UDC 547.759.32 + 541.64

RESEARCHES ON STRUCTURAL PECULIARITIES AND CHEMICAL REACTIONS OF CARBAZOLE AND SOME OF ITS DERIVATIVES

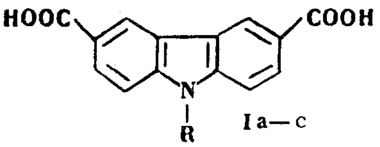
XIV. Dipropargyl Esters of 9-Alkylcarbazole-3, 6-dicarboxylic acids*

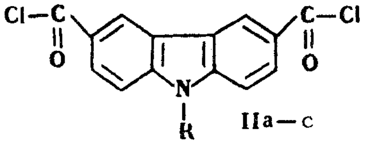
N. D. Negodyaev and Z. V. Pushkareva

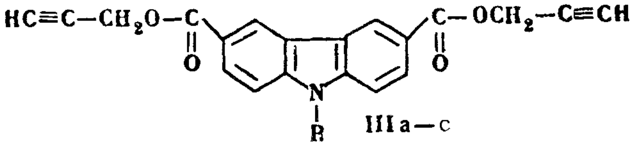
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 2, No. 4, pp. 586-589, 1966

Dipropargyl esters of 9- ethyl, 9-n-butyl, and 9-isoamylcarbazole-3, 6-dicarboxylic acids, not hitherto described in the literature, are synthesized. It is shown that, in the presence of tert-butyl peroxide, these esters can polymerize to infusible and insoluble products.

Information was previously published [1] concerning the synthesis and certain properties of diallyl esters of 9-alkylcarbazole-3, 6-dicarboxylic acid (Ia-c):


Ia—c


IIa—c


IIIa—c

a $R=C_2H_5$; b $R=n\text{-}C_4H_9$; c $R=i\text{-}C_5H_{11}$

As the available data [2, 3] show that dipropargyl esters of aliphatic and aromatic dicarboxylic esters can be converted by polydehydrocondensation into polymers with enhanced thermal stability, it was of interest to prepare the dipropargyl esters of the above-mentioned carbazole acids.

Diacid chlorides IIa-c were prepared from Ia-c, and with propargyl alcohol in the presence of pyridine gave the dipropargyl esters IIIa-c. Table 1 gives some data for the diacid chlorides and diethers synthesized.

Esters IIIa and IIIb are shown to be capable of undergoing homopolymerization. Heating the molten esters with small amounts of tert-butyl peroxide at 200° C gives polymers, infusible and undecomposed at 280° C, and insoluble in boiling dimethylformamide, dioxane, acetone, benzene, and other organic solvents.

The IR spectra of the monomers and polymers had absorption bands corresponding to C—O, > C=O, and C—O—C groups. The spectra of the polymers lack bands characteristic of the C≡C and ≡C—H groups. Table 2 gives the most characteristic IR spectrum data of monomers and polymers.

Experimental

9-Ethylcarbazole-(IIa), 9-n-butylcarbazole-(IIb), and 9-isoamylcarbazole-3, 6-dicarbonyl chloride (IIc). These were prepared from the corresponding acids Ia-c by the previously described method [1]. The crude diacid chlorides were purified by recrystallization from benzene.

Dipropargyl 9-ethylcarbazole-3, 6-dicarboxylate (IIIa). 3.2 g (0.01 mole diacid chloride IIa was slowly added, with stirring, to a mixture of 20 ml propargyl alcohol and 2 ml pyridine. The mixture was refluxed for 30 min, then cooled, the precipitate filtered off, and recrystallized from EtOH. The dipropargyl esters of IIIb and IIIc were prepared similarly.

Polymerization of dipropargyl 9-ethylcarbazole-3, 6-dicarboxylate (IIIa). A dry tube was charged with 5 g ester, and heated in a Wood's metal bath at 200° C. After it had been there for 5 min, 0.5 ml tert-butyl peroxide was pipetted

---

* For Part XIII see [1].

Table 1

Properties of Diacid Chlorides and Diesters Synthesized

Compound	Mp • C	Formula	C, %		H, %		Cl, %		N, %		Solubility	Yield, %
			Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.		
9-Ethylcarbazole-3, 6-dicarbonyl chloride (IIa)	203	$C_{16}H_{11}Cl_2NO_2$	—	—	—	—	21.92; 22.20	22.19	4.64; 4.30	4.40	Soluble in benzene, dichloroethane, $CHCl_3$, acetone, etc.	80
9-N-Butylcarbazole-3, 6-dicarbonyl chloride (IIb)	218	$C_{18}H_{15}Cl_2NO_2$	—	—	—	—	20.70; 20.90	20.40	4.01; 3.81	4.02		80
9-Isoamylcarbazole-3, 6-dicarbonyl chloride (IIc)	214	$C_{19}H_{17}Cl_2NO_2$	—	—	—	—	20.00; 20.20	19.60	4.10; 4.20	3.86		80
Dipropargyl 9-ethylcarbazole-3, 6-dicarboxylate (IIIa)	183	$C_{22}H_{17}NO_4$	73.63; 73.50	73.54	4.62; 4.90	4.77	—	—	4.09; 4.26	3.90	Soluble in benzene, dioxane, acetone, $CHCl_3$ etc.	75
Dipropargyl 9-n-butyl-carbazole-3, 6-dicarboxylate (IIIb)	125	$C_{24}H_{21}NO_4$	74.49; 74.63	74.41	5.59; 5.70	5.42	—	—	3.70; 3.75	3.62		73
Dipropargyl 9-isoamylcarbazole-3, 6-dicarboxylate (IIIc)	128	$C_{25}H_{23}NO_4$	74.71; 75.08	74.81	5.55; 5.64	5.73	—	—	3.54; 3.60	3.49		73

Table 2

Vibration Frequencies of Individual Bands in the IR Spectra of Monomers and Polymers

Compound number	Vibration frequencies of bonds, cm^{-1}				
	C≡C	≡C—H	C—O	>C=O	C—O—C
IIIa	2135	3275; 3285	1147	1706	1099; 1085
Polymer IIIa	—	—	1147	1712	1096; 1079
IIIb	2127	3259; 3290	1147	1717; 1705	1096; 1066
IIIc	2130	3270; 3285	1147	1707	1095
Polymer IIIc	—	—	1147	1715	1088

into the bottom, the tube corked, and the mixture kept in the bath at the same temperature for 4 hr. After an hour the mixture ceased to be liquid and solidified. After 4 hr the contents were cooled and the tube broken. The brown cylindrical block was powdered and 3 g of the powdered polymer extracted for 10 hr with dioxane in a Soxhlet apparatus. After drying, the extracted sample was weighed, and its weight found to be the same as that of the starting powder. Mp > 280° C. Found: C 72.63, 73.00; H 4.76, 4.97; N 3.81, 3.90%. Calculated for $C_{22}H_{17}NO_4$: C 73.54; H 4.77; N 3.90%.

Polymerization of dipropargyl 9-isoamylcarbazole-3,6-dicarboxylate (IIIc). This and the working up of the product were carried out similarly. Weight loss on extraction was 0.5%. Mp > 280° C. Found: C 74.16, 74.30; H 5.95, 5.90; N 3.69, 3.90%. Calculated for the $C_{25}H_{23}NO_4$ unit: C 74.81; H 5.73; N 3.49%.

The IR absorption spectra of the dipropargyl esters and polymers obtained from them, were measured with a UR-10 spectrophotometer, in vaseline (700–1800 cm^{-1}) and perfluorohydrocarbon (1800–3500 cm^{-1}).

REFERENCES

1. N. D. Negodyaev and Z. V. Pushkareva, KhTS, 46, 1966.
2. A. M. Sladkov, V. V. Korshak, and A. G. Makhsumov, Izv. AN SSR, OKhN, 1343, 1963.
3. V. V. Korshak, A. M. Sladkov, and A. G. Makhsumov, Uzb. khim. zh., 1, 67, 1964.

6 March 1965

Kirov Ural Polytechnic Institute, Sverdlovsk