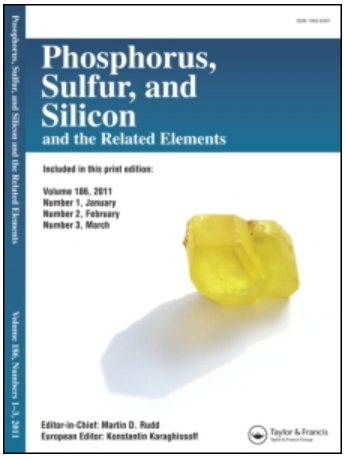

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SYNTHESIS OF 2-AMINO-5-ARYL-1,3,4-THIADIAZOLES FROM TRICHLOROMETHYLARENES: THE EFFECT OF REACTION CONDITIONS

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Abstract The factors have been considered controlling the course of the interaction between trichloromethylarenes and thioacylhydrazines.

INTRODUCTION

Trichloromethylarenes (TCMA) being synthetic equivalents of carboxylic acids are promising starting compounds for various syntheses, particularly for heterocyclizations. However, the susceptibility of TCMAs to hydrolysis or alcoholysis and their rather ready reduction can hinder the use of TCMAs in organic synthesis. Recently we have found that on interaction of $ArCCl_3$ (**1**, Ar = a Ph, b 2,4-$Me_2C_6H_3$, c 2,4,5-$Me_3C_6H_2$, d 2,4,6-$Me_3C_6H_2$) with hydroxylamine or hydrazines in pyridine solution an unconventional reductive condensation takes place which leads to derivatives of respective aldehydes, particularly oximes and aldazines or hydrazones.[1] Besides these products benzotrichloride **1a** gives 3,5-diphenyl-1,2,4-oxadiazole with hydroxylamine and 2,5-diphenyl-1,3,4-oxadiazole with hydrazine.

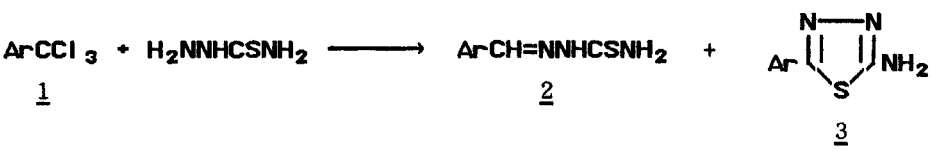
RESULTS AND DISCUSSION

Our initial attempts to prepare substituted 1,3,4-oxa- and thiadiazoles were unsuccessful: only very low yields (~10%) of 2,5-diaryl-1,3,4-oxadiazoles were obtained by us in reactions of benzotrichloride with benzhydrazide or its 4-substituted derivatives in alcohol solutions in the presence of sodium hydrocarbonate, we failed also to prepare 2-amino-5-phenyl-1,3,4-thiadiazole from benzotrichloride and thiosemi-

carbazide in ethanol in the presence of sodium carbonate. In both cases the major part of starting TCMA was converted to respective alkyl benzoate, no products of reductive condensation being formed. To exclude undesired alcoholysis pyridine was used both as a solvent and a base. Corresponding thiosemicarbazones (2) were obtained but in cases of 1a,b considerable amounts of thiodiazoles (3) were isolated (Table). Recently we have found that the actual reducing agent in the reductive condensation is not hydroxylamine or hydrazines but pyridine.[2] However, the use of methanol-pyridine ethanol-pyridine mixtures as solvents makes it possible to transform TCMAs 1a,b into desired 1,3,4-oxadiazoles in 65-95% yields. Under similar conditions TCMAs 1a,b were transformed into diaryl-1,3,4-thiadiazoles (65-70% yields) when reacted with thiobenzhydrazide. In the case of chloride 1d the competition between heterocyclization and reductive condensation results in the only products of the latter reaction which were obtained in high yields (Table).

Table

Effect of Solvent on Yields of Products



1 2 3

1, Ar	Yields, %			
	in Py		in MeOH-Py	
	2	3	2	3
Ph	10	30	-	60
2,4-$Me_2C_6H_3$	18	15	5	30
2,4,6-$Me_3C_6H_2$	70	-	55	-

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