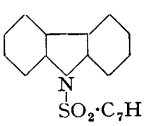
94. *The Nitration of* 9-p-*Toluenesulphonylcarbazole.*

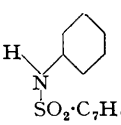
By B. K. Menon, E. V. Menon, and David H. Peacock.

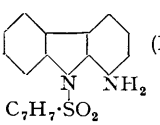
9-*p*-Toluenesulphonylcarbazole is nitrated in the 1-position apparently exclusively; bromination, however, occurs only in the 3-position and by the action of iodine monochloride only the 3 : 6-di-iodo-compound could be obtained. The 1-*nitro*-compound gave a mixture of two *dinitro*-compounds, neither of which was identical with the 3 : 6-*dinitro*-compound produced by nitration of 3-*nitro*-9-p-*toluenesulphonylcarbazole*. The resolution of the 1-amino-compound is being attempted.

The nitration of 3-*nitro*-9-p-*toluenesulphonylcarbazole* gave the 3 : 6-*dinitro*-compound, and nitration of the 1-nitro-compound and dinitration of 9-*p*-toluenesulphonylcarbazole gave in each case a mixture of the same two compounds, which are probably the 1 : 6- and the 1 : 8-compound. 1-*Nitro*-9-p-*toluenesulphonylcarbazole* is nitrated much more readily than the 3-nitro-compound. Treatment of 9-*p*-toluenesulphonylcarbazole with sulphuric acid effected simultaneous sulphonation and hydrolysis of the *p*-toluenesulphonyl group; pyridine–sulphur trioxide gave similar results.

The 1-nitro-compound was hydrolysed with difficulty to 1-nitrocarbazole and this in turn was reduced to 1-aminocarbazole (Lindemann, *Ber.*, 1924, **57**, 1316; Morgan and Mitchell, J., 1931, 3284). On diazotisation a crystalline diazonium salt was obtained which did not give a triazole when treated with ammonia (Morgan and Mitchell, *loc. cit.*). 1-*Amino*-9-p-*toluenesulphonylcarbazole* (III) was obtained on reduction of the nitro-compound. If the three valencies of the ring nitrogen atom are not coplanar, the compound (III) should be capable of resolution.

(I.) 

(II.) 

(III.) 

The formation of the 1-nitro-derivative from (I) corresponds to the formation of an *o*-nitro-derivative from (II). Nitration in the *o*-position to an amino-group appears to be facilitated by the conversion of the amino-group into the *p*-toluenesulphonamido-group (Reverdin and Crépieux, *Ber.*, 1902, **35**, 1440; D.R.-P. 157,859 and 163,516), but in those cases where the *p*-position is free a mixture of the *o*- and the *p*-isomer is obtained. In the present instance no other isomer has been observed, although the 3-position is open to nitration and this is the position attacked by bromine and by iodine monochloride. In other cases where only one isomer has been obtained, the *p*-position, corresponding to the 3- and the 6-position in carbazole, has been occupied as in the *p*-toluenesulphonyl derivatives of *p*-toluidine (Reverdin and Crépieux, *loc. cit.*), 4-aminodiphenyl (Bell and Kenyon, J., 1926, 2708), and 4-methylaminodiphenyl (Bell and Robinson, J., 1927, 1129).

The toluenesulphonyl group is a strongly polar group and association with a polar reagent, such as nitric acid, may assist substitution in the adjacent positions as suggested by Lapworth and Robinson (*Mem. Manchester Phil. Soc.*, 1928, **72**, 43). In this connection it is noteworthy that bromine, a non-polar reagent, substitutes in the 3-position. On the other hand, iodine monochloride, a polar reagent, reacted in the 3- and the 6-position. Nitration in the 1-position seems to be bound up with the strong polarity of the sulphonyl group, as 9-benzoyl- and 9-acetyl-carbazole are nitrated in the 3-position.

The difference in behaviour of (I) and (II) may also be due to the restriction of rotation about the C–N–C bond in (I) as compared with the free rotation possible in (II). The inductive effect exerted by the sulphonyl group on positions 1 and 8 in (I) will therefore be greater than its effect on positions 2 and 6 in (II). It is hoped to study the nitration of similar compounds in which free rotation has been prevented.

Unsuccessful attempts to resolve the alkaloidal salts of 9-ethyl-, 9-methyl-, and 9-benzyl-carbazolesulphonic acid have been made (cf. Peacock, Dissert., London, 1927). The introduction of the sulphonyl group, by lowering the mesomeric effect of the nitrogen atom, may stabilise the dissymmetric forms and 1-amino-9-*p*-toluenesulphonylcarbazole is being examined. It has, however, been found that, in a somewhat similarly constituted

compound, 2-*m*-carboxybenzenesulphonyl-**1** : **2** : **3** : 4-tetrahydro*iso*quinoline, where mesomerism with an adjacent benzene ring is excluded, no active forms could be isolated (Peacock, unpublished results).

Experimental.

9-p-*Toluenesulphonylcarbazole.*—Carbazole (33·7 g.) was fused with potassium hydroxide (17 g.) at 230°, the powdered product mixed with solvent naphtha (200 c.c.), and the solvent distilled to remove water. The residue was mixed with *p*-toluenesulphonyl chloride (40 g.) in toluene (200 c.c.), left overnight, and then stirred at 140—150° for 6 hours. After cooling, the solid was collected and washed with toluene and the combined toluene solutions were steam-distilled. The residue, after crystallisation from rectified spirit, had m. p. 137—138° (40 g.) (D.R.-P. 224,951; Stevens and Tucker, J., 1923, **123**, 2140). The solid was boiled with water and left 10 g. of carbazole.

1-*Nitro*-9-p-*toluenesulphonylcarbazole.*—A solution of the preceding compound in glacial acetic acid (300 c.c.) at 60° was treated with 98% nitric acid (12·0 g.), added during ½ hour, and then allowed to cool after 6 hours' stirring. The crystalline solid (38 g.) was collected, and the filtrate poured into ice-water, giving a further crop (14·0 g.). The combined crops, crystallised from glacial acetic acid, had m. p. 134°; yield, 45 g. (Found : N, 7·3. $C_{19}H_{14}O_4N_2S$ requires N, 7·65%).

1-*Nitrocarbazole.*—When heated with (*a*) 60% sulphuric acid at 160—170°, (*b*) 60% sulphuric acid at 140—150°, and (*c*) syrupy phosphoric acid at 170—180°, the preceding nitro-compound was charred in (*a*) and recovered unchanged in (*b*) and (*c*). The nitro-compound (15 g.) was hydrolysed by heating with concentrated hydrochloric acid (30 c.c.) for 10 hours in a sealed tube at 120—140°. The blackish product was extracted with boiling benzene, the residue dissolved in aniline (5 c.c.), and absolute alcohol (10 c.c.) added. 1-Nitrocarbazole (2 g.), m. p. 187—188°, then separated [Found : N, 13·4, 13·7 (W. and S.). Calc. : N, 13·2%]. Morgan and Mitchell (*loc. cit.*) give m. p. 186·5—187·5°.

1-*Benzamidocarbazole,* prepared from 1-aminocarbazole and benzoyl chloride in pyridine and crystallised from ethanol, had m. p. 242° (Found : N, 9·95. $C_{19}H_{14}ON_2$ requires N, 9·8%).

1-*Amino*-9-p-*toluenesulphonylcarbazole.*—1-Nitro-9-*p*-toluenesulphonylcarbazole (25 g.) was boiled with rectified spirit (400 c.c.), tin (25 g.) and concentrated hydrochloric acid (50·0 c.c.) added during 1 hour, and the mixture heated on a boiling water-bath for 11 hours. The alcohol was distilled off, and the residual solution basified with caustic soda; the precipitate was extracted with hot alcohol, which deposited, on cooling, 6·2 g. of the *amino*-compound. The alcoholic mother-liquor on addition of water gave an oily product, which after crystallisation as the hydrochloride gave another 12 g. of the amine. It formed crystals from ethanol, m. p. 134° [Found : N, 8·5, 8·2 (W. and S.). $C_{19}H_{16}O_2N_2S$ requires N, 8·3%].

The amino-compound was decomposed, not hydrolysed, by hydrochloric acid and by 50% sulphuric acid.

1-*Acetamido*-9-p-*toluenesulphonylcarbazole,* m. p. 8·8° (Found : N, 7·7. $C_{21}H_{18}O_3N_2S$ requires N, 7·4%), 1-*benzamido*-9-p-*toluenesulphonylcarbazole,* m. p. 165° (Found : N, 6·5. $C_{26}H_{20}O_3N_2S$ requires N, 6·4%), and 1-p-*toluenesulphonamido*-9-p-*toluenesulphonylcarbazole,* m. p. 241° (Found : N, 6·0; S, 12·95. $C_{26}H_{22}O_4N_2S_2$ requires N, 5·7; S, 13·1%), were prepared by the action of acetic anhydride, benzoyl chloride and pyridine, and *p*-toluenesulphonyl chloride and pyridine, respectively, and crystallised from ethanol.

3-*Bromo*-9-p-*toluenesulphonylcarbazole.*—A solution of 9-*p*-toluenesulphonylcarbazole (10 g.) in glacial acetic acid (60 c.c.) at 60° was stirred while bromine (5·2 g.) in acetic acid (10 c.c.) was added (1 hour); the mixture was then stirred at 70° for 2 hours. After cooling, the crystals were removed and the mother-liquor added to ice-water, giving more of the bromo-compound (total yield, 12 g.), m. p. 148° after crystallisation from ethanol (Found : Br, 20·0. $C_{19}H_{14}O_2NBrS$ requires Br, 20·0%). The same *substance,* m. p. and mixed m. p. 148° (Found : Br, 20·0%), was obtained by converting 3-bromocarbazole into its *p*-toluenesulphonyl derivative.

Dinitro-9-p-*toluenesulphonylcarbazole.*—A solution of the sulphonylcarbazole (10 g.) in glacial acetic acid (60 c.c.) at 70°, after addition of 98% nitric acid (5·0 g.) during 40 minutes, was kept at 70—80° for 3 hours, at 80—85° for 2 hours, cooled, and poured on ice. The nitro-compound (11 g.) was extracted with boiling toluene (200 c.c.). The residue and the crystals from the toluene solution were crystallised from nitrobenzene, giving 6·1 g., m. p. 207° (Found : N, 10·25; *M*, ebullioscopic in acetone, 405·8. $C_{19}H_{13}O_6N_3S$ requires N, 10·2%; *M*, 411), and 2·0 g., m. p. 271° (Found : N, 10·3%), very sparingly soluble in acetone. Neither compound could be hydrolysed by normal methods.

Nitration of 1-*Nitro*-9-p-*toluenesulphonylcarbazole.*—The carbazole (1 g.) was nitrated in glacial acetic acid (6 c.c.) at 80° (97% nitric acid, 0·45 g.) and after ½ hour the temperature was kept at 100° for 1 hour, and the mixture then poured into ice-water. The product (1 g.) was fractionally crystallised from amyl alcohol and acetone–ether, giving 0·4 g., m. p. 203°, and 0·2 g., m. p. 268°, identical with the two *dinitro*-compounds described above, and a product (0·2 g.) m. p. 120—130°, from the mother-liquors.

Nitration of 3-*Nitro*-9-p-*toluenesulphonylcarbazole.*—This *compound,* prepared from 3-nitrocarbazole by the usual acetone method, crystallised from amyl alcohol in fine needles, m. p. 211° (Found : N, 7·4. $C_{19}H_{14}O_4N_2S$ requires N, 7·65%). It (1 g.) was nitrated in glacial acetic acid (3 c.c.) and acetic anhydride (3 c.c.) at 30° (98% nitric acid, 1 c.c.) and after 1 hour the mixture was heated to 100° during 5 hours and poured into ice-water. The product (1·0 g.), crystallised from amyl alcohol and then from nitrobenzene, had m. p. 304° (Found : N, 10·3. $C_{19}H_{13}O_6N_3S$ requires N, 10·2%).

3 : 6-*Dinitro*-9-p-*toluenesulphonylcarbazole* was prepared from 3 : 6-dinitrocarbazole by the acetone method and crystallised from aniline and then from nitrobenzene; it had m. p. 302—303° and was apparently identical with the product obtained above.

The rates of nitration of 1- and 3-nitro-9-*p*-toluenesulphonylcarbazole were compared by mixing 1·0 g. of each substance with acetic acid (6 c.c.) and 98% nitric acid (0·5 c.c.) and stirring while the temperature was raised in 4 hours from 30° to 90°. The products were isolated, and the approximate extent of dinitration determined by (1) the titanous chloride method, (2) the percentage of nitrogen, (3) the molecular weight. The 1-nitro-compound gave roughly 60%, and the 3-nitro-compound only about 15%, of dinitro-product.

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University College, Rangoon.
University Chemical Laboratories, Cambridge.

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