SYNTHESIS OF NEW FLUORENE DERIVATIVES

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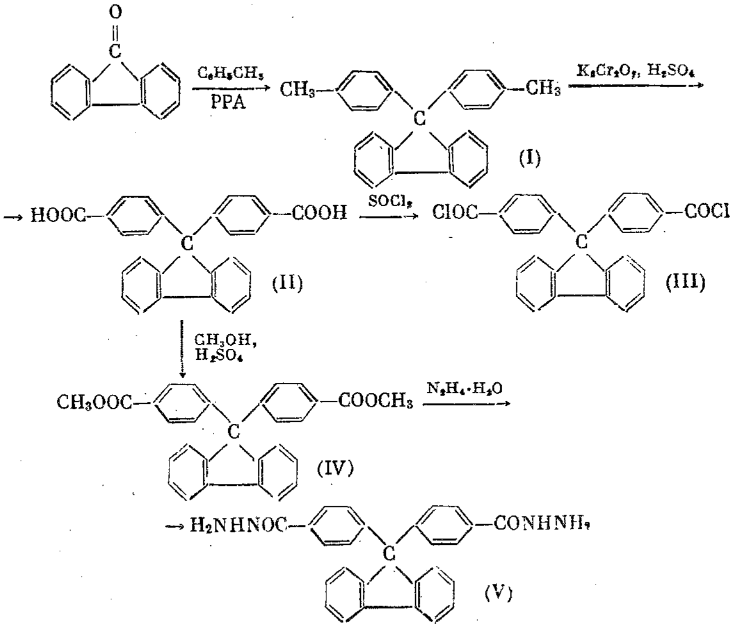
Methods are known for the preparation of such aromatic bifunctional fluorene derivatives as 9,9-bis-(4-hydroxyphenyl)fluorene [1] and 9,9-bis-(4-aminophenyl)fluorene [2]. The synthesis of 9,9-diphenylfluorene is also described [3-5].

The present paper is devoted to the synthesis of 9,9-ditolylfluorene (I), 9,9-bis-(4-carboxyphenyl)-fluorene (II), and its acid chloride (III), dimethyl ester (IV), and dihydrazide (V) by the following scheme



To synthesize (I) we used the acid-catalyzed condensation of ketones with aromatic compounds. As the catalyst we used HCl, $AlCl_3$ or polyphosphoric acid (PPA). Only when the condensation was run in PPA medium were we able to obtain (I) in ~30% yield. To oxidize (I) we used a sulfuric acid solution of potassium dichromate at 270-280°C [6], in which connection (II) was obtained in good yield.

The 9,9-bis-(4-carboxyphenyl)fluorene derivatives were synthesized in the same manner as the corresponding known aromatic dicarboxylic acid derivatives. Acid chloride (III) was obtained by refluxing (II) with $SOCl_2$. The dimethyl ester (IV) was obtained by the esterification of (II) with methanol in the presence of conc. H_2SO_4. Dihydrazide (V) was synthesized from the dimethyl ester (IV) by refluxing with hydrazine hydrate in methanol.

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EXPERIMENTAL METHOD

9,9-Ditolylfluorene. A mixture of 36.0 g (0.2 mole) of fluorene, 64.0 ml (0.6 mole) of absolute toluene, and 700 g of PPA was heated at 140° (in the bath) for 5 h, cooled to 80°, and poured into 4 liters of ice water. The PPA was neutralized by adding $NaHCO_3$. The obtained precipitate was filtered, washed on the filter with water, then with 700 ml of ethanol, and dried in the air at 60°. Then the product was extracted with 300 ml of glacial CH_3COOH and dried at 80°. The yield after extraction was 19.6 g (28%), mp 164-165° (from ethanol). Found: C 93.58; H 6.35%. $C_{27}H_{22}$. Calculated: C 93.60; H 6.40%.

9,9-Bis-(4-carboxyphenyl)fluorene (II). Into a rocking 0.5-liter autoclave were charged 12 g of 9,9-bis-4-(tolyl)fluorene, 21 g of $K_2Cr_2O_7$, 2 ml of H_2SO_4 (94%), and 180 ml of water. The oxidation was run at 270-280° for 5 h. The reaction mass was dumped, and the aqueous solution of the K salt of the acid was filtered from the Cr_2O_3 and acidified with HCl solution. The obtained precipitate was filtered and washed with water until neutral. The obtained acid was dried at 120°. The yield of (II) was 9.8 g (69%), mp 345-347° (from ethanol); acid number = 196 mg of NaOH/g of acid (theory 197). Found: C 79.38; H 4.70%. $C_{27}H_{18}O_4$. Calculated: C 79.79; H 4.46%.

Acid Chloride of 9,9-Bis-(4-carboxyphenyl)fluorene (III). A mixture of 4.0 g of 9,9-bis-(4-carboxyphenyl)fluorene and 7.0 ml of $SOCl_2$ was refluxed until all of the dicarboxylic acid had dissolved (~10 h). Then the excess $SOCl_2$ was distilled off and the acid chloride was recrystallized from dichloroethane. The yield of (III) was 3.6 g (82%), mp 155-157°. Found: C 73.15; H 3.62; Cl 15.83%. $C_{27}H_{16}Cl_2O_2$. Calculated: C 73.16; H 3.64; Cl 15.99%.

Dimethyl Ester of 9,9-Bis-(4-carboxyphenyl)fluorene (IV). A mixture of 3.0 g of 9,9-bis-(4-carboxyphenyl)fluorene, 10 ml of absolute methanol, and 0.1 ml of conc. H_2SO_4 was refluxed for 10 h. The precipitate obtained on cooling was filtered, washed with chilled water, and dried at ~80°. Yield 3.0 g (94%), mp 178-180°. Found: C 80.10; H 5.07%. $C_{29}H_{22}O_4$. Calculated: C 80.17; H 5.10%.

Dihydrazide of 9,9-Bis-(4-carboxyphenyl)fluorene (V). A mixture of 3.6 g of the methyl ester of 9,9-bis-(4-carboxyphenyl)fluorene, 25 ml of methanol, and 10 ml of hydrazine hydrate was refluxed for 20 h. The precipitate obtained on cooling was filtered, washed with water, and recrystallized from 400 ml of aqueous ethanol. The yield of dihydrazide (V) was 3.2 g (89%), mp 295-296°. Found: C 74.48; H 5.20; N 12.91%. $C_{27}H_{22}N_4O_2$. Calculated: C 74.64; H 5.20; N 12.89%.

CONCLUSIONS

9,9-Ditolylfluorene was synthesized by the condensation of fluorenone with toluene in polyphosphoric acid medium, the oxidation of which gave 9,9-bis-(4-carboxyphenyl)fluorene. The acid chloride, dimethyl ester, and dihydrazide of 9,9-bis-(4-carboxyphenyl)fluorene were synthesized.

LITERATURE CITED

1. V. V. Korshak, S. V. Vinogradova, V. A. Pankratov, A. P. Suprun, and V. V. Golubev, USSR Patent 172,775 (1964); Byull. Izobr., No. 14, 22 (1965).
2. British Patent 467,824 (1935); C. A., 31, 8944 (1937).
3. F. Ulmann and R. Wurstenberger, Ber., 38, 4105 (1905).
4. E. Khotinsky and R. Patzewitch, Ber., 42, 3106 (1909).
5. W. E. Bachman, J. Am. Chem. Soc., 52, 3287 (1930).
6. V. V. Korshak, S. V. Vinogradova, and S. N. Salazkin, USSR Patent 192,791 (1966); Byull. Izobr., No. 6, 23 (1967).