Novel Reaction of 4-Methyl- and 4-t-Butyl-phenols with Tetrasulphur Tetranitride affording 2,1,3-Benzothiadiazoles[1]

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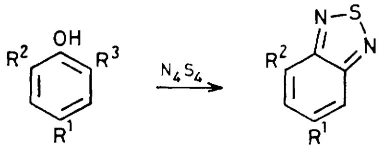
Reaction of tetrasulphur tetranitride (N_4S_4) with 4-methyl- (**1a, b**) and 4-t-butyl-phenols (**1c—j**) gave the 2,1,3-benzothiadiazoles (**2a—e**).

Recently, the use of sulphur nitrides in the preparation of nitrogen–sulphur heterocycles has been intensively investigated.[2—10] The reaction of tetrasulphur tetranitride (N_4S_4) with acetylenes[8,9] and ketones[10] is useful for the preparation of 1,2,5-thiadiazoles. It was reported that *N,N'*-thiobis-(2,6-dimethyl-1,4-benzoquinone imine) was obtained in the reaction of 2,6-xylenol with N_4S_4, $N_3S_4Cl_3$, and $N_3S_3Cl_3$ in 9, 17, and 25% yields, respectively.[5] Expecting that *N,N'*-thiobis(1,2-benzoquinone imines) would be formed, we treated the 4-methyl- (**1a**, **b**) and 4-t-butyl-phenols (**1c—j**) with N_4S_4; unexpectedly, however, the 2,1,3-benzothiadiazoles (**2a—e**) were formed, as we now report.

An equimolar mixture of N_4S_4 and the appropriate compound (**1**) in toluene was heated at reflux for 6 h and compounds (**2**) were isolated following chromatography (Table 1).†



(**1**) (**2**)

Reaction with 2-methyl- (**1a**) and 2-t-butyl-*p*-cresol (**1b**) gave the 2,1,3-benzothiadiazoles (**2a**) and (**2b**) in 37 and 24% yields, respectively. The 4-t-butylphenols (**1c—e**) afforded compounds (**2c—e**) in better yields. Interestingly, the t-butyl group was eliminated in the reaction with (**1f**) to give (**2e**) in 52% yield. Halogen atoms were also removed and (**2e**) was obtained in 43—86% yields, in reactions with the 2-halogenophenols (**1g—j**). Phenol gave only tarry materials.

Though anisole and *p*-t-butylanisole did not react in refluxing toluene, anisole reacts with N_4S_4, as reported,[7] when heated at 120 °C without solvent, giving benzobis- and benzotris-1,2,5-thiadiazole in poor yields.

As 1,2,5-thiadiazoles give vicinal diamines on reductive

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† Column chromatography was carried out on silica gel (Wako gel, C-300). Sulphur was eluted with hexane, and then (**2**) was obtained from the fraction eluted with a 3 : 1-mixture of hexane–benzene. Compounds (**2**) gave satisfactory elemental analyses and spectral data.

Table 1. Preparation of 2,1,3-benzothiadiazoles (**2**).

(**1**)	R^1	R^2	R^3	% Yield of (**2**)[a]	
a	Me	Me	H	(**2a**),	37
b	"	Bu^t	"	(**2b**),	24
c	Bu^t	Me	"	(**2c**),	65
d	"	H	"	(**2d**),	33[b]
e	"	Bu^t	"	(**2e**),	68
f	"	"	Bu^t		52[c]
g	"	"	F		63
h	"	"	Cl		50
i	"	"	Br		43
j	"	"	I		86

[a] (**2a**), (**2b**), and (**2d**) are oils; (**2c**) had m.p. 48.5—50 °C and (**2e**) m.p. 78—79 °C. [b] (**1d**) was recovered in 22% yield. [c] (**1f**) was recovered in 20% yield.

ring-cleavage, this reaction provides a novel procedure for transforming phenols into *o*-phenylenediamines.

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