

INVESTIGATION OF FEATURES OF THE STRUCTURE AND CHEMICAL TRANSFORMATIONS OF CARBAZOLE AND SOME OF ITS DERIVATIVES

XXIV. Diazotization of 3,6-Diaminocarbazole*

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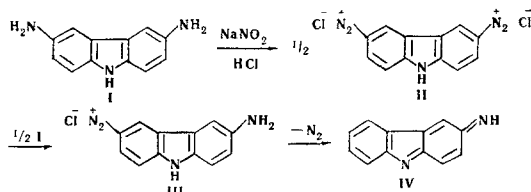
It has been shown that in the diazotization of 3,6-diaminocarbazole, regardless of the ratio of the components, both amino groups are diazotized. When the diazonium salt obtained is coupled with azo components, regardless of the molar ratio of the components bis-azo dyes are obtained.

3-Amino- and 3,6-diaminocarbazoles can be used to obtain azo dyes with a wide range of colors [1, 2].

It was interesting to compare the nature of the diazotization of the amino group in 3,6-diaminocarbazole with the diazotization of benzidine, which takes place smoothly with the formation of bis-diazo compounds [3]. For this purpose we have performed the diazotization of 3,6-diaminocarbazole with the amount of sodium nitrite calculated for one amino group. The decomposition of the resulting diazonium salt led to the formation of two substances: 3-imino-3H-carbazole [4] and 3-aminocarbazole. In addition to this, the dye obtained by coupling the diazonium solution with β -naphthol was identified by IR spectroscopy as the bis-azo dye of known structure. This permits the conclusion that both amino groups of 3,6-diaminocarbazole are diazotized regardless of the amount of diazotizing reagent.

The formation of 3-imino-3H-carbazole (IV) with a deficiency of sodium nitrite can be explained by an exchange reaction between the carbazolebis-diazonium salt II and 3,6-diaminocarbazole (I) with the formation of the 3-aminocarbazole-6-diazonium salt III, in a similar manner to the formation of 4-aminobiphenyl-4'-diazonium salts when benzidine is diazotized under similar conditions [5].

Taking into account the tendency of 3-aminocarbazole to undergo oxidation, the conversion of the 3-aminocarbazole-6-diazonium salt into the imino compound on decomposition may be considered probable:



In actual fact, the prolonged interaction of solutions of a carbazole-3,6-bis-diazonium salt and 3,6-diaminocarbazole hydrochloride in equimolecular amounts

also forms a black crystalline precipitate of 3-imino-3H-carbazole.

The azo coupling of carbazole-3,6-bis-diazonium salts with β -naphthol or other azo components forms only the bis-azo dyes, regardless of the molar ratios of the components. This distinguishes carbazole-3,6-bis-diazonium salts from biphenyl-4,4'-bis-diazonium salts, which are capable of stepwise azo coupling.

EXPERIMENTAL

Diazotization of 3,6-diaminocarbazole and decomposition of the diazonium salt. A solution of 2 g (0.01 mole) of 3,6-diaminocarbazole in 3 ml of conc HCl and 25 ml of water was filtered and to it, at 0-5° C, was rapidly added a solution of 0.69 g of sodium nitrite (0.01 mole) in 20 ml of water. The filtered solution was stirred at 0-4° C for 2 hr and was left to stand for 2 days. Then it was heated in the water bath at 50-60° C until foaming ceased. The precipitate that had deposited was filtered off and was washed successively with dilute HCl, water, ethanol, and ether. The compound was recrystallized from acetone to form black lustrous crystals. From the analytical data and IR spectrum, it was 3-imino-3H-carbazole. Yield 1.5 g (82%). Found, %: N 14.92, 14.80. Calculated for $C_{12}H_8N_2$, %: N 15.5. From the acid filtrate, ammonia liberated 0.1 g of 3-aminocarbazole, mp 242-245° C (from benzene).

Azocoupling of diazotized 3,6-diaminocarbazole with β -naphthol. The diazonium salt obtained from 2 g (0.01 mole) of 3,6-diaminocarbazole by the above-described method was treated with an alkaline solution of 1.44 g (0.01 mole) of β -naphthol. The mixture was stirred at 10° C for 1.5 hr and was neutralized with HCl, after which the precipitate was filtered off and was washed with dil HCl, water, and dil ethanol. Small dark red crystals (from ethanol). Yield 2.5 g (48%). The same compound was obtained by coupling diazotized 3,6-diaminocarbazole with β -naphthol in a molar ratio of 1:2 (in this case, the diazonium salt was obtained by diazotizing 3,6-diaminocarbazole with sodium nitrite in a molar ratio of 1:2). Found, %: C 75.70; H 4.10; N 12.99%. Calculated for $C_{32}H_{21}N_5O_2$, %: C 75.74; H 4.14; N 13.80.

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*For part XXIII, see [6].