A CONVENIENT METHOD FOR OBTAINING 3-CHLORO- AND 3,6-DICHLOROCARBAZOLES

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It has been shown that the reaction of carbazole and some of its derivatives with phosphorus pentachloride in 1,2-dichloroethane leads predominantly to 3-chloro- and 3,6-dichlorocarbazoles, depending on the reaction conditions.

In the chlorination of carbazole and of 9-methylcarbazole, which is usually effected with sulfuryl chloride [1], N-chlorosuccinimide [2], or gaseous chlorine [3], mixtures of mono- and polychloro derivatives are formed [4-6].

The use of phosphorus pentachloride (PCl_5) in 1,2-dichloroethane (DCE) as a chlorinating agent has enabled us to obtain, depending on the reaction conditions, 3-chlorocarbazole (I) and 3-chloro-9-methylcarbazole (II) or 3,6-dichlorocarbazole (III) and 3,6-dichloro-9-methylcarbazole (IV) with satisfactory yields (Table 1). With a twofold amount of PCl_5 (moles) in boiling DCE, 9-methyl-3-trifluoroacetylcarbazole (V) gave 6-chloro-9-methyl-3-trifluoroacetylcarbazole (VI) in a yield of 85%, the carbonyl group remaining unchanged.

The replacement of the oxygen atoms of the carbonyl groups in perhalogenoketones by chlorine atoms under the action of PCl_5 takes place with difficulty at 250-300°C [7]. The analogous reaction with 1,1,1-trifluoroacetophenone takes place more readily [8]. The reaction of PCl_5 with acetophenone [9] and pentafluoroacetophenone [10] not only replaced the carbonyl function by chlorine but also led to the chlorination of the methyl group, but no chlorination of the aryl fragment took place. The presence of the π-electron-excessive carbazole substituent [11] in the case of the ketone (V) led, on its reaction with PCl_5, to the exlcusive chlorination of the aromatic ring. Under these conditions the unfluorinated analog of ketone (V) — 3-acetyl-9-methylcarbazole — resinified.

The products obtained were identified from their melting points, R_f values and IR and PMR spectra in comparison with those of authentic samples synthesized by known methods.

EXPERIMENTAL

The course of the reactions was followed with the aid of TLC on Silufol plates with hexane–ether (1:1) as eluent. IR spectra were taken in paraffin oil on a UR-20 instrument, and PMR spectra on a Tesla BS-487c (80 MHz) instrument with HMDS as internal standard.

3-Chlorocarbazole (I) and 3-Chloro-9-methylcarbazole (II). At 20°C with vigorous stirring, half a volume of a solution of PCl_5 in DCE containing a double (with respect to the substrate) amount of chlorinating agent was added dropwise to a solution of the initial carbazole in DCE. The mixture was heated at 60°C for 5-7 min, and the second half of the PCl_5 solution was added. After cooling to room temperature, the mixture was washed four times with water and the solvent was distilled off. The solid residue of the chlorine derivative was purified by recrystallization from benzene. Somewhat higher yields of the chlorine derivative can be obtained by adding the second half of the PCl_5 solution at room temperature and keeping the mixture under these conditions for one day (Table 1).

3,6-Dichlorocarbazole (III) and 3,6-Dichloro-9-methylcarbazole (IV). Solutions of the initial carbazole and of PCl_5 in a ratio of 1:3 (molar) in DCE were mixed and boiled for 5 min. After the solution had been cooled, the product was isolated as described above.

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TABLE 1. 3-Chloro- and 3,6-Dichlorocarbazoles

Compound	Reaction conditions		mp, °C (from benzene)	R_f	Yield, %
	temperature, °C	time, min			
I [4, 6]	60	7 (1 day*)	191—192	0,33	60 (65*)
II [1]	60	7 (1 day*)	57—58	0,53	52 (60*)
III [4, 6]	83	5	201—202	0,23	66
IV [1]	83	5	156—157	0,38	58

*At room temperature.

6-Chloro-9-methyl-3-trifluoroacetylcarbazole (VI). A solution of 0.55 g (2 mmole) of the ketone (V) in 10 ml of DCE was treated with 10 ml of a solution containing 0.83 g (4 mmole) of PCl_5 and DCE, and the mixture was boiled for 10 min. The resulting solution was poured into 200 ml of water, and the organic layer was separated off and evaporated. The solid residue was dried at 120°C, and the compound (VI) was extracted with boiling hexane. Yield 0.53 g (85%), mp 115.5-116.5°C (from hexane), R_f 0.13. IR spectrum, cm^{-1}: 1700 (C═O); 1230, 1200-1140 (C—F); 810, 770, 735, 675 (C—H). PMR spectrum ($CDCl_3$), ppm: 3.69 (3 H, s, NCH_3); 7.35-7.60 (2 H, m); 8.07-8.05 (3 H, m); 8.81 (1 H, d). Found: C 57.7, H 2.9, Cl 11.2, N 4.5%. $C_{15}H_9ClF_3NO$. Calculated: C 57.7; H 2.8; Cl 11.4; N 4.5%.

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