Simple New Synthesis of 4,6-Diaryl-2-hydroxy-s-triazines and Amidines

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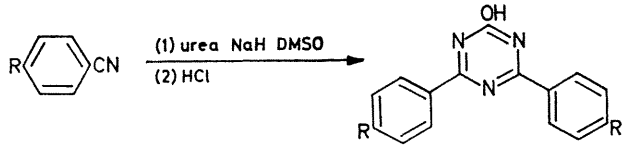
Summary The anions of urea and amines add to nitriles in dimethyl sulphoxide to afford 4,6-diaryl-2-hydroxy-*s*-triazines and amidines respectively.

THE first synthesis of 4,6-diaryl-2-hydroxy-*s*-triazines from benzamidines and phosgene or ethyl chloroformate was reported in 1890 by Pinner[1] and recently Japanese workers[2] obtained several of these compounds by the Friedel–Crafts reaction of chloro-*s*-triazines with aromatic compounds. The second method gives poor yields and the purificaton of the products is laborious. A convenient new approach is as follows. A mixture of arylnitrile (0·2 mol), urea (0·1 mol), sodium hydride (0·1 mol), and dimethyl sulphoxide (200 ml) was stirred at room temperature for 2 h and then for 32 h on a steam bath. After cooling to room temperature, the slurry was poured into ice-cold water and acidified (HCl). The white solid was washed with methanol and dried to afford analytically pure material (50%). The mass spectra of compounds (**1**)—(**3**) showed M^+ at m/e 249, 317, and 277, respectively; m.p.s.: 296—298° (lit.,[1] 289°); (**2**) m.p. 372—374° (lit.,[3] 374°); (**3**) m.p. 342–344° (lit.,[2] 316—317°).

The two most common preparative methods for amidines are: (a)[4] addition of amines to nitriles in the presence of aluminium chloride and (b)[5] reaction of amines with iminoether hydrochlorides. Both methods employ high temperatures and the yields vary from low to moderate depending upon the basicity of the amine and the stability of the amidine. Since the DMSO–NaH method required mild

TABLE

Compound	R^1	$R^1C(=NH)NHR^2$ R^2	Yield (%)	M.p. °C
(**1**)	Phenyl	Phenyl	86	113—116[6]
(**2**)	*p*-Anisyl	*o*-Tolyl	89	133—134[7]
(**3**)	3-Pyridyl	Phenyl	80	135—136[8]
(**4**)	Phenyl	5-Methyl-2-pyridyl	88	88—90[9]
(**5**)	*o*-Chlorophenyl	Phenyl	87	101—102[8]
(**6**)	*o*-Tolyl	Phenyl	85	123—125[6]
(**7**)	2,6-Dichlorophenyl	Phenyl	50	116—118[10]



(**1**) R = H
(**2**) R = Cl
(**3**) R = Me

conditions and afforded high yields, we prepared a variety of amidines (Table).

A slurry of amine (0·1 mol), nitrile (0·1 mol), sodium

$$R^1CN + R^2NH_2 \xrightarrow[(2)\ H_2O]{(1)NaH,\ DMSO} R^1C(=NH)NHR^2$$

hydride (0·1 mol), and dimethyl sulphoxide (50 ml) was stirred in an ice bath for 2—3 h and then at room temperature for several h until the reaction was complete (t.l.c.). The resulting suspension was poured into 500 ml of ice-cold water. The solid filtered off, dried, and recrystallized from n-hexane–propan-2-ol.

(*Received, March 15th*, 1971; *Com.* 278.)

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