PREPARATION OF 2,4-DIALKYLIDENE-1,3-DITHIETANES FROM YNAMINES AND CARBON DISULFIDE

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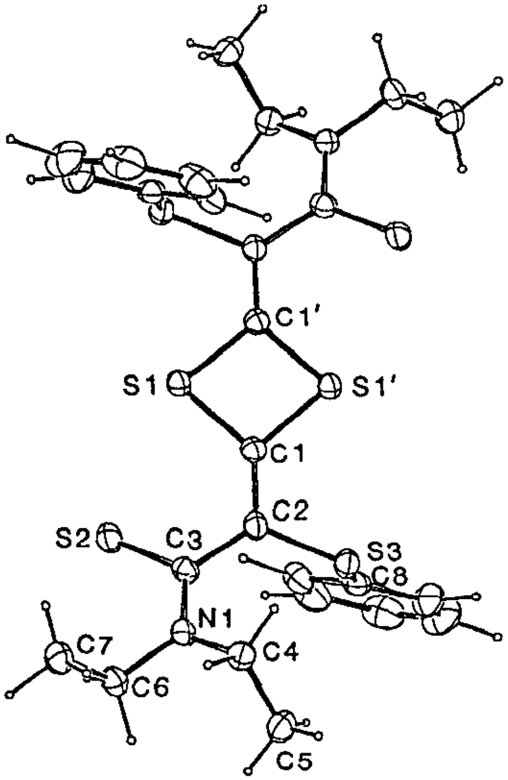
Abstract - Aminoacetylenes $R_2N\text{-}C{\equiv}C\text{-}R'$(**1**) afforded 2,4-dialkylidene-1,3-dithietanes (**2**) on compressing or heating with carbon disulfide. The structure of **2** was determined by X-ray crystal structure analysis. Thiocarbamoylthioketenes, 1:1 adducts of the ynamine and carbon disulfide were proposed as the probable intermediates leading to **2**. The present results indicate that the reactivities of ynamines toward carbon disulfide are different from those of electron-deficient acetylenes.

Reactions of acetylene derivatives with carbon disulfide have been investigated extensively in the last two decades. Hexafluoro-2-butyne or dimethyl acetylenedicarboxylate afforded the tetrathiafluvalene derivatives (TTF) and some other adducts on heating at 100 °C with carbon disulfide.[1] Rice and Okamoto reported that electron-deficient acetylenes such as dimethyl acetylendicarboxylate, acetylenedicarboxylic acid, methyl propiolate, and propiolic acid gave the corresponding TTF's in excellent yields, on compressing with carbon disulfide under 500 MPa at 100 °C.[2] In these reactions, carbon disulfide behaves as an electron donor toward acetylenes, and affords TTF's *via* 1:1 carbene-like adducts.

However, the reaction of carbon disulfide with other acetylenes, especially electron-rich acetylenes such as ynamines, has not been studied. Since ynamines are iso-electronic with disubstituted cyanamides, reactivities of the both compounds are expected to be similar to each other. On the other hand, we have reported previously that the reaction of carbon disulfide with dimethyl cyanamide under 500 MPa at 70 °C gave 2,6-bis(dimethylamino)-4-(dimethylthiocarbamoyl)imino-4*H*-1,3,5-thiadiazine,[3] thus providing a new route to the thiadiazine. So we had an interest in the reactivities of ynamines and then attempted the high pressure or thermal reaction of carbon disulfide with 1-diethylamino-2-phenylthioacetylene(**1 a**)[4] and 1-dimethylamino-2-phenylacetylene (**1 b**),[5] which has led to some new information.

Compressing **1 a** and **1 b** with an excess of carbon disulfide at 800 MPa, 70 °C gave **2 a** and **2 b**, respectively, nearly quantitatively. Meanwhile, on heating at the same temperature under ordinary pressure, they were also given in moderate yields.[6] Since their ir spectra resemble each other and had a strong absorption assignable to their C=C stretching at 1512 or 1510 cm^{-1}, respectively, both compounds are assumed to have the same skeletal structure. The ^1H nmr spectra did not provide any important information. However the ^{13}C nmr spectrum suggested that **2 a** has two quaternary carbons (δ = 117.75, 143.96), and a thiocarbonyl carbon (δ = 190.78) besides ethyl and aromatic carbons. In the mass spectra of **2 a** and **2 b**, the M^+ were observed at 562 and 442 m/z, respectively, indicating that these compounds are the adducts of two molecules of carbon disulfide and two molecules of acetylenes.

The molecular structure of **2 a** was unequivocally established by a single crystal X-ray diffraction structure analysis,[7] and identified to be 2,4-bis[diethylthiocarbamoyl(phenylthio)methylidene]-1,3-dithietane, which satisfies the spectral data described above. The molecule has a center of symmetry and contains a planar 4-membered C_2S_2 ring. An ORTEP drawing[8] is shown in Figure 1.



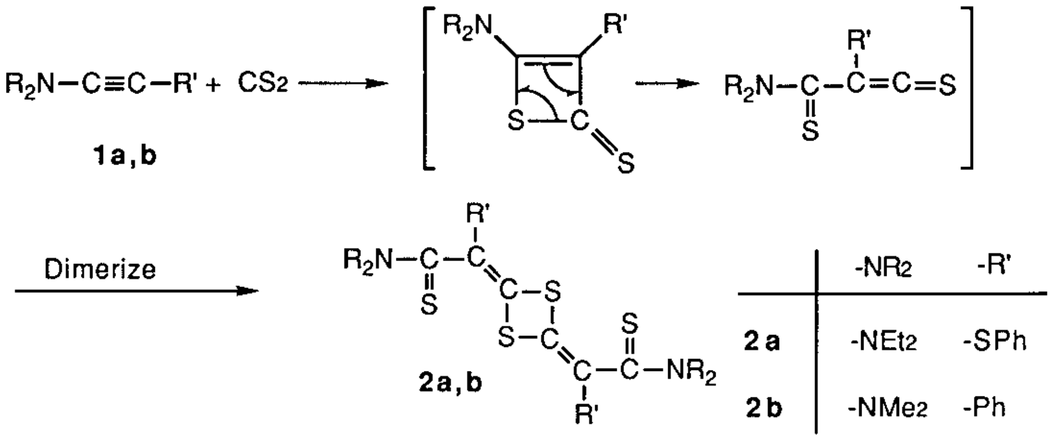
Bond distances(Å); S1-C1 1.755(7), S1-C1'1.769(7), C1-C2 1.349(9), S2-C3 1.686(7), C2-C3 1.473(9), N1-C3 1.335(8), N1-C4 1.476(9), N1-C6 1.483(8), C4-C5 1.518(12), C6-C7 1.510(10), S3-C2 1.770(7), S3-C8 1.785(7).

Bond angles(°); C1-S1-C1' 81.2(3), S1-C1-S1' 98.8(3), C2-C1-S1' 127.6(5), S1-C1-C2 133.5(5), C1-C2-C3 120.7(6), S3-C2-C3 124.9(5), S2-C3-C2 117.3(5), S2-C3-N1 122.2(5), S3-C2-C1 114.3(5), C2-S3-C8 103.3(3).

Figure 1 An ORTEP drawing of the molecule (**2a**)

It was thus found that **2 a** and **2 b** are formed from two carbon disulfides and two acetylenes like as the formation of TTF's. However, they have a 1,3-dithietane structure, quite different from a TTF skeleton. The plausible reaction path to lead to **2 a** and **2 b** was speculated as shown in Scheme 1.

At the first stage, [2+2] cycloaddition takes place, thereby the ynamines acting as electron donor, which is followed by ring-opening leading to, 1:1 adducts, 3-dialkylamino-1-propene-1,3-dithiones, in the same way that disubstituted cyanamides afford thiocarbamoyl isothiocyanates as the intermediates.[3] This addition would be markedly accelerated under high pressure. Then the resulting thioketenes are so reactive that dimerize immediately to give dithietanes (**2 a**) and (**2 b**), respectively, like as most thioketenes do so.[9]



	-NR2	-R'
2a	-NEt2	-SPh
2b	-NMe2	-Ph

Scheme 1

In conclusion, ynamines are very reactive to carbon disulfide and give 1,3-dithietanes in good yields. The addition mode of electron-rich acetylenes to carbon disulfide, described here, is novel and quite different from that of electron-deficient acetylenes which lead to TTF's. The former reaction is rather similar to that observed with disubstituted cyanamides. These facts suggest that ynamines may show unique reactivity toward other thiocarbonyl compounds that leads to many other novel derivatives, and the study in this line is in progress.

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6. Reaction of ynamines with carbon disulfide: A mixture of 2 mmol of 1-diethylamino-2-phenylthioacetylene or 1-dimethylamino-2-phenylacetylene and carbon disulfide (1 ml) in dichloromethane (2 ml) was sealed in a flexible tube. Method A; the tube was placed in a reaction vessel[10] and pressurized at 800 MPa, 70 °C for 20 h. The reaction mixture was purified on a silica-gel column (hexane : AcOEt = 1 : 1) to afford **2a** (533 mg, 95%) or **2b** (415 mg, 94%). Method B; the tube was heated 70 °C for 20 h in an autoclave. The reaction mixture was treated in the same way as described above to give **2a** (253 mg, 45%), or **2b** (160 mg, 36%).

2a: Orange needles, mp 162~163 °C (AcOEt); ir (KBr) 2989, 1512, 1421, 1265, 1222, 738 cm^{-1}; ^1H

nmr ($CDCl_3$) δ = 1.20 (t, 12 H, J = 7.0 Hz, 4 CH_3), 3.77 (q, 8 H, J = 7.0 Hz, 4 CH_2), 7.20~7.55 (m, 10 H, Ar H); ^{13}C nmr δ = 12.51 (CH_3), 47.38 (CH_2), 117.75 (quat C), 127.01, 129.10, 129.18, 134.08 (quat C), 143.96 (quat C), 190.78 (C=S); ms m/z 562 (M^+), 498 (M^+- 2 S), 469, 453 (M^+- SPh), 281 (M^+/2), 140 (base). Anal. Calcd for $C_{26}H_{20}N_2S_6$: C, 55.47; H, 5.37; N, 4.98; S, 34.18. Found: C, 55.25; H, 5.31; N, 4.89; S, 34.04.

2b: Yellow powder, mp 190 °C (acetonitrile); ir (KBr) 2829, 1510, 1386, 1271, 696 cm^{-1}; ^1H nmr δ = 3.24 (br s, 12 H, 2 $(CH_3)_2N$), 7.24~7.73 (m, 10 H, Ar H); ms m/z 442 (M^+), 378 (M^+- 2 S), 221 (M^+/2), 88(base, $(CH_3)_2NCS^+$). Anal. Calcd for $C_{22}H_{22}N_2S_4$: C, 59.69; H, 5.01; N, 6.33; S, 28.97. Found: C, 59.86; H, 4.86; N, 6.16; S, 28.67.

7. X-ray Crystallographic Analysis of **2a**: An orange needle-like crystal of having approximate dimension of 0.1 x 0.7 x 0.06 mm was used. X-ray data were collected on an Enraf-Nonius CAD4 diffractometer by using graphite-monochromatized CuKα radiation (λ=1.5418Å). Crystal data : $C_{26}H_{30}N_2S_6$, orthorhombic, space group Pbcn, a=24.471 (3), b=9.910(2), c=11.393 (1)Å, V=2762.7 (7)$Å^3$, Z=4, ρ_{calc}=1.353g/cm^3, μ=45.2cm^{-1}. Data were collected $4° \leq 2\theta \leq 120°$, with θ/ω scan, ω=(0.80+0.15tanθ)°, Empirical absorption corrections using ψ-scans were applied. (transmittion factors 0.74/1.00); no decay. A total 2487 reflections were collected and 1838 ($|Fo| \geq 3\sigma|Fo|$) reflections were used. The structure was solved by MULTAN 78[11] and difference Fourier synthesis. Eight hydrogen atoms were revealed in the difference Fourier map and the remainder were placed at the ideal positions. The refinement was carried out by full-matrix least squares with anisotropic temperature factors for the non-H atoms. The positions and the thermal parameters of the H atoms were not refined. (R = 0.083, Rw = 0.083, w =1/(0.00267$|Fo|^2$+0.0948$|Fo|$+2.831). Calculations were carried out on a FACOM M-1800/30 with UNICSIII.[12]
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