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STUDIES OF THE STRUCTURAL PECULIARITIES AND CHEMICAL CHANGES OF CARBAZOLE AND OF SOME OF ITS DERIVATIVES

XIII. Diallyl Esters of 9-Alkylcarbazole-3, 6-dicarboxylic Acids*

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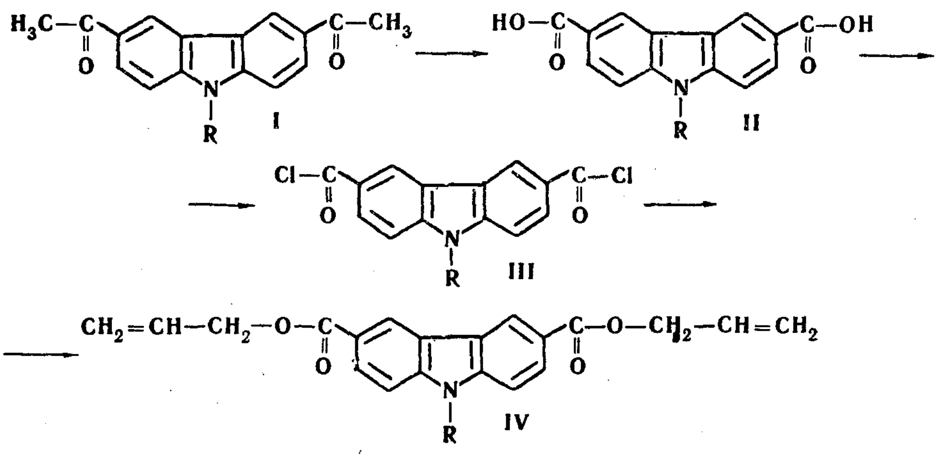
Oxidation of the corresponding 3, 6-diacetylcarbazoles gives 9-n-butyl- and 9-isoamylcarbazole-3, 6-dicarboxylic acids. 9-Alkylcarbazole-3, 6-dicarboxylic acids are converted to acid chlorides, which are esterified with allyl alcohol without being isolated pure. Allyl 9-ethyl-, 9-n-butyl- and 9-isoamylcarbazole-3, 6-dicarboxylates are synthesized. The ability of these esters to polymerize and to undergo copolymerization with methyl mercaptan is demonstrated with the example of diallyl 9-ethylcarbazole-3, 6-dicarboxylate.

In addition to the known dielectric polyvinylcarbazole, prepared from 9-vinylcarbazole, polymers of 3-monovinyl- and 3, 6-divinyl-9-alkylcarbazoles which are thermostable dielectrics, have been described. The monomers were prepared from the corresponding mono- and diacetylcarbazoles by reduction and dehydration [1, 2].

The present paper describes another method of preparing carbazole containing monomers with two double bonds, comprising oxidation of 3, 6-diacetyl derivatives (I) to carboxylic acids (II), followed by esterification of the acid chlorides (III) to give allyl esters (IV).



The 3, 6-diacetyl derivatives I were prepared in 65-75% yield by alkylating 3, 6-diacetylcarbazole [3] in acetone solution with alkyl iodides in the presence of sodium hydroxide, and among them was the hitherto undescribed 3, 6-diacetyl-9-propylcarbazole. The melting points of the compounds described agree with those given in the literature [4-7]. The 9-alkylcarbazole-3, 6-dicarboxylic acids II were synthesized by oxidizing the corresponding diacetylcarbazoles in dioxane solution with sodium hypobromite, like the preparation of 9-ethylcarbazole-3, 6-dicarboxylic acid [4]. In addition to 9-ethylcarbazole-3, 6-dicarboxylic acid, which has previously been described, the reaction made it possible to obtain smoothly, and in 85-90% yield, 9-butyl- and 9-isoamylcarbazole-3, 6-dicarboxylic acid. When other diacetylcarbazoles (I, R = Me, n–Pr, $CH_2-CH=CH_2$) were oxidized, the acids could not be isolated.

The acid chlorides III were prepared by treating the acids with thionyl chloride in the presence of pyridine, and used crude for the esterifications, being identified only as the esters. The allyl esters IV, formed by reacting the acid chlorides derived from the acids with allyl alcohol in the presence of pyridine, formed colorless crystals, readily soluble in ethanol, acetone, dioxane, and benzene. The table gives some constants for the esters obtained.

Ability to polymerize and copolymerize was investigated for the example of diallyl 9-ethylcarbazole-3, 6-dicarboxylate. Polymerization of this ester by fusing it at 160° with benzoyl peroxide did not give any infusible material after 72 hr, whereas with tert-butyl peroxide, formation of a transparent brown block occurred in 15-20 min, this being unmelted up to 300°, and insoluble in boiling ethanol, acetone, benzene, and toluene. 8% by weight on the second

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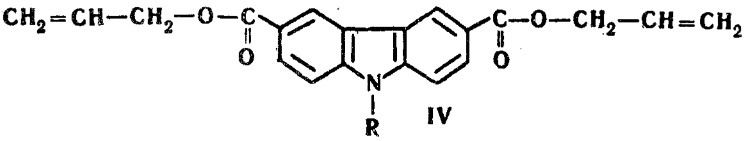
*For Part XII see [8].

monomer of diallyl 9-ethylcarbazole-3, 6-dicarboxylate copolymerizes with methyl methacrylate in the presence of benzoyl peroxide, but there is no copolymerization with styrene.

Diallyl 9-Alkylcarbazole-3, 6-Dicarboxylates (IV)



IV

R	Mp, °C	Formula	Found, %			Calculated, %			Bromine number		Yield, %
			C	H	N	C	H	N	Found	Calculated	
C_2H_5	140—141	$C_{22}H_{21}NO_4$	72.31 72.83	5.73 5.75	3.95 3.95	72.45	5.78	3.85	87.4	88.1	57
n-C_4H_9	81—82	$C_{24}H_{25}NO_4$	73.32 73.44	6.48 6.44	3.84 3.90	73.66	6.39	3.58	81.2	81.8	55
i-C_5H_{11}	82—83	$C_{25}H_{27}NO_4$	73.51 73.89	6.57 6.68	3.68 3.67	74.07	6.66	3.46	81.7	79.0	55

Experimental

3, 6-Diacetyl-9-n-propylcarbazole. 4 g 3, 6-diacetylcarbazole, 4 ml propyl iodide, 1 g powdered NaOH, and 100 ml acetone were refluxed for 8 hr together in a round-bottomed flask fitted with a reflux condenser. Pouring the solution into water precipitated an oily material, which was pressed out on a filter, washed and dried. Crystallization from ethanol gave 3 g compound (64%), mp 162-163°. Found: C 77.68, 78.08; H 6.53, 6.51; N 4.56, 5.15%. Calculated for $C_{19}H_{19}NO_2$: C 77.81; H 6.48; N 4.78%.

9-n-Butylcarbazole-3, 6-dicarboxylic acid. A solution of NaOBr was prepared from 3 ml Br_2 and 6 g NaOH, with water to 100 ml, and added to a solution of 3 g 3, 6-diacetyl-9-n-butylcarbazole in 100 ml dioxane. The mixture was stirred from some minutes and left overnight. The reaction products were diluted, and the precipitate formed filtered off. When the filtrate was acidified with HCl, the acid was precipitated; it was filtered off, and purified by reprecipitation from dilute sodium carbonate solution. The yield was 2.7 g (85%) of an amorphous powder, soluble in dilute aqueous solutions of sodium carbonate, ammonia, alkali, as well as in pyridine and dimethylformamide, but insoluble in most organic solvents. Mp 320° (decomp). Found: C 69.30, 69.70; H 5.48, 5.55; N 4.40, 4.65%. Calculated for $C_{18}H_{17}NO_4$: C 69.45; H 5.56; N 4.49%.

9-Isoamylcarbazole-3, 6-dicarboxylic acid. This was obtained similarly, in 90% yield, mp 318° (decomp). Found: C 69.90, 70.23; H 5.70, 5.80; N 4.10, 4.20%. Calculated for $C_{19}H_{19}NO_4$: C 70.13; H 5.88; N 4.30%..

9-Alkylcarbazole-3, 6-dicarbonyl chlorides. 0.01 mole acid and 75 ml $SOCl_2$ plus a few drops of pyridine were refluxed for 2 hr, excess thionyl chloride then distilled off, dry benzene added to the residue, and the benzene in its turn distilled off. After vacuum-drying the acid chlorides were reacted with allyl alcohol.

Diallyl 9-ethylcarbazole-3, 6-dicarboxylate. 30 ml allyl alcohol and 1 ml pyridine were added to the solid acid chloride (0.01 mole), and the mixture refluxed for 2 hr. Then, for example, half the allyl alcohol was distilled off, and on cooling, a crystalline precipitate separated from what remained. This was filtered off. Diallyl 9-n-butylcarbazole-3, 6-dicarboxylate and 9-isoamylcarbazole-3, 6-dicarboxylate were prepared similarly. The yields of the esters amounted to 55-57% (Table). The materials obtained were purified by recrystallization from ethanol.

Fusion (block) polymerization of diallyl 9-ethylcarbazole-3, 6-dicarboxylate. 2 g ester and a few grains of benzoyl peroxide or 2-3 drops of tert-butyl peroxide were placed in an ampul, which was then flushed with nitrogen and sealed. The ampul was placed in a Wood metal bath at 160° for 72 hr when benzoyl peroxide was used, and 15-20 min with tert-butyl peroxide. Then the ampuls were cooled and broken and the melting points and solubilities were determined. The product formed using benzoyl peroxide was soluble in benzene, did not dissolve in boiling ethanol and melted at 80-100°. The product formed using tert-butyl peroside did not dissolve in boiling ethanol, acetone, benzene or toluene, and did not melt up to 300°

Copolymerization of diallyl 9-ethylcarbazole 3, 6-dicarboxylate with methylmethacrylate and styrene. 1 g ester, 12.5 g freshly distilled methylmethacrylate and 0.27 g benzoyl peroxide were placed in an ampul, which was then flushed with nitrogen and sealed. A control without ester was run simultaneously; both ampuls were put in a Wood metal bath held at 70° for 4 hr and then at 100° for 10 hr. Using the same amounts by weight, runs were carried out with styrene, which was held at 100° for 20 hr, and then at 150° for 4 hr. After cooling the ampuls were broken, the polymers powdered and vacuum-dried, then extracted in a Soxhlet. In the control 8 g polymethylmethacrylate completely dissolved in acetone in 24 hr extraction. Under the same conditions polymer from mixed ester-methylmethacrylate only swelled to a limited extent, but did not dissolve (weight loss on drying 0.05 g). 6 hr extraction with benzene completely dissolved weighed-out 4 gm portions of polystyrene from the control and of polymer from mixed styrene-ester.

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