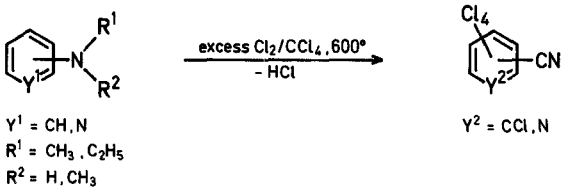

A New Synthesis of Perchlorinated Aromatic Nitriles

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Chlorination of *N*-alkylamino-arene derivatives in vapor phase at 600° has been found to yield perchlorinated aromatic nitriles.

The reaction did not need a catalyst and it was carried out in the presence of carbon tetrachloride diluent to modify the exothermic halogenation. The Table summarizes the compounds and the reactor conditions used in the study. The design of the chlorinator has been described in a previous communication[1]. Reaction variables were not investigated to optimize the yield of perchlorinated aromatic nitriles. Major impurities, which were identified in the crude product mixtures, were the chlorinolysis products, hexachlorobenzene or pentachloropyridine. The purified aromatic perchloronitriles were identified by their melting points and I.R. spectra.

General Procedure for Perchlorinated Aromatic Nitriles:

The vapor phase reactor has been described previously[1]. A pressurized solution of 10% by weight of the educt in carbon tetrachloride is forced at constant rate through a flowmeter into the tubular Vycor®-glass vaporizer, which is wired and insulated similar to the reactor. The vapors from the preheater are mixed with chlorine in the nozzle and jetted through the small orifice into the heated reactor at 600–605°. The chlorine gas is introduced into the nozzle at a constant rate to give a 19 : 1 to 45 : 1 molar ratio of halogen to educt. After a 10–14 second residence time, the hot reactor effluent is collected in a series of two Dry Ice traps. The crude products are recovered by evaporating excess chlorine, hydrogen chloride, and carbon tetrachloride on a steam bath. Further purification is accomplished by recrystallization from carbon tetrachloride.

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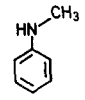
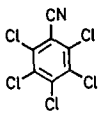
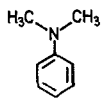
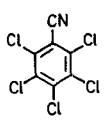
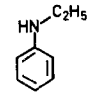
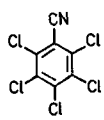
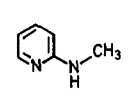
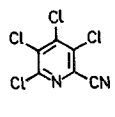
[1] S. H. Ruetman, *Synthesis* **1973**, 680.
[2] V. Merz, W. Weith, *Ber. Dtsch. Chem. Ges.* **16**, 2869 (1883).
[3] R. M. Bimber, *U.S. Patent* 3,325,503 Diamond Alkali Co., (1967); *C. A.* **68**, 68896 (1968).

Table. High Temperature Chlorination of Alkylaminoarenes

Educt	Product	b.p. of educt	Reaction conditions				Yield [%]	m.p.[a] (CCl_4)	Molecular formula
			Reactor temp.	Vaporizer temp.	Chlorine: educt ratio	Residence time			
		196°	605°	215°	20 : 1	13 sec	69	215–216.5° (Lit.[2] 210°)	C_7Cl_5N[b] (275.3)
		193–194°	600°	220°	22 : 1	14 sec	48	—	
		205°	600°	230°	19 : 1	13 sec	31	204–207°	
		200–201°	600°	225°	45 : 1	10 sec	24	150.5–151.5° (Lit.[3] 148–150°)	$C_6Cl_4N_2$[c] (241.9)

[a] Uncorrected.

[b] calc. C 30.5 Cl 64.4 N 5.1
found 30.8 64.6 5.0

[c] calc. C 29.8 Cl 58.6 N 11.6
found 30.2 58.6 11.7