Polyesters Containing Carbazole Rings in the Main Chain. I. Syntheses of Diacylcarbazoles and Carbazoledicarboxylic Acids*

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Despite the numerous heterocyclic compounds such as thiophene-, furan-, and pyridinedicarboxylic acids that have been claimed to be useful in the preparation of high melting polyesters suitable for fibermaking, the carbazole derivatives have never been in much demand as starting materials for such a purpose.

To prepare polyesters containing carbazole rings in the main chains, the authors first synthesized a series of carbazole derivatives and several carbazoledicarboxylic acids by oxidizing the corresponding diacylcarbazoles.

Descriptions appearing in the literature on the synthesis of 3, 6-diacetylcarbazole (I) usually give neither exact yields nor information on 3-acetyl- or 9-acetylcarbazoles which has been shown to be one of the main acylation products. By carefully following the methods of Plant et al.,[1, 2] we have found that under the described conditions, I was obtained only in poor yields, while a large amount of monoacetylcarbazole was isolated. The experimental data also indicated that at higher reaction

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[1] S. G. P. Plant, K. M. Rogers and S. B. C. Williams, *J. Chem. Soc.*, **1935**, 741.

[2] D. R. Mitchell and S. G. P. Plant, ibid., **1936**, 1295.

temperatures, acylation of carbazole tended to give more 9-acetylcarbazole, though carbazole is considered to resemble a secondary aromatic amine in chemical reactivity, with substitution groups preferably entering into para positions to the nitrogen. In the syntheses of 3, 6-diacetyl-9-alkylcarbazoles, however, the sole product was the disubstituted 9-alkylcarbazole.

Of the three acylating agents employed, acetyl bromide appeared to be best suited for the preparation of diacetylcarbazoles.

Oxidation of 3, 6-diacetyl- and 3, 6-diacetyl-9-alkylcarbazoles with an appropriate amount of sodium hypochlorite solution, as shown in Table III, yielded almost quantitatively carbazole-3, 6-dicarboxylic and 9-alkylcarbazole-3,6-dicarboxylic acids, previously reported as being obtained only in much lower yields via other reactions.[1-3]

TABLE I. MOLECULAR PROPORTIONS OF CATALYST AND ACETIC ANHYDRIDE PER MOLE OF CARBAZOLE*

$AlCl_3$*	$(CH_3CO)_2O$*	Yield, %		
		a	b	c
4.2	2.3	6.4	12.4	d
5.3	2.8	14.1	4.9	11.3
5.3	4.6	0.2	15.6	4.9
4.2	2.3	—	—	23.2**
6.3	2.3	14.8	5.2	10.5

a, 3, 6-Diacetylcarbazole ; b, 3-Acetylcarbazole ; c, 9-Acetylcarbazole ; d, Isolation procedure was omitted. ; ** Reaction temperature was 5°C.

TABLE II. MOLECULAR PROPORTIONS OF CATALYST AND ACETYL HALIDE PER MOLE OF CARBAZOLE*

$AlCl_3$*	CH_3COCl*1 or CH_3COBr*2	Yield, %	
		a	b
2.1	2.1[1]	33.5	19.1
2.1	2.1[1]	34.1**	15.4**
2.1	2.0[2]	6.7	4.7
2.1	2.0[2]	8.4**	c

a, 3, 6-Diacetylcarbazole ; b, 9-Acetylcarbazole ; c, Isolation procedure was omitted. ; ** Reaction time was two hours.

TABLE III. SYNTHESES OF 9-ALKYLCARBAZOLE-3, 6-DICARBOXYLIC ACIDS

a g.	b cc.	Pyridine cc.	Yield %
2.5*	22	15	95
2.5*	25	15	98
2.5**	25	18	91
2.5**	30	18	99

a, 3, 6-Diacetyl-9-alkylcarbazole (* 9-ethyl ; and ** 9-methyl) ; b, Sodium hypochlorite solution, 6 N.

Experimental

3, 6-Diacetylcarbazole (I).—A mixture of 6.0 g. of carbazole (m. p. 245°C), 9.0 g. of acetyl bromide, 50 cc. of dry carbon disulfide, and 10 g. of pulverized aluminum chloride was refluxed at the boiling point of the solvent for an hour and then the solvent was distilled off. By treating the residue with ice-dilute hydrochloric acid, I was obtained as a brown solid, which gave almost colorless crystals, 3.0 g. ; m. p. 235—237°C, after two recrystallizations from ethanol (decolorizing charcoal added). The reaction of carbazole and acetyl chloride, however, gave I in much poorer yields in the presence of the same catalyst. As shown in Table I, the reaction of 60 g. of carbazole with 105 g. of acetic anhydride at 0 ± 1°C for 6 hr. with stirring also afforded I in 14.1% yield. Use of about two molecular proportions of aluminum chloride per mole of anhydride as a catalyst at 0°C gave 3-acetyl- and 9-acetylcarbazoles besides I, whereas at 5°C the reaction led mainly to 9-acetylcarbazole. An increase in the amount of catalyst, as recommended by Groggins and Nagel,[4] did not increase the yields of I. Prolonging the reaction time also did not cause much improvement of the yield ; even the yield from a reaction of 6 hr. compared favorably with that of 8 hr. or longer. Acetylation of carbazole with acetic anhydride in the presence of 3.5 mol. of aluminum chloride gave more 9-acetylcarbazole.

Found : C, 76.46 ; H, 5.16 ; N, 5.45. Calcd. for $C_{16}H_{13}O_2N$: C, 76.55 ; H, 5.17 ; N, 5.58%.

During crystallization of the crude acylation product from ethanol, 3-acetylcarbazole, m.p. 166—168°C, came out first ; concentration of the filtrate afforded I. After removal of the solvent by distillation, the residue, temperature range of m. p. 69—115°C, was recrystallized from methanol to give 9-acetylcarbazole as light yellowish white crystals, m. p. 77—78°C. When a solution of 9-acetylcarbazole in benzene was passed through a column (1.8 cm. inner diameter) packed with alumina (15 cm. in height), and the column successively eluted with benzene, 9-acetylcarbazole was recovered as carbazole.

Carbazole-3, 6-dicarboxylic Acid (II).*—A solution of 5 g. of I in 30 cc. of pyridine was poured into a flask containing 100 cc. of 5% aqueous sodium hydroxide solution. This mixture was kept at 20°C while 44 cc. of 6 N sodium hypochlorite solution was added with stirring. The reaction mixture was stirred for an additional 100 min. and the excess of oxidizing agent decomposed by pouring the product into sodium bisulfite solution, after unaltered I had been removed by filtration. On addition of hydrochloric acid to the filtrate, II came out as a white precipitate, 5.1 g., m. p. above 375°C (decomp.)

Found : C, 65.51 ; H, 3.63 ; N, 5.33. Calcd. for $C_{14}H_9O_4N$: C, 65.84 ; H, 3.55 N, 5.49%.

Diethyl Carbazole-3, 6-dicarboxylate (III).—A suspension of 10 g. of II in a mixture of 200 cc. of dry ethanol and 30 cc. of concentrated sulfuric acid was refluxed with stirring for 6 hr. and then

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[3] H. Gilman and S. M. Spatz, *J. Am. Chem. Soc.*, **63**, 1553 (1941).

[4] P. H. Groggins and R. H. Nagel, *Ind. & Eng. Chem.*, **1934**, **26**.

* According to the modified method of Uematsu, unpublished paper, this laboratory.

the excess of ethanol removed by distillation. The residue was treated with dilute aqueous sodium carbonate solution to dissolve unchanged acid, and the insoluble residue was recrystallized from ethanol (decolorizing charcoal added) to give III as almost colorless crystals, 8.0 g., m. p. 206—207°C.

Found: C, 69.32; H, 5.49; N, 4.38. $C_{18}H_{17}O_4N$ requires C, 69.47; H, 5.51; N, 4.49%.

3, 6-Diacetyl-9-methylcarbazole (IV) and 3, 6-Diacetyl-9-ethylcarbazole (V).—A solution of 1 g. of I in 30 cc. of acetone and aqueous potassium hydroxide (1.5 g. of potassium hydroxide in 1 cc. of water) was refluxed with stirring for 5 min.; then 2.2 g. of dimethyl sulfate was added and the mixture was allowed to react at 35°C for 10 min. The reaction product was poured into 300 cc. water to give a white precipitate, 1.1 g., m. p. 198—200°C.

Found: C, 76.85; H, 5.59; N, 5.23. Calcd. for $C_{17}H_{15}O_2N$: C, 76.98; H, 5.66; N, 5.28%.

IV was also obtained by reaction of 9-methylcarbazole with an acyl halide, such as acetyl chloride or acetyl bromide, in the presence of aluminum chloride. A mixture of 14 g. of I in 280 cc. of acetone with aqueous potassium hydroxide (21 g. of potassium hydroxide in 10 cc. of water) and diethyl sulfate was stirred at room temperature for 10 min.; subsequent dilution of the product with water precipitated V, 15 g., m. p. 181—182°C.

Found: C, 77.16; H, 5.89. Calcd. for $C_{18}H_{17}O_2N$: C, 77.42; H, 6.09%.

V was also synthesized from the reaction of 9-ethylcarbazole with acyl halides, such as acetyl chloride or acetyl bromide, using aluminum chloride as a catalyst. Acetyl bromide reacted with 9-ethylcarbazole and gave V usually in higher yields than did acetyl chloride.

9-Methylcarbazole-3, 6-dicarboxylic Acid (VI).—A solution of 1 g. of IV in 10 cc. of pyridine was poured into 20 cc. of 5% aqueous sodium hydroxide solution, and the temperature of the mixture maintained at 20°C while 12 cc. of NaOCl solution (6 N) was added; the reaction mixture was then stirred for one hour and forty minutes at 25°C. Unchanged material was filtered off and the filtrate treated with sodium bisulfite solution. Addition of hydrochloric acid to the filtrate precipitated VI as a white powder, 1.0 g., m. p. above 395°C (decomp.).

Found: C, 66.78; H, 4.21. $C_{15}H_{11}O_4N$ requires C, 66.92; H, 4.09%.

Diethyl 9-Methylcarbazole-3, 6-dicarboxylate (VII).—After a suspension of 1.0 g. of VI in a mixture of 25 cc. of ethanol and 2.5 cc. of concentrated sulfuric acid had been refluxed for 6 hr. with stirring, the excess ethanol was removed by distillation. The residue was then treated with 5% aqueous sodium carbonate solution to dissolve unchanged acid and the mixture filtered. The residue after crystallization (decolorizing charcoal added) yielded VII as light yellowish white crystals, 0.7 g., m. p. 163—165°C.

Found: C, 70.18; H, 5.61. Calcd. for $C_{19}H_{19}O_4N$: C, 70.16; H, 5.85%.

9-Ethylcarbazole-3, 6-dicarboxylic Acid (VIII).—A mixture of 1.0 g. of V in 7 cc. of pyridine and 200 cc. of 5% sodium hydroxide solution was treated with 14 cc. of 3 N sodium hypochlorite solution at 20°C under stirring for one hour and forty minutes. The resulting reddish orange solution was filtered to remove any unaltered V and discharged into sodium bisulfite solution. VIII was obtained as a white precipitate upon addition of hydrochloric acid. Yield, 1.0 g., m. p. above 380°C (decomp.).

Found: C, 67.22; H, 4.63. $C_{16}H_{13}O_4N$ requires C, 67.56; H, 4.57%.

Diethyl 9-Ethylcarbazole-3, 6-dicarboxylate (IX).—The procedure for the preparation of IX was similar to that used in the synthesis of III. Yield, 83%; melting point after crystallization from ethanol (decolorizing charcoal added), 173—174°C.

Found: C, 70.95; H, 6.18. Calcd. for $C_{20}H_{21}O_4N$: C, 70.80; H, 6.19%.

Summary

Acetylation of carbazole with acetyl halide or acetic anhydride gave both monoacetyl- and diacetylcarbazoles. Several carbazoledicarboxylic acids were prepared in quantative yields by oxidizing the corresponding diacetylcarbazoles.

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