SULFUR NITRIDE IN ORGANIC CHEMISTRY. 12.[1] THE REACTION OF N_4S_4 WITH 1-ARYL-1-TRIMETHYLSILYLOXYETHYLENES AFFORDING 3-HYDROXY-4-ARYL-1,2,5-THIADIAZOLES

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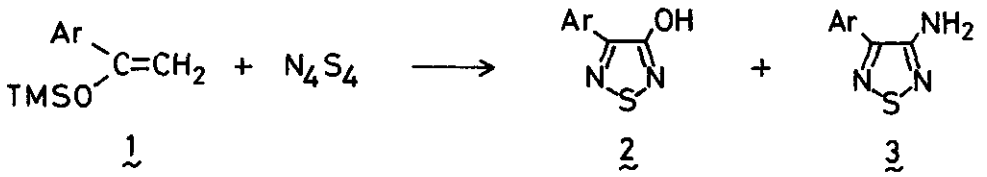
Abstract ——— Reaction of N_4S_4 with 1-aryl-1-trimethylsilyloxyethylenes (1a-1e) gave 3-hydroxy-4-aryl-1,2,5-thiadiazoles (2a-2e) though the yields were low. 3-Amino-4-thienyl-1,2,5-thiadiazole (3) was obtained as a minor product.

Reaction of N_4S_4 with acetylenes are useful for the preparation of symmetrically 3,4-disubstituted 1,2,5-thiadiazoles, while the reaction with monosubstituted acetylenes gave the corresponding 1,2,5-thiadiazoles in low yields, accompanied by side products.[2,3] On the other hand, hindered olefins such as norbornadiene and trans-cyclooctene form 2:1-adducts with N_4S_4.[4-7] The formation of 1,2,5-thiadiazoles by the reaction of N_4S_4 with olefinic compounds is scarcely known, though $N_3S_3Cl_3$ afforded 1,2,5-thiadiazoles in the reaction with trans-stilbene, acenaphthylene and cholestenone in 19, 31 and 6 % yields, respectively.[8] Recently, organosilicone is well-recognized as one of the most versatile reagents in organic synthesis.

Expecting the formation of 3-aryl-1,2,5-thiadiazoles, we undertook the reaction of N_4S_4 with 1-aryl-1-trimethylsilyloxyethylenes (1a-1e) and the results are reported in the present paper.

Reaction of N_4S_4 with 1 was carried out in dry xylene at reflux under nitrogen atmosphere and the results are summarized in Table.



1 2 3

Table. Reaction of N_4S_4 with 1

1	Ar	Products Yield[a] (%) 2	3
1a	C_6H_5-	2a (12)	---
1b	4-Cl-C_6H_4-	2b (19)	---
1c	4-CH_3-C_6H_4-	2c (14)	---
1d	2-Pyridyl-	2d (18)	---
1e	2-Thienyl-	2e (11)	3 (4)

a) Isolated yields are given.

Unexpectedly, 3-hydroxy-4-phenyl-1,2,5-thiadiazole (2a)[9] was obtained in 12 % yield in the reaction with 1a. Formation of 3-phenyl-1,2,5-thiadiazole and 3-amino-4-phenyl-1,2,5-thiadiazole in trace amounts, respectively, was detected by means of GC-Mass. In the reaction with 1b and 1c, the corresponding 1,2,5-thiadiazoles 2b and 2c were obtained in 19 and 14 % yields, respectively. The reaction with 1d and 1e gave pyridyl- (2d) and thienyl-1,2,5-thiadiazole (2e) in 18 and 11 % yields. 3-Amino-4-thienyl-1,2,5-thiadiazole (3) was isolated in 4 % yield as a side product in the reaction with 1e.

Aryl methyl ketones were isolated in the above reactions, however, 2 is not formed via the ketone, because acetophenone did not react with N_4S_4 under the above conditions.

Trimethylsilyloxycyclohexene gave only tarry materials. 3,4-Diphenyl-1,2,5-thiadiazole (4) was formed in 13 % yield in the reaction with 1-trimethylsilyloxy-trans-stilbene accompanied with 13 % yield of desoxybenzoin which is reported to give 4 in 42 % yield on the reaction with N_4S_4.[10]

Ethyl 2-trimethylsilyloxycinnamate did not give 1,2,5-thiadiazole and ethyl benzoyl-acetate was obtained in 75 % yield, which might be formed by hydrolysis during

work-up.

EXPERIMENTAL

All melting points are uncorrected. Ir spectra were measured on a Nippon Bunko IR-A-102 spectrophotometer as potassium bromide pellets. Mass spectra were recorded on a Nippon Denshi JMS-01SG-2 mass spectrometer at 75 eV using a direct inlet system. Column-chromatography was carried out on silica gel (Wako gel, C-300).

General procedure. A mixture of N_4S_4 (5.4 mmol) and 1 (5.4 mmol) in dry xylene (30 ml) was heated at reflux for 6 h and it was allowed to cool to room temperature. Precipitated sulfur and inorganics were filtered off and the filtrate was condensed to about 5 ml. The condensate was column-chromatographed using hexane at first, then benzene and finally chloroform as eluents. Sulfur was eluted with hexane. The ketones and 2d were obtained from benzene eluent. Compounds 2a-2c, 2e and 3 were eluted with chloroform.

Physical and spectral properties of 2 and 3 are given below.

3-Hydroxy-4-phenyl-1,2,5-thiadiazole (2a): mp 165-167°C (lit.[9],166-168°C).

3-Hydroxy-4-p-chlorophenyl-1,2,5-thiadiazole (2b): colorless needles (benzene), mp 241-242°C; ir ν_{OH} 3200-2400 cm^{-1}; ms: m/e 224, 222 (M^+). Anal. Calcd for $C_8H_5ClN_2OS$: C, 45.18; H, 2.37; N, 13.17. Found: C, 45.40; H, 2.56; N, 12.97.

3-Hydroxy-4-p-tolyl-1,2,5-thiadiazole (2c): colorless plates (benzene), mp 212-213 °C; ir ν_{OH} 3200-2400 cm^{-1}; ms: m/e 192 (M^+). Anal. Calcd for $C_9H_8N_2OS$: C, 56.23; H, 4.19; N, 14.57. Found: C, 56.18; H, 4.15; N, 14.42.

3-Hydroxy-4-α-pyridyl-1,2,5-thiadiazole (2d): straw-colored needles (hexane), mp 100-102°C; ir ν_{OH} 3100-2500 cm^{-1}; ms: m/e 179 (M^+). Anal. Calcd for $C_7H_5N_3OS$: C, 46.92; H, 2.81; N, 23.45. Found: C, 46.92; H, 2.82; N, 23.36.

3-Hydroxy-4-α-thienyl-1,2,5-thiadiazole (2e): pale yellow plates (hexane), mp 220-221°C; ir ν_{OH} 3100-2400 cm^{-1}; ms: m/e 184 (M^+). Anal. Calcd for $C_6H_4N_2OS_2$: C, 39.12; H, 2.19; N, 15.20. Found: C, 39.14; H, 2.38; N, 15.05.

3-Amino-4-α-thienyl-1,2,5-thiadiazole (3): colorless needles (hexane:benzene = 5:1), mp 117-118°C; ir ν_{NH} 3500, 3320, 3200 cm^{-1}; ms: m/e 167 (M^+). Anal. Calcd for $C_6H_5N_3OS_2$: C, 39.35; H, 2.75; N, 22.94. Found: C, 39.23; H, 2.91; N, 22.80.

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