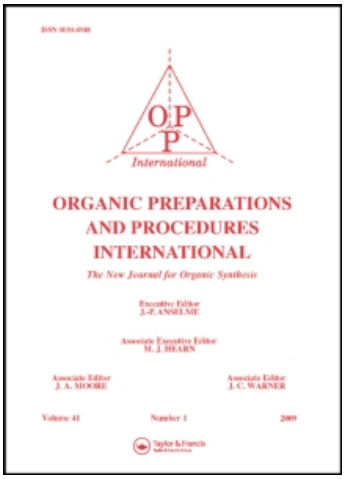

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3-ARYL-1,2,5-THIADIAZOLES FROM THE REACTION OF TETRASULFUR TETRANITRIDE WITH ARYL METHYL KETONES†

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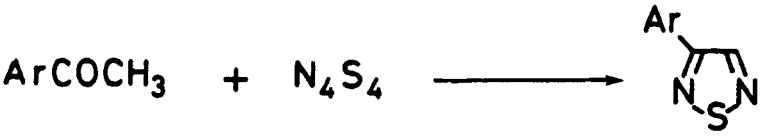
The characteristic feature of the reaction of N_4S_4 with organic substrates is the formation of 1,2,5-thiadiazoles.[1] The reactions with diaroyl- and diarylacetylenes are useful for the preparation of 3,4-disubstituted 1,2,5-thiadiazoles,[2] while mono arylacetylenes gave the corresponding 3-aryl-1,2,5-thiadiazoles (IIa-c) in poor yields.[2] We now report a convenient albeit low yield preparation of II by the reaction of N_4S_4 with aryl methyl ketones (I).



I II

a) Ar = C_6H_5 b) Ar = 4-$CH_3C_6H_4$ c) Ar = 4-BrC_6H_4
d) Ar = 4-ClC_6H_4 e) Ar = 3-BrC_6H_4 f) Ar = 3-$O_2NC_6H_4$
g) Ar = 2-BrC_6H_4 h) Ar = 2-ClC_6H_4 i) Ar = 2-thienyl

As N_4S_4 did not react with acetophenone (Ia) in refluxing xylene, the reactions were carried out in excess I without solvent to yield the expected 3-aryl-1,2,5-thiadiazoles (II). Although a vigorous reaction occurred with 2-furyl and 2-pyridyl methyl ketones, only large amounts of resinous materials were formed. No 1,2,5-thiadiazole was detected from the reaction of N_4S_4 with 2- and 4-hydroxyacetophenones.[3]

EXPERIMENTAL SECTION

All melting points are uncorrected. Column chromatogrpahy was carried out on silica gel (Wako-gel, C-300).

TABLE. Yields, mps and Analytical Data of 3-Aryl-1,2,5-Thiadiazole (II).

compd	mp. (°C)	Yield[a] (%)	Elemental Analysis (Found) C	H	N
IIa	42-44°	35	lit.[2] mp. 43-44°		
IIb	56-57°	15	lit.[2] mp.56-57°		
IIc	120-121°	30	lit.[2] mp. 120-121°		
IId	101-102°	25	48.86(48.89)	2.56(2.72)	14.29(14.23)
IIe	40-42°	41	39.85(39.74)	2.09(2.02)	11.62(11.42)
IIf	108-109°	30	46.37(46.76)	2.43(2.65)	20.28(20.42)
IIg	63-64°	13[b,d]	39.85(40.28)	2.09(2.25)	11.62(11.29)
IIh	88-89°	25[b,c]	48.86(48.66)	2.56(2.68)	14.29(14.04)
IIi	38-39°	10	42.86(42.93)	2.40(2.54)	16.67(16.37)

a) Carried out at 85-95° for 7 hrs unless otherwise noted; b) Carried out at 110-120° for 3 hrs.; c) Nitrile formed in 13%; d) Small amount of nitrile product.

General Procedure.- A mixture of N_4S_4 (1.00 g) and I (4.00 g) was heated at the specified temperature. After the reaction was over, benzene (4 ml) was added to the reaction mixture and it was allowed to cool to room temperature. Precipitated sulfur and inorganics were collected and the filtrate was chromatographed. Sulfur was eluted with hexane and the mixture of I and II was eluted with benzene, which was chromatographed again with hexane as an eluent to give II. Compounds II were purified by recrystallization from hexane or by sublimation under reduced pressure.

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