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SYNTHESIS OF 9-ALKYLCARBAZOLE-3,6-DICARBOXYLATE DIPHENYL ESTERS

N. D. Negodyaev, G. D. Mel'nikov, and Z. V. Pushkareva

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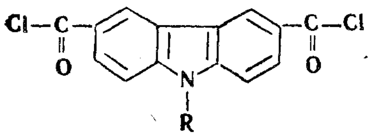
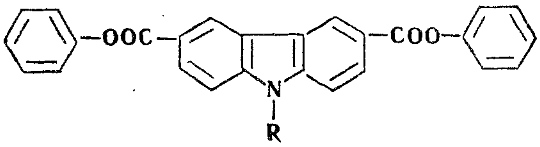
Diphenyl esters of dicarboxylic acids are of interest as starting materials for synthesizing thermostable polymers with chains containing heterocyclic rings [1, 2]. Diphenyl esters of 9-alkylcarbazole-3,6-dicarboxylic acids, having the formula B, have now been prepared by reacting dicarbonyl chlorides of acids, of formula A, with phenol, using the method described in [3], the yields being 73-75% theory.



A

Ia $R=C_2H_5$
Ib $R=n\text{-}C_4H_9$
Ic $R=i\text{-}C_5H_{11}$



B

IIa $R=C_2H_5$
IIb $R=n\text{-}C_4H_9$
IIc $R=i\text{-}C_5H_{11}$

Carbonyl chlorides of acids Ia-c have previously been described [4, 5]. Diphenyl 9-ethylcarbazole-3,6-dicarboxylate (IIa), colorless fine crystals, crystallizable from benzene, mp 204° C (decomp). Found: C 77.35; H 4.74; N 3.07%. Calculated for $C_{28}H_{21}NO_4$: C 77.24; H 4.82; N 3.21%. Diphenyl 9-n-butylcarbazole-3,6-dicarboxylate (IIb), mp 203-204° C (ex benzene). Found: C 77.83; H 5.62; N 3.10%. Calculated for $C_{30}H_{25}NO_4$: C 77.75; H 5.40; N 3.02%. Diphenyl 9-isoamylcarbazole-3,6-dicarboxylate (IIc), mp 175-176° C (ex benzene). Found: C 78.30; H 5.72; N 3.13%. Calculated for $C_{31}H_{27}NO_4$: C 77.99; H 5.66; N 2.93%.

The esters were readily soluble in many organic solvents.

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Kirov Ural Polytechnic Institute

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SYNTHESIS OF THIONAPHTHENO [3,2-b] PYRROLE

O. P. Shkuro and V. P. Mamaev

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The interest shown in the preparation of new heterocyclic systems, and functional derivatives of them, led us to synthesize a new condensed ring system, which included the thionaphthene and pyrrole ring systems.

Condensation of 3-nitrothionaphthen-2-aldehyde, which we previously synthesized [1], with nitromethane in the presence of KOH gave β-hydroxyl-β-(3-nitrothionaphthenyl-2)nitroethane (I), $C_{10}H_8N_2O_5S$, mp 141-142° C (ex MeOH). Heating I in Ac_2O in the presence of fused NaOAc gave 3-nitro-2-(ω-nitrovinyl) thionaphthene (II), $C_{10}H_6N_2O_4S$, mp 165-166.5° C (ex MeOH-dioxane 3:1). Unlike I, the IR spectrum of II had bands at 950-980 cm^{-1} (C-H of vinyl group) and 1630 cm^{-1} (C=C conjugation). Reductive cyclization, using conditions repeatedly employed in synthesizing various indoles [2], gave thionaphtheno [3,2-b] pyrrole (III), isolated from the reaction products by preparative thin-layer chromatography on alumina oxide (activity III), the mobile phase being benzene. Thionaphtheno [3,2-b] pyrrole (III) formed colorless needles mp 120-121° C (ex isooctane). Found: N 7.80, 7.86%;