

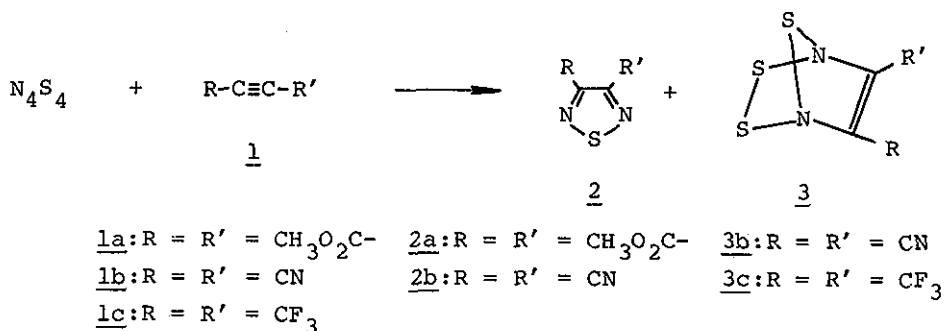
THE REACTION OF N_4S_4 WITH PHENYLACETYLENE AND METHYL PROPIOLATE¹⁾

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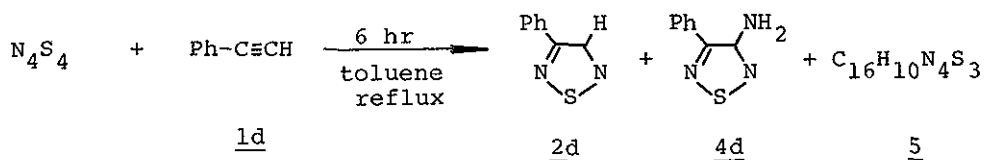
The reaction of N_4S_4 with phenylacetylene (1d) and methyl propiolate (1e) was investigated. The reaction with 1d gave 3-phenyl- (2d), 3-amino-4-phenyl-1,2,5-thiadiazole (4d) and [1,2,5-thiadiazolo]dithiatriazapentalene (5) in 15, 5 and 8% yields respectively. The reaction with 1e afforded the corresponding 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 $C\equiv C$ bond of 1e with N_3S_3 .

In 1968, the reaction of N_4S_4 with electron deficient acetylenes (1a-c) was reported²⁾ 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.

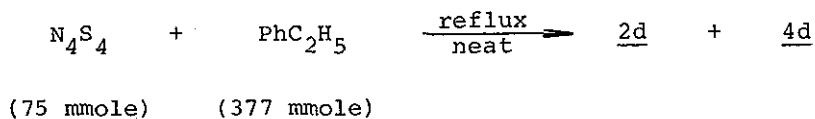


Our interests in N_4S_4 as a synthetic reagent prompted us to investigate the reaction of N_4S_4 with various acetylenes and we now report the reaction of N_4S_4 with monosubstituted acetylenes, 1d (R = Ph, R' = H) and 1e (R = CH_3O_2C , R' = H), to give 3-amino-1,2,5-thiadiazoles (4d and 4e) together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



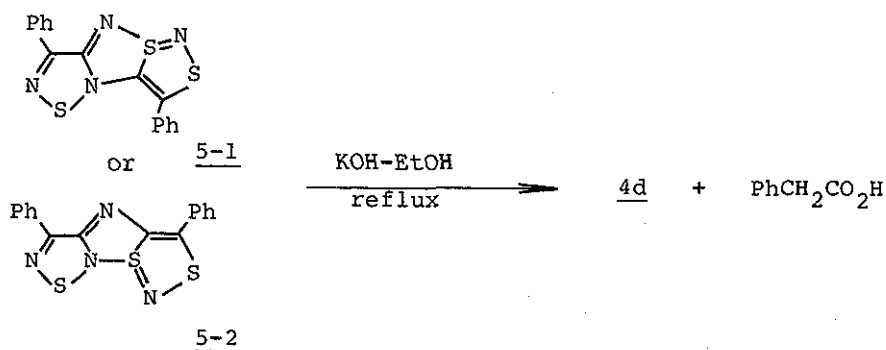
The compound 2d is identical with an authentic specimen prepared by the reaction of N_4S_4 with ethylbenzene³⁾. Although Bertini and Pino did not mention the formation of 4d, we isolated 4d in 0.7% yield in addition to 2d which was obtained in 4% yield.



The compound 4d, mp 100-102 °C, was deduced to have the aminothiadiazole structure from elemental analysis and spectral

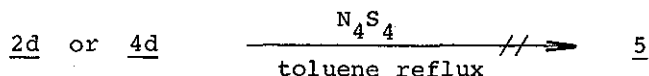
data⁴⁾. Of the six possible structures, 3-amino-5-phenyl- (mp 139 °C)⁵⁾ and 5-amino-3-phenyl-1,2,4-thiadiazole (mp 160 °C)⁶⁾, and 2-amino-5-phenyl-1,3,4-thiadiazole (mp 223-224 °C)⁷⁾ are excluded. Two 1,2,3-thiadiazoles are also rejected from the inspection of the fragmentation of mass spectrum of 4d⁴⁾.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

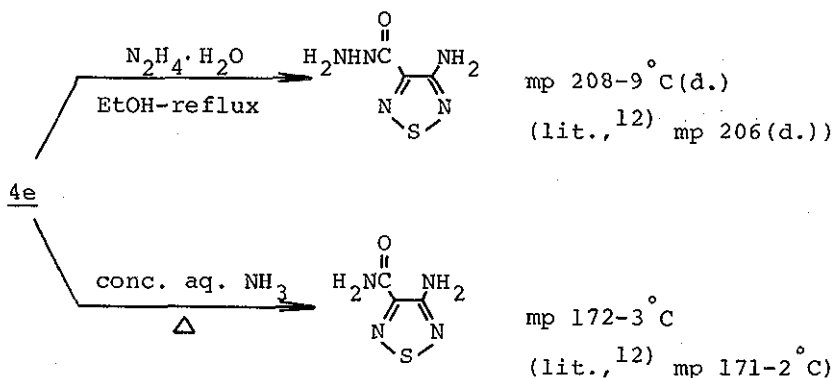
The molecular formula of 5, C₁₆H₁₀N₄S₃, corresponds to the 2:1-adduct of 1d and N₄S₄ with a loss of hydrogen sulfide. Its structure was deduced from the spectral data⁸⁾ and hydrolysis with ethanolic potassium hydroxide, affording 4d in 64% yield with a trace amount of phenylacetic acid.



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

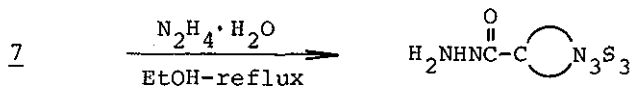
Although the pathway of the formation of the products is still unknown, 5d was not obtained when 2d or 4d was heated with N₄S₄ in toluene.





The compound 6 has the molecular formula¹³⁾ of the adduct of 1e with N_2S_3 , which is corresponding to the compound 3 reported by Josey²⁾. 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 $\text{C}\equiv\text{C}$ 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 phenylacetylenecarboxylate¹⁴⁾. 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.

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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):
 $\nu_{(\text{NH})}$ 3420, 3290, 3200 cm^{-1} . NMR (CDCl_3): δ_{ppm} 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 ($\text{H}_2\text{N-CNS}$, 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.
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- 8 5, deep violet needles (n-hexane), mp 187-189° C, NMR (CDCl_3):
 δ_{ppm} 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} (log ϵ) 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): δ_{ppm}
4.05 (3, s, $-\text{OCH}_3$), 9.11 (1, s, $-\text{N}=\text{CH}-$).
- 10 4e, colorless needles (n-hexane), mp 142-143° C, IR (KBr):
 $\nu_{(\text{C}=\text{O})}$ 1710 cm^{-1} . NMR (CDCl_3) δ_{ppm} 4.01 (3, s, $-\text{OCH}_3$),
6.00 (2, b.s., $-\text{NH}_2$).

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- 13 6, colorless needles (n-hexane), mp 109-110°C, IR (KBr): $\nu_{(C=O)}$ 1695 cm^{-1} . NMR (CDCl_3) δ_{ppm} 3.98 (3, s, $-\text{OCH}_3$), 8.90 (1, s, $-\text{N}=\text{CH}-$). 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.

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