, and **3** were obtained.

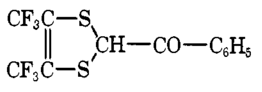
In none of these reactions have products derived from nucleophilic attack of the 1,3-dithiolium carbene at the carbonyl group been found. The absence of a general reaction for acidic hydrogen compounds indicates that a direct insertion of the carbene into a CH bond is an unlikely mechanism. Reaction of the carbene with the enol form of the aldehyde or ketone also appears unlikely because of the low concentration of enol under the essentially neutral reaction conditions.

The most likely mechanism for the alkylation reaction is given in Scheme I. That the dithiolium carbene is generated under the reaction conditions is demonstrated by the fact that products derived from it and the acetylene are also obtained in many of the reactions. Although in many cases the carbene reacts as a nucleophile the carbon atom still has a vacant orbital and the potential for electrophilic reaction. Electrophilic attack at the carbonyl oxygen would lead to the enol ether. The initial dipolar ion need not be an antiaromatic species. The negative charge could overlap with the d orbitals of sulfur and not enter into the π system of the dithiolium ring. Under the neutral reaction conditions the more stable enol would be formed and this would lead to the orientation observed with 2-butanone and 2,4-pentanedione. The isomerization of the enol ether to the observed product could occur by either a homolytic or a heterolytic process.

Scheme I



Hexafluoro-2-butyne reacted with carbon disulfide and benzaldehyde to give **17** and **18**. Cinnamaldehyde reacted analogously as did other aromatic aldehydes. It is believed that **18** is formed from **17** by the type of reaction discussed above for aldehydes and ketones.



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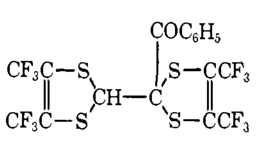

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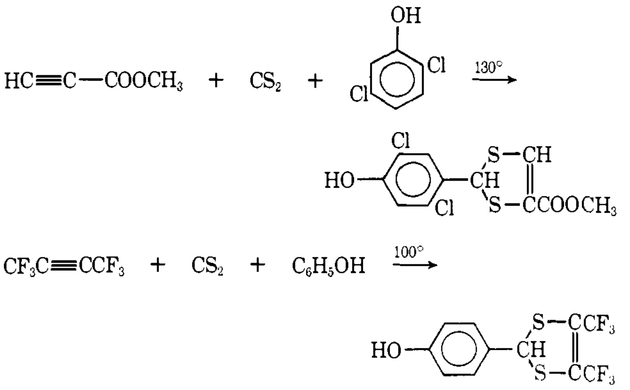
The mechanism of formation of **17** is not known, but a likely possibility would be nucleophilic attack of the 1,3-dithiolium carbene at the carbonyl carbon followed by a hydride shift.

Another type of alkylation reaction was observed with acetylenes, carbon disulfide, and phenols. This reaction evidently results from formation of the 1,3-dithiolium carbene, protonation to give the corresponding cation, and a Friedel–Crafts type alkylation of the phenol (or phenolate ion). In some cases the addition of acid (such as trifluoroacetic acid) is needed to suppress the addition of the phenol to the acetylene.



The thermal carbon disulfide–acetylene reaction permits the investigation of a wide variety of reactions of a carbene which is probably unencumbered with solvent or other complexing materials.

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[2] The numbering of compounds is the same as in ref 1.

Stereochemistry of the Alkylation of Cobalt(I)

Sir:

In the first reported alkylations of vitamin B_{12s},[1] the reactions were formulated as additions to a cobalt hydride. Later it was proposed that B_{12s} is a nucleophilic Co(I) species and the alkylations are S_N2 processes.[2] Recent evidence has shown that B_{12s} and the related cobaloxime(I) react with alkylating agents *via* bimolecular processes.[3] The variation in rate upon changing the alkylating agent is similar to that of known S_N2 reactions. However, the mechanism cannot be considered established until the stereochemical fate of the reacting carbon is known.

We wish to report that the reaction of cobaloxime(I) with typical alkylating agents (epoxides, bromides, and

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[1] (a) O. Müller and G. Müller, *Biochem. Z.*, **336**, 299 (1962); (b) O. Müller and G. Müller, *ibid.*, **337**, 179 (1964), (c) A. W. Johnson, L. Mervyn, N. Shaw, and E. L. Smith, *J. Chem. Soc.*, 4146 (1963).

[2] G. N. Schrauzer, R. I. Windgassen, and J. Kohnle, *Chem. Ber.*, **98**, 3324 (1965).

[3] G. N. Schrauzer and E. Deutsch, *J. Am. Chem. Soc.*, **91**, 3341 (1969).