

4*N*-orbital, 4*N*-electron system which will be excited state forbidden.¹⁰

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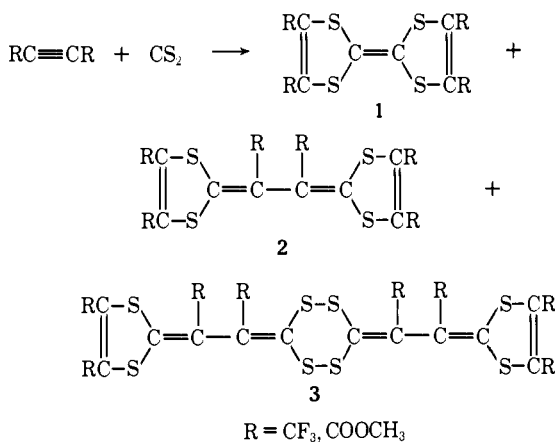
(10) (a) H. E. Zimmerman, *J. Amer. Chem. Soc.*, **88**, 1564 (1966); (b) *Angew. Chem.*, **81**, 45 (1969); *Angew. Chem. Int. Ed. Engl.*, **8**, 1 (1969).

Howard E. Zimmerman, Gary A. Epling
Chemistry Department, University of Wisconsin
Madison, Wisconsin 53706
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Nucleophilic 1,3-Dithiolium Carbenes

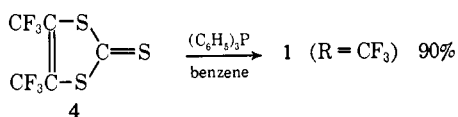
Sir:

At 100° carbon disulfide was added to acetylenes having at least one electron-attracting substituent to give products 1, 2, and 3, any one of which can be made the predominant product by variation of re-



action conditions. Compound 3 (R = CF₃) was obtained in 60% yield when a sevenfold excess of carbon disulfide was employed. With a 3.5-fold excess of carbon disulfide a 40% yield of 2 (R = CF₃) and a 20% yield of 3 were obtained. Compound 1 (R = CF₃) was normally formed in yields of the order of 2%, but could be produced quantitatively in the presence of trifluoroacetic acid. Compounds 1, 2, and 3 are stable under the reaction conditions. A mixture of 1, 2, and 3 (R = COOCH₃) was heated with hexafluoro-2-butyne and carbon disulfide and no cross products were formed.

The bidithiole 1 (R = CF₃) was prepared in 90% yield by desulfurization of the known trithiocarbonate 4 with triphenylphosphine. Compound 2 was identical with material previously prepared.¹ The structures of 3 are consistent with all analytical and spectral data and are assigned for reasons given below.



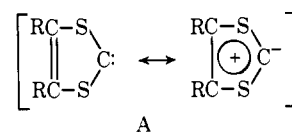
The reaction of hexafluoro-2-butyne, carbon disulfide, and methanol gave no 1, 2, or 3, but only

(1) C. G. Krespan and D. C. England, *J. Org. Chem.*, **33**, 1850 (1968).

the methoxydithiole 5 (R = CF₃). A similar reaction with dimethyl acetylenedicarboxylate gave principally 5 (R = COOCH₃) along with small amounts of 1 (R = COOCH₃). Completely analogous reactions occurred with esters of propionic acid.

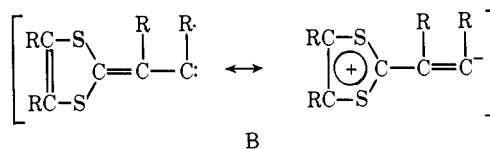
The reaction of hexafluoro-2-butyne, carbon disulfide, and olefins gave cyclopropanes 7. Yields of 7 as high as 77% (R = OCH₃) have been obtained.

These data suggest that acetylenes and carbon disulfide generate 1,3-dithiolium carbenes (A) and that the carbenes react as nucleophiles. Such a species has a 6- π -electron system and would be expected to



be greatly stabilized by electron delocalization. Stable, aromatic, 1,3-dithiolium cations are well known²⁻⁴ and 1,3-dithiolium carbenes have been suggested as intermediates in reactions of the ions with bases.^{5,6} The formation of alkoxydithioles 5 indicates that alcohols can very effectively capture A, presumably by protonation.

In the presence of olefins, A preferentially reacts with the electron-deficient triple bond of the acetylene to generate a new carbene B which is trapped with the olefin to form cyclopropanes 7. These reactions of A are again those of a nucleophile. Interaction



of A with electron-deficient olefins can occur. The reaction of hexafluoro-2-butyne, carbon disulfide, and dimethyl maleate gave 1, 2, and 3 (R = CF₃) and dimethyl fumarate. Control experiments demonstrated that neither the acetylene nor carbon disulfide caused isomerization of dimethyl maleate under reaction conditions. It seems most reasonable that A underwent reversible Michael-type addition to the ester to give zwitterion C which lived long enough to allow bond rotation.

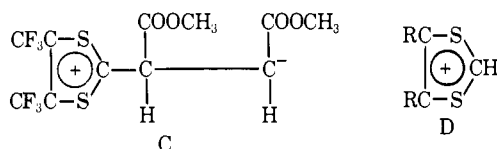
(2) D. Leaver, W. A. H. Robertson, and D. M. McKinnon, *J. Chem. Soc.*, 5104 (1962).

(3) E. Klingsberg, *J. Amer. Chem. Soc.*, **84**, 3410 (1962).

(4) The parent 1,3-dithiolium perchlorate² undergoes rapid deuterium exchange at C-2 and reacts with triethylamine to give a high yield of $\Delta^{2,2}$ -bi-1,3-dithiole.

(5) H. Prinzbach, H. Berger, and A. Lüttringhaus, *Angew. Chem.*, **77**, 453 (1965).

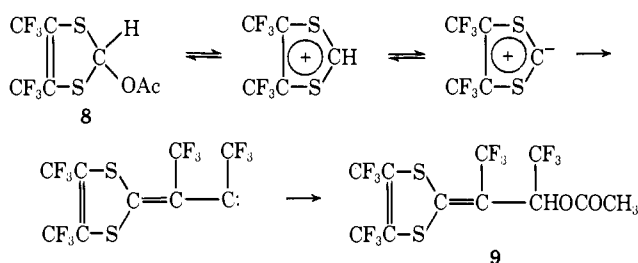
(6) H. Prinzbach and E. Futterer, *Advan. Heterocycl. Chem.*, **7**, 121-124 (1966).



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**.

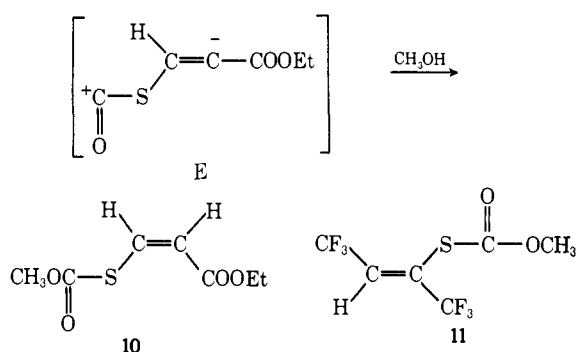
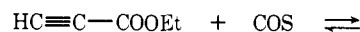
If carbene **B** reacted with carbon disulfide analogously to the known reactions of diarylcarbenes with carbon disulfide,⁷ the result would be **3**. All analytical and spectral properties of **3** are in agreement with this structural formulation.

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

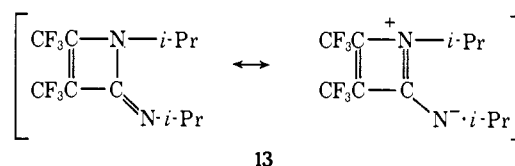
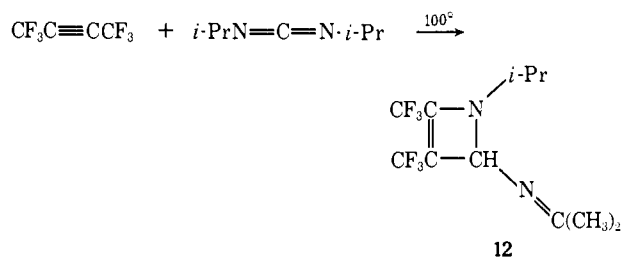


additions would rationalize the need for an electron-attracting substituent on the acetylene. If such a

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

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.



H. D. Hartzler

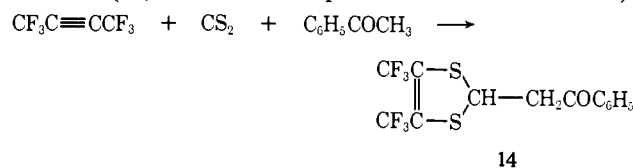
Contribution No. 1649, Central Research Department
E. I. du Pont de Nemours and Company, Experimental Station
Wilmington, Delaware 19898
Received December 6, 1969

Alkylations and Acylations with 1,3-Dithiolium Carbenes

Sir:

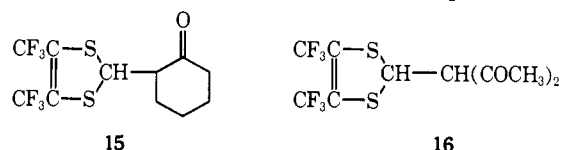
The thermal reaction of carbon disulfide with acetylenes having at least one electron-attracting substituent has been shown¹ to generate 1,3-dithiolium carbenes which have been captured by a variety of electrophilic reagents. Another general reaction of 1,3-dithiolium carbenes has been found in the α -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%



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