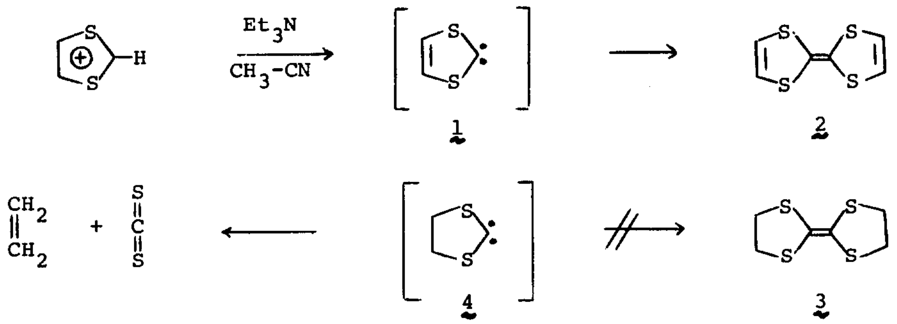
Tetrahedron Letters No.30, pp. 2633-2636, 1970. Pergamon Press. Printed in Great Britain.

CONDENSATION OF CARBON DISULFIDE WITH DIMETHYL ACETYLENEDICARBOXYLATE

D.L. Coffen
Department of Chemistry, University of Colorado
Boulder, Colorado 80302

(Received in USA 13 April 1970; received in UK for publication 29 May 1970)

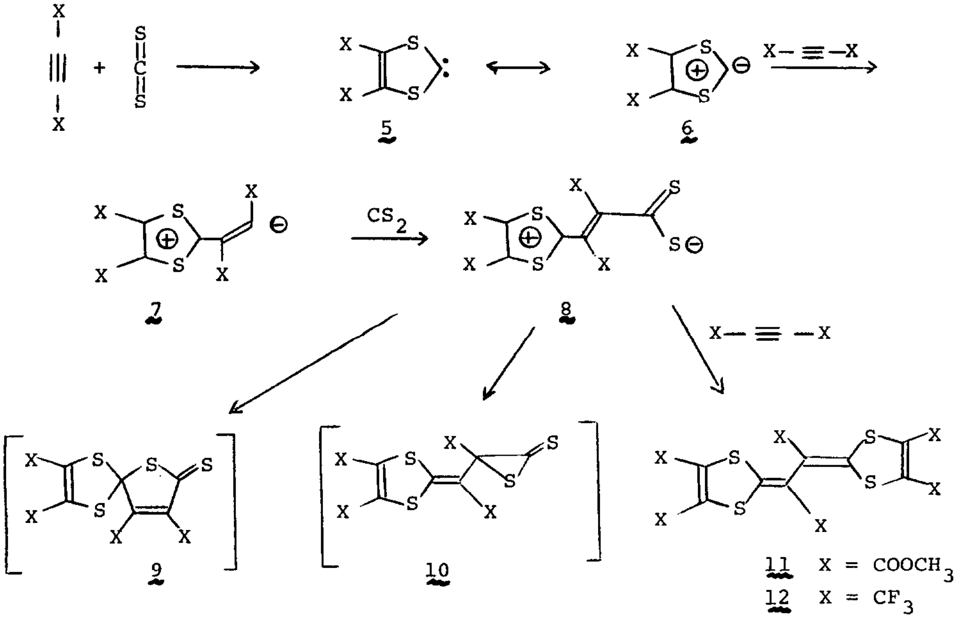
A study of the chemistry of tetrathioethylenes, now in progress, entailed the investigation of several methods for their synthesis. The generation of sulfur stabilized carbenes is a well established route to these compounds[1] and we have successfully applied this method to the synthesis of tetrathiafulvalene (2).[2] Other methods were necessary for the synthesis of tetrathioethylene 3[3] however, as

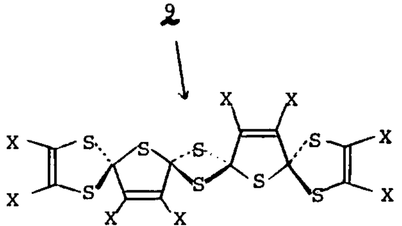


the carbene 4 undergoes rapid and facile decomposition to ethylene and carbon disulfide.[4] These observations suggested: (a) that a low energy pathway (symmetry allowed)[5] exists between carbenes of type 1 and 4 and their C_2 and CS_2 components, (b) that carbene 1 is in a more favorable thermodynamic relationship to these components by virtue of resonance stabilization, and (c) that carbenes of type 1 might conceivably be generated by a cycloaddition reaction between carbon disulfide and acetylenes.

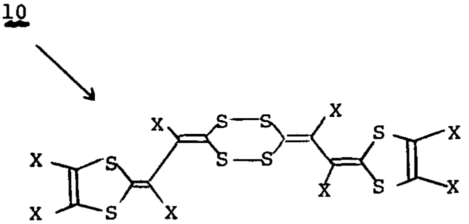
In view of possibility (c) a reaction between dimethyl acetylenedicarboxylate and carbon disulfide was sought with the following result.[6] A solution of the acetylene (5 g.) in carbon disulfide (200 ml) was heated under reflux for sixteen days. During this time a crystalline precipitate formed and the solution became dark red. The cooled solution was decanted from the precipitate and, after evaporation of carbon disulfide, 3.7 g. of the acetylene was recovered by vacuum distillation. The distillation residue consisted of a dark red tar. The precipitate was triturated with cold chloroform, filtered and washed with chloroform giving 228 mg. (13%) of creamy white powder. Recrystallization from chloroform/methanol gave fine white crystals with m.p. 258-260°. A high resolution infrared spectrum of this product exhibited four C=O bands at 1687, 1713, 1727, and 1743 cm^{-1} and a C=C band at 1545 cm^{-1}. The 100 Mc nmr spectrum (recorded at 140° in p-dichlorobenzene) consisted of four lines of equal intensity at 3.77, 3.91, 3.93 and 3.95 ppm. The molecular weight and elemental analysis (C, 38.43%; H, 2.79%; S, 29.03%, and mol. wt. 811) establish that a 4:4 adduct of the acetylene with carbon disulfide was formed (Calcd. C, 38.52%; H, 2.77%; S, 29.38%; and mol. wt. 872).

The task of assigning a structure to this 4:4 adduct was approached with the mechanistic considerations set forth in the first paragraph of this Letter. It is assumed that the condensation could begin with the cycloaddition of the acetylene to carbon disulfide producing as a first intermediate the carbene 5. The resonance structure 6 concommitantly stabilizes and confers nucleophilic character on this carbene whence it adds to the electrophilic acetylene. The resulting carbanion 7 can (and probably does) react with more of the acetylene yielding net polymerization, or it can react with carbon disulfide to give the dithiocarboxylate ion 8. Addition of a third molecule of the acetylene would produce the 3:2 adduct 11 and the formation of an adduct of this type (12) from hexafluoro-2-butyne and carbon disulfide, recently reported by Krespan and England,[7] lends considerable credence to this portion of the proposed condensation pathway.

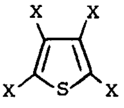




13



14 X = COOCH$_3$



15 X = COOCH$_3$

Alternatively the zwitter ion 8 can undergo internal charge neutralization via either of two possible modes producing intermediate 9 or 10. The well known propensity of thiocarbonyl compounds to dimerize suggests that 13, derived from 9, is one possible structure for the 4:4 adduct. Intermediate 10 is of the type advanced by Schönberg and coworkers[8] as an intermediate in the reaction of diaryldiazomethanes and certain ylids with carbon disulfide, a reaction which produces 1,2,4,5-tetrathiacyclohexane derivatives of type 14. Thus 14 is a second possible structure for the 4:4 adduct (in terms of this condensation mechanism). A decision between structures 13 and 14 can be made on the basis of the infrared and nmr spectra of the adduct. The presence of four different carbonyl bands in the former and four different methyl ester resonances in the latter indicate that the adduct contains four pairs of structurally different methyl ester functions. This is the case with structure 14 but the symmetry of 13 is such that all four ester groups on the terminal rings are identical, i.e., there are three kinds of ester groups in a 4:2:2 ratio.

Modest support for structure 14 is available from the vacuum pyrolysis of the adduct. Pyrolysis at its melting point (0.001 mm) yields the tetramethyl ester of thiophenetetracarboxylic acid (15). This substance is readily formed from dimethyl acetylenedicarboxylate and sulfur.[9] Most of the steps in the proposed condensation sequence are undoubtedly reversible and, in addition, pyrolysis of organic disulfides is known to yield elemental sulfur in some instances.[10] Pyrolysis into a mass spectrometer gives a mass spectrum with intense peaks at m/e 301 (31%, c.f. Ref. 7) and 578 (100%) suggesting that the 3:2 adduct 11[6] is also a pyrolysis product of the 4:4 adduct.

In an effort to substantiate the proposed condensation mechanism, 1,3-dithiolium bisulfate[11] was treated with triethylamine in a carbon disulfide-dimethyl acetylenedicarboxylate solvent mixture. As expected the yield of tetrathiafulvalene, (2) dropped to a trace amount but a plethora of other colored products precluded a meaningful interpretation of the experiment.

Research support from the National Science Foundation (GP-10950) is gratefully acknowledged.

REFERENCES

1. See for examples D. Seebach, Angew. Chem. internat. ed., **6**, 443 (1967); R.A. Olofson, S.W. Walinsky, J.P. Marino, and J.L. Jernow, J. Am. Chem. Soc., **90**, 6554 (1968).

2. Various substituted tetrathiafulvalenes have also been prepared by this method; H. Prinzbach, H. Berger, and A. Lüttringhaus, Angew. Chem. internat. ed., **4**, 435 (1965); K.M. Pazdro, Roczniki Chem., **43**, 1089 (1969); A. Takamizawa and K. Hirai, Chem. Pharm. Bull. Japan, **17**, 1931 (1969).

3. D.L. Coffen and P.E. Garrett, Tetrahedron Letters, 2043 (1969).

4. D.M. Lemal and E.H. Banitt, *ibid.*, 245 (1964).

5. The fragmentation of carbene **4** and formation of carbene **5** can be viewed in terms of the orbital symmetry considerations advanced for 1,3-dipolar addition reactions by A. Eckell, R. Huisgen, R. Sustmann, E. Wallbillich, D. Grashey, and E. Spindler, Chem. Ber., **100**, 2192 (1967).

6. The results of a similar investigation were recently communicated by H.D. Hartzler, J. Am. Chem. Soc., **92**, 1412 (1970).

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

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

9. A. Michael, *ibid.*, **28**, 1633 (1895).

10. For example E. Fromm and O. Achert, *ibid.*, **36**, 534 (1903).

11. E. Klingsberg, J. Am. Chem. Soc., **86**, 5290 (1964).