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THE CHEMISTRY OF CYANOACETYLENES VI.
THE REACTIONS WITH THIOCARBONYL COMPOUNDS

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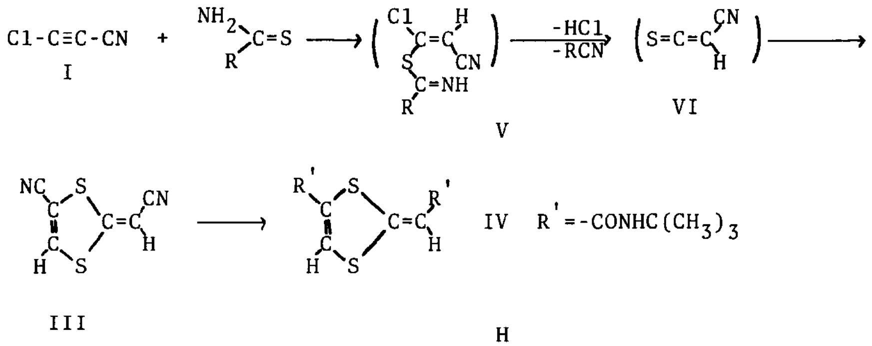
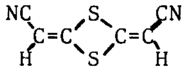
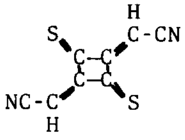
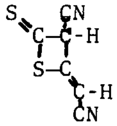
We now wish to report a novel synthesis of dithiafulvene by the reactions of chlorocyanoacetylene (I) with various thiocarbonyl compounds, while the similar reactions of cyanoacetylene (II) afford either thiodiacrylonitrile or 2,3-dihydro-1,3-thiazin.

When one mole of chlorocyanoacetylene (I) was treated with one mole of thioacetamide in methanol at 0°, a yellow product (III) of mp 201° (Found: C, 43.32; H, 1.28; N, 16.90%. M^+ 166. Calcd for $C_6H_2N_2S_2$. M.W. 166: C, 43.38; H, 1.21; N, 16.87%) was obtained in a 60% yield, which, upon treatment with t-butanol in sulfuric acid under the Ritter reaction conditions, gave the corresponding diamide (IV), mp 303°, in an almost quantitative yield. Found: C, 53.45; H, 7.09; N, 8.85%. Calcd for $C_{14}H_{22}N_2O_2S_2$: C, 53.49; H, 7.05; N, 8.91%. The diamide structure in IV was confirmed by the IR spectrum showing a broad absorption at around 1625 cm^{-1} due to carbonyls disappearing that of 2230 cm^{-1} due to nitriles in the starting material III. Both III and IV were considerably insoluble in common organic solvents. The NMR spectrum of III in DMSO-d6 showed only two signals at τ 1.76 (singlet) and 3.80 (singlet) with the relative intensities of 1:1 and both could be assigned to vinyl protons. The UV spectrum of III in ethanol exhibited a strong absorption at 309 mμ ($\log\varepsilon$ = 4.16) with a shoulder at 326 (4.01), indicating the presence of dithiafulvene ring system (1). The Mass spectrum of III showed two characteristic peaks at the most abundance, a molecular ion peak M^+ as well as the base peak at m/e 166 and that at m/e 83 (rel. int. 43%), supporting the dimer structure (Figure). On the basis of the above spectral evidences, 2-cyano-5-cyanomethylene-1,4-dithiafulvene was concluded to be the most probable structure for III among other possible structures, IIIa, IIIb and IIIc. The similar reactions of I with thiourea, N,N'-dimethyl-, or N-phenylthiourea afforded all the same product III in the yields of 65, 50, and 50% respectively, but no reaction was observed with S-methylthiourea, indicating that the reactions were initiated by nucleophilic attack of the thiocarbonyl to the triple bond in I to form a 1:1 adduct V as an intermediate, from which hydrogen chloride and RCN (for instance, acetonitrile when R is CH_3-) were eliminated to give unstable thioaldoketene VI. Similar mechanism has been proposed by us (2) for the formation of cyanoynamines from I and several secondary amines. VI is assumed to be readily dimerized to a stable compound III.



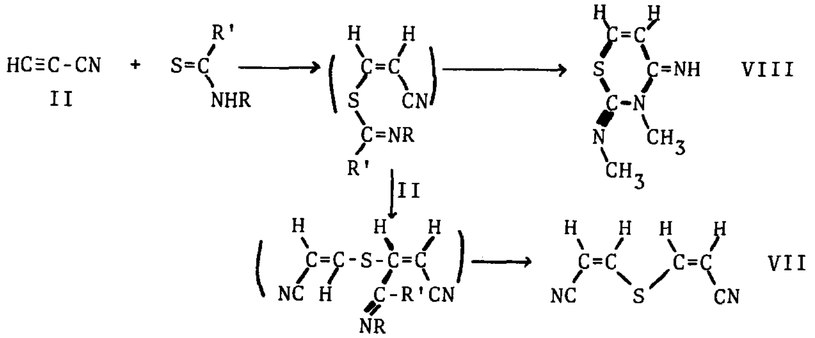

IIIa

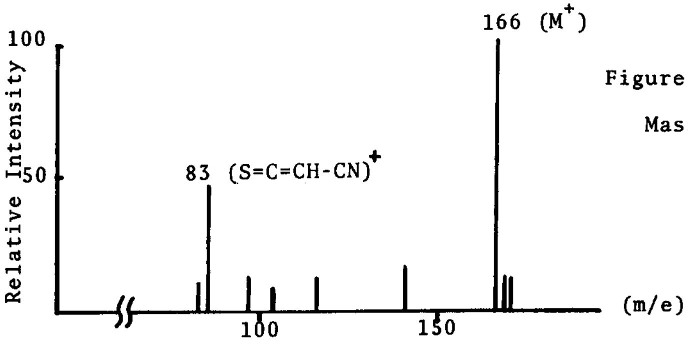

IIIb


IIIc

Since dithiafulvenes are known to be prepared by the reactions of acetylenic compounds with sulfur and carbon disulfide (3), I was heated with sulfur in carbon disulfide under refluxing, but no reaction was observed and furthermore, heating of I with sulfur without solvent resulted in drastic explosion. According to the general procedure for the preparation of the dithiafulvene system by dimerization of thiolized enamines (4), 1-cyano-2-morpholinoethylene wastreated with sulfur, but this thiolation was failed to recovery the starting materials (5).

Similarly, cyanoacetylene was treated with thioactamide, N-phenyl-, N-phenyl-N'-methyl- and N,N'-diphenylthiourea to afford all thiodiacrylonitrile (VII), the same product from II and thiourea as reported by Kishida and Terada (6). The yields in the above reactions were 95, 70, 70, snd 70% respectively. When treated with N,N'-dimethylthiourea in methanol or in acetone, II afforded a colorless crystal (VIII), mp 160°, in a 60% yield, which precipitated in the reaction mixture. This compound was characterized as 2-methylimino-3-methyl-4-imino-2,3-dihydro-1,3-thiazin from the analytical (Found: C, 46.60; H, 5.79; N, 27.13%. Calcd for $C_6H_9N_3S$: C, 46.44; H, 5.85; N, 27.08%) and the following NMR spectral data: the NMR spectrum in deuteriochloroform showed signals at τ 3.23 (1 H, doublet, J = 7.5 c.p.s.) and at 4.21 (1 H, doublet, J = 7.5 c.p.s.) both attributable to olefinic protons of the ring in cis-configuration besides those at 6.15 (3 H, singlet, C=NCH_3), 6.34 (3 H, singlet, NCH_3) and 3.55 (1 H, broad singlet, C=NH). The similar formation of 2,3-dihydro-1,3-thiazin derivatives from thiocarbonyl compounds has been documented on dimethyl acetylenedicarboxylate (7) and ethyl propiolate (8). The reason why cyclized 2,3-dihydro-1,3-thiazin was produced from N,N'-dimethylthiourea, but not from N-phenyl-N'-methyl- or N,N'-diphenylthiourea is uncertain at the present stage of the investigation. However, the formation of VII or VIII from II and thiocarbonyl compounds shall be explained as the following scheme.





Figure

Mass spectrum of III

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