

REACTION OF CARBAZOLE WITH FORMALDEHYDE. REACTIONS OF N-HYDROXYMETHYLCARBAZOLE IN THE PRESENCE OF ACIDS

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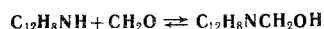
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Formation of the reaction product from carbazole and formaldehyde (CF condensate) in the presence of hydrochloric acid takes place via a stage of equilibration between processes of formation and decomposition of N-hydroxymethylcarbazole.

The individual primary products of reaction of secondary amines with formaldehyde, N-hydroxymethylamines, can be isolated only if the reaction is carried out in alcoholic alkali [1]. They are unstable in acid solution, undergoing further changes [2, 3] (condensation, isomerization, etc) to aminoformaldehyde resins.

In the course of a study of the decomposition of N-carbazolylacetylchloride in Friedel-Crafts acylation reactions, results were obtained relating to reactions undergone by N-hydroxymethylcarbazole in the presence of strong acids. Concentrated hydrochloric acid at 20° C converts N-hydroxymethylcarbazole to symmetrical N, N'-dicarbazolyldimethylether (I) and CF condensate, the product of reaction of carbazole with formaldehyde [4]. Under the same conditions, but in the presence of a considerable excess of resorcinol, N-hydroxymethylcarbazole rapidly forms carbazole (after 15 minutes the carbazole yield is 50%, and after 3 hr 80%). CF condensate is not formed in the presence of resorcinol, and a low molecular product of reaction of formaldehyde with resorcinol is obtained. At a carbazole:formaldehyde ratio of 1:1, the reaction products contain only CF condensate, when the ratio is 1:5 compound I is also found (due to conversion of the N-hydroxymethylcarbazole originally formed under those conditions).

From these results it can be concluded that formation of CF condensate, both from carbazole and formaldehyde, and from N-hydroxymethylcarbazole in the presence of concentrated hydrochloric acid is accompanied by establishment of the equilibrium:



When treated with polyphosphoric acid at 100° C, N-hydroxymethylcarbazole gives a high yield (up to 90%) I. Those conditions were used to prepare and identify the latter (in concentrated HCl the yield of I does not exceed 10%).

EXPERIMENTAL

N-Hydroxymethylcarbazole. Prepared as described in [5], mp 127°-128° C (ex MeOH).

Symmetrical N, N'-dicarbazolyldimethyl ether (I).

A solution of polyphosphoric acid was prepared from 14 g P₂O₅ and 12 ml 87% H₃PO₄, and 1.97 g (0.01 mole)

N-hydroxymethylcarbazole introduced into it, and the whole heated at 100° C for 6 hr, cooled, the polyphosphoric acid decomposed with ice, the solid filtered off, washed with water, dried and extracted with benzene. On evaporation the extract gave 1.68 g white amorphous powder, compound I. After recrystallization from benzene it formed white needles mp 226°-227° C. Found: C 83.1; 82.9; H 5.52; 5.73%; M 356; 364. Calculated for C₂₆H₂₀N₂O: C 83.0; H 5.32; M 376. IR spectrum, very intense band 1025 cm⁻¹ (-CH₂-O-CH₂-)^[6], 1620, 1491, 1330, 1244, 1162, 1138, 1092, 1068, 917, 788, 749, 727 cm⁻¹; N-H valence vibrations band lacking.

Conversion of N-hydroxymethylcarbazole in the presence of concentrated hydrochloric acid. A solution of 3.94 g (0.02 mole) N-hydroxymethylcarbazole in 100 ml acetone was added to 300 ml conc. HCl at 20° C, with vigorous stirring. After 3 hr the products were poured into 500 ml water, the solid filtered off, washed with water, dried, and extracted with hot benzene. The extract was chromatographed (Al₂O₃, benzene) to give a white amorphous substance, mass 0.38 g. Undepressed mixed mp with authentic I. The residue remaining after the extraction was CF condensate, an infusible amorphous material with a very low solubility in organic solvents. IR spectrum: 2925, 2855, 1604, 1492, 1460, 1380, 1328, 1278, 1234, 1212, 1154, 1026, 924, 878, 800, 744, 722 cm⁻¹ (cf. the corresponding data in [4]).

Conversion of N-hydroxymethylcarbazole in the presence of concentrated hydrochloric acid and resorcinol. A solution of 3.94 g (0.02 mole) N-hydroxymethylcarbazole and 15.4 g (0.14 mole) resorcinol in 100 ml acetone was stirred with 300 ml conc. HCl at 20° C. After 3 hr the products were diluted with water, the solid filtered off, washed with water to remove unreacted resorcinol, and the residue treated with 2% NaOH, then filtered. The filtrate was acidified, the precipitate filtered off, and dried; it was an amorphous substance, the low-molecular product of reaction of resorcinol with formaldehyde, mp 190°-200° C. Found: M 335; 360. Calculated for C₂₀H₁₈O₆: M 354. The solid insoluble in the NaOH solution was dissolved in benzene and chromatographed (Al₂O₃, C₆H₆) to give two fractions: a) compound I, yield 0.1 g; b) carbazole, yield 2.68 g (80%) (undepressed mixed mp with authentic compound identified it).

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