HETEROCYCLES, Vol. 6, No. 7, 1977

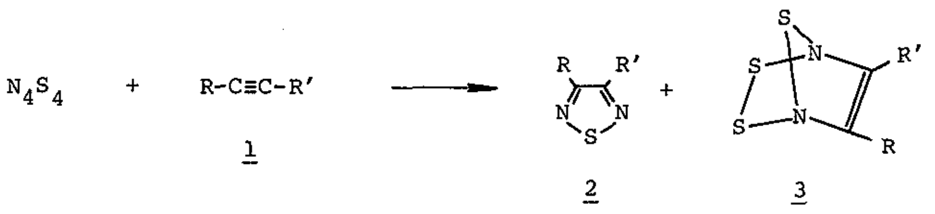
THE REACTION OF N_4S_4 WITH PHENYLACETYLENE AND METHYL PROPIOLATE[1)]

Masashi Tashiro*, Shuntaro Mataka and Kazufumi Takahashi

Research Institute of Industrial Science, Kyushu University 86,
Hakozaki, Higashi-ku, Fukuoka 812, Japan

The reaction of N_4S_4 with phenylacetylene (1d) and methyl propiolate (1e) was investigated. The reaction with 1d gave 3-phenyl- (2d), 3-amino-4-phenyl-1,2,5-thiadiazole (4d) and [1,2,5-thiadiazolo]dithiatriazapentalene (5) in 15, 5 and 8% yields respectively. The reaction with 1e afforded the corresponding 1,2,5-thiadiazoles, 2e and 4e in 7 and 5% yields respectively, together with a small amount of trithiadiazepine (6) and the adduct (7) of the fragment arising from the cleavage of the C≡C bond of 1e with N_3S_3.

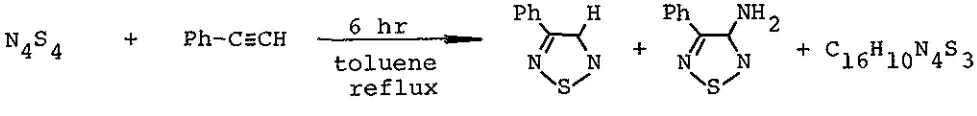
In 1968, the reaction of N_4S_4 with electron deficient acetylenes (1a-c) was reported[2)] to give 3,4-disubstituted-1,2,5-thiadiazoles (2a,b) and/or the adducts (3a,b) of 1 with N_2S_3, to which was proposed the bicyclic structure shown below. However, no paper has been published to our knowledge up to date.



1a:R = R' = CH_3O_2C- 2a:R = R' = CH_3O_2C- 3b:R = R' = CN
1b:R = R' = CN 2b:R = R' = CN 3c:R = R' = CF_3
1c:R = R' = CF_3

Our interests in N_4S_4 as a synthetic reagent prompted us to investigate the reaction of N_4S_4 with various acetylenes and we now report the *reaction of* N_4S_4 with monosubstituted acetylenes, 1d (R = Ph, R′= H) and 1e (R = CH_3O_2C, R′= H), to give 3-amino-1,2,5-thiadiazoles (4d and 4e) together with other products.

A mixture of 1d (22 mmole) and N_4S_4 (11 mmole) in toluene (40 ml) was heated at reflux for 6 hr. After removal of the solvent in vacuo, the residue was *columnchromatographed* on silica gel (Wako gel, C-300) and 2d and 5 were isolated from the benzene eluate, and 4d from $CHCl_3$ in 16, 8 and 5% yields, respectively.



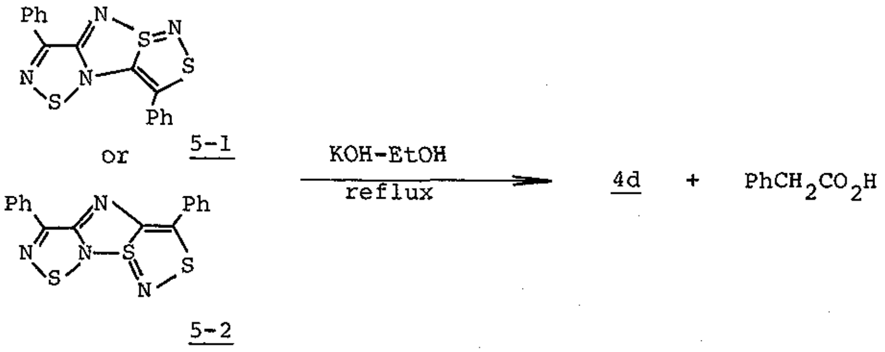
1d 2d 4d 5

The compound 2d is identical with an authentic specimen prepared by the reaction of N_4S_4 with ethylbenzene[3]. Although Bertini and Pino did not mention the formation of 4d, we isolated 4d in 0.7% yield in addition to 2d *which was obtained in 4% yield.*

$$\underset{(75\ \text{mmole})}{N_4S_4} + \underset{(377\ \text{mmole})}{PhC_2H_5} \xrightarrow[\text{neat}]{\text{reflux}} \text{2d} + \text{4d}$$

The compound 4d, mp 100-102°C, was deduced to have the aminothiadiazole structure from elemental analysis and spectral data4). Of the six possible structures, 3-amino-5-phenyl- (mp 139 °C)5) and 5-amino-3-phenyl-1,2,4-thiadiazole (mp 160 °C)6), and 2-amino-5-phenyl-1,3,4-thiadiazole (mp 223-224 °C)7) are excluded. Two 1,2,3-thiadiazoles are also rejected from the inspection of the fragmentation of mass spectrum of 4d4). Therefore, 4d is determined to be 3-amino-4-phenyl-1,2,5-thiadiazole.

The molecular formula of 5, $C_{16}H_{10}N_4S_3$, corresponds to the 2:1-adduct of 1d and N_4S_4 with a loss of hydrogen sulfide. Its structure was deduced from the spectral data8) and hydrolysis with ethanolic potassium hydroxide, affording 4d in 64% yield with a trace amount of phenylacetic acid.

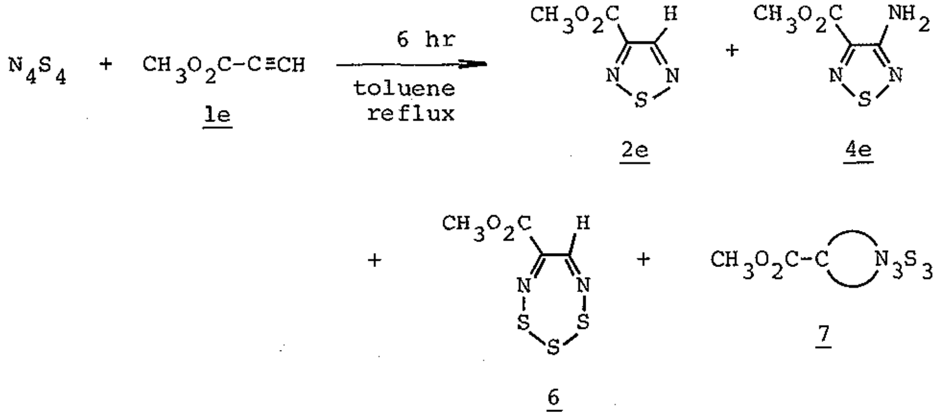


However, it was not determined which structure 5-1 or 5-2 is correct based on the available data.

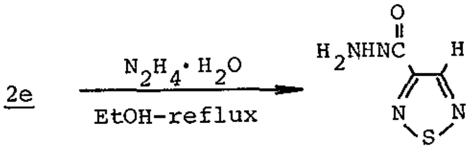
Although the pathway of the formation of the products is still unknown, 5d was not obtained when 2d or 4d was heated with N_4S_4 in toluene.

$$\underline{2d}\ \text{or}\ \underline{4d}\ \xrightarrow[\text{toluene reflux}]{N_4S_4\qquad /\!/}\ \underline{5}$$

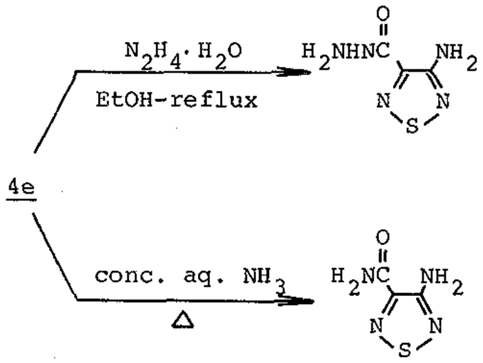
When methyl propiolate (1e; R = CH_3O_2C-, R'= H) was allowed to react with N_4S_4 under the conditions mentioned above and the reaction mixture was columnchromatographed on silica gel (Wako gel, C-300), isolated were 7 from the n-hexane eluate, 2e and 6 from benzene, and 4e from chloroform in 1, 7, 1 and 5% yields, respectively.



The structures of 2e and 4e were deduced from their spectral data[9,10] and further confirmed by their reaction with hydrazine hydrate and conc. aqueous ammonia, affording the corresponding hydrazides and amide in high yields.



mp 155-7 °C
(lit.,[11] mp 155-6 °C)

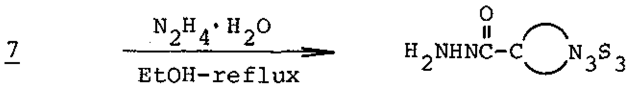


mp 208-9°C(d.)
(lit.,[12] mp 206(d.))

mp 172-3°C
(lit.,[12] mp 171-2°C)

The compound 6 has the molecular formula[13] of the adduct of 1e with N_2S_3, which is corresponding to the compound 3 reported by Josey[2]. The nmr spectrum of 6 shows a singlet at δ 8.90 ppm which is ascribable to an azomethine proton. Therefore, the bicyclic structure proposed by Josey for 3 is not suitable for 6 and we now propose the trithiadiazepine structure for 6.

The molecular formula of 7 is interestingly corresponding to the adduct of a fragment arising from the cleavage of the C≡C bond of 1e and N_3S_3, which is also obtained when N_4S_4 is allowed to react with dimethyl acetylenedicarboxylate (1a)[14] or with methyl phenylacetylenecarboxylate[14]. Although the structure of 7 could not be determined, the presence of the ester group was confirmed by the reaction with hydrazine hydrate, affording the corresponding hydrazide in high yield.



Studies on the reaction of N_4S_4 with other acetylenes are in progress.

REFERENCES

1 Part 3 of the series of "Sulfur Nitride in Organic Chemistry". Part 2: *M. Tashiro and S. Mataka*, Heterocycles, 1976, 4, 1243.

2 A. D. Josey, Abstract, The 155th National Meeting of the American Chemical Society, San Francisco, Calif., April, 1968, Division of Organic Chemistry, p. 14.

3 V. Bertini and P. Pino, Corsi. Semin. Chem., 1968, 82; C.A., 1970, 72, 43575v.

4 4d, straw-colored plates (n-hexane), mp 100-102°C, IR (KBr): $\nu_{(NH)}$ 3420, 3290, 3200 cm^{-1}. NMR ($CDCl_3$): δppm 4.92 (2, s, NH_2), 7.43-7.51 (3, m, aromatic), 7.61-7.80 (2, m, aromatic). Ms: m/e(rel. int., %), 177 (M^+, 100), 135 (PhCNS, 36), 103 (PhCN, 8), 74 (H_2N-CNS, 94).

5 J. Goerdeler and P. Mertens, Chem. Ber., 1970, 103, 1805.

6 A. E. Siegrist, E. Maeder, M. Duennenberger and P. Liechti, Swiss Pat., 426,848; C.A., 1968, 68, 69002y.

7 E. Grigat and R. Puetter, Chem. Ber., 1965, 98, 1359.

8 5, deep violet needles (n-hexane), mp 187-189°C, NMR ($CDCl_3$): δppm 7.35-7.64 (6, m, aromatic), 7.90-8.21 (2, m, aromatic), 8.41-8.62 (2, m, aromatic). UV (EtOH): λ_{max} (logε) 520(3.49), 364(4.04), 322(3.98), 255(4.12), 237(4.21)nm. Ms: m/e (rel. int., %) 354 (M^+, 36), 121 (PhCS, 100), 77 (Ph, 10).

9 2e, colorless prisms (n-hexane), mp 42°C, NMR ($CDCl_3$): δppm 4.05 (3, s, $-OCH_3$), 9.11 (1, s, -N=CH-).

10 4e, colorless needles (n-hexane), mp 142-143°C, IR (KBr): $\nu_{(C=O)}$ 1710 cm^{-1}. NMR ($CDCl_3$) δppm 4.01 (3, s, $-OCH_3$), 6.00 (2, b.s., $-NH_2$).

11 M. Carmack and L. Weistock, U.S. Pat., 3060187; C.A., 1963, 58, 9089g.

12 Y. F. Shealy and J. D. Clayton, J. Org. Chem., 1963, 28, 1491.

13 6, colorless needles (n-hexane), mp 109-110°C, IR (KBr): $\nu_{(C=O)}$ 1695 cm^{-1}. NMR ($CDCl_3$) δppm 3.98 (3, s, $-OCH_3$), 8.90 (1, s, -N=CH-). Ms: m/e (rel. int., %) 208 (M^+, 81), 162 (M^+-NS, 60), 78 (NS_2^+, 100).

14 M. Tashiro, S. Mataka and K. Takahashi, Unpublished results.

15 All compounds gave the satisfactory elemental analyses.

Received, 9th April, 1977