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

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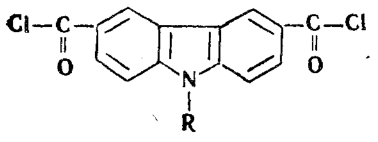
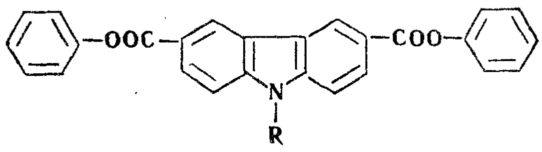
Diphenyl esters of dicarboxylic acids are of interest as starting materials for synthesizing thermostable polymers with chains containing heterocyclic rings [1, 2]. Diphenyl esters of 9-alkylcarbazole-3, 6-dicarboxylic acids, having the formula B, have now been prepared by reacting dicarbonyl chlorides 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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UDC 547.735 + 547.759

SYNTHESIS OF THIONAPHTHENO [3, 2-b] PYRROLE

O. P. Shkuro and V. P. Mamaev

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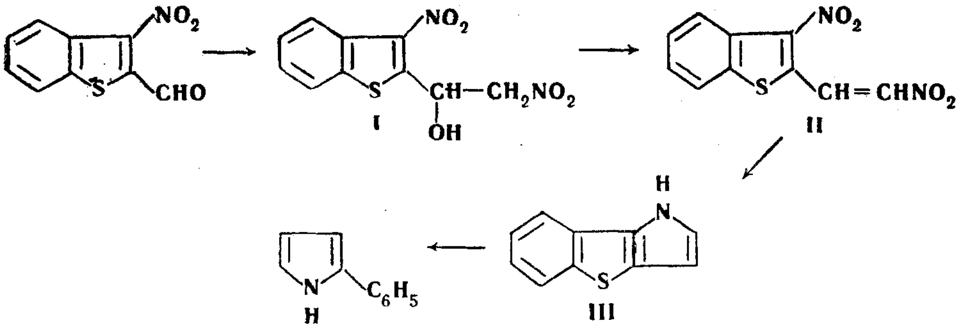
The interest shown in the preparation of new heterocyclic systems, and functional derivatives of them, led us to synthesize a new condensed ring system, which included the thionaphthene and pyrrole ring systems.

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%;

M 173.* Calculated $C_{10}H_7NS$: N 8.08%; M 173. UV spectrum (EtOH), λ_{max} mμ (lg ε): 250 (4.28), 262 (4.33), 286 (4.13). IR spectrum (KBr), ν cm^{-1}: 3410 (indole N–H). The properties of this heterocyclic system closely resemble



those of thieno [3, 2-b] pyrrole [3]. III gives a dark blue color with Erlich's reagent. It decomposes rapidly when stored in the light. It readily sublimes in a vacuum. The structure of III is checked by reductive desulfurization with Raney Ni to 2-phenylpyrrole, identified by mp, IR spectrum, and behavior on chromatographing with an authentic specimen [4].

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*Molecular weight found mass-spectrometrically.

UDC 547.722

REACTION OF FURAN AMINES WITH ACROLEIN

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The present work represents a first synthesis of furan derivatives with carbonyl and amino groups at positions 2 and 5. To achieve the goal, a study was made of the reaction of various N-substituted furan amines with acrolein in the presence of AcOH. It was shown that furan amines with a tertiary amino group at position 3 in the side chain react with acrolein to give the corresponding furan 2, 5-substituted aldehydoamines. For example, 24 g (0.4 mole) AcOH was added to a mixture of 25 g (0.121 mole) 2-[3'-(methyl-β-cyanoethylamino) butyl] furan [bp 121° C (3 mm); n_D^{20} 1.4815; d_4^{20} 1.0040. Found: C 69.48, 69.48; H 8.65, 8.49%. Calculated for $C_{12}H_{18}N_2O$: C 69.86; H 8.79%], 16 g (0.286 mole) acrolein, and 0.2 g hydroquinone. After stirring for 2 hr, the products were diluted with water, neutralized with $NaHCO_3$, and extracted with ether. After distilling off the ether, there was obtained 8 g (26%) 2-(3'-oxopropyl)-5-[3'-methyl-β-cyanoethylamino)butyl] furan, bp 124°C (3.5 mm); n_D^{20} 1.4850; d_4^{20} 1.0193. Found: C 68.72, 68.80; H 8.42, 8.51%. Calculated for $C_{15}H_{22}N_2O_2$: C 68.66; H 8.45%.

It was shown that under these conditions, N-substituted furan amines, with the amino group next to the furan ring, does not react with acrolein. For example, N-methyl (β-cyanoethyl) furfurylamine [bp 101° (3 mm); n_D^{20} 1.4825; d_4^{20} 1.0335. Found: C 65.40, 65.20; H 7.56, 7.35%. Calculated for $C_9H_{12}N_2O$: C 65.82; H 7.36.] is unchanged on treatment with acrolein.

There is complete polymerization of furan amines with a hydrogen atom at the nitrogen atom, e.g., 2-[3'-