REACTION OF INDOLYLPYRYLIUM SALTS WITH SOME HYDRAZINE DERIVATIVES

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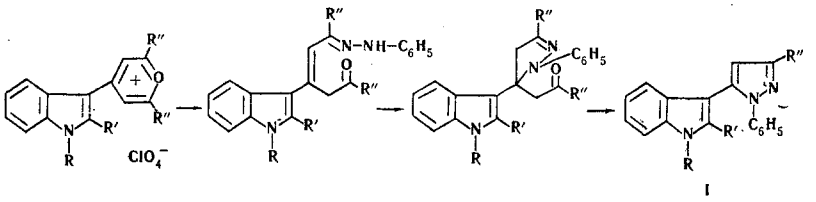
The reaction of 4-(3-indolyl)pyrylium salts with phenylhydrazine in alcohol gives 5-(3-indolyl)pyrazoles. The pyrylium salts react with acid hydrazides in refluxing dimethylformamide to give monohydrazones of the pseudobases of these salts (unsaturated 1,5-diketones).

The literature contains information relative to the preparation of pyrazolylindoles from β-diketones of the indole series [1, 2]. With the idea of synthesizing these compounds from more accessible substances, we studied the reaction of indolylpyrylium salts with hydrazine derivatives, since it is known that pyrylium salts react readily with phenylhydrazine to give pyrazoles [3]. We were able to show that pyrazolylindoles I are formed by refluxing indolylpyrylium perchlorates with excess phenylhydrazine in a small volume of alcohol.



I

R=H, CH_3, $CH_2C_6H_5$; R′=H, CH_3; R″=C_6H_5

It is known [4] that 2,4,6-trimethylpyrylium perchlorate reacts with benzhydrazide in acetic acid to give a 1-benzoylaminocollidinium salt. We demonstrated that the pyrylium salt reacts differently with hydrazides in refluxing dimethylformamide. For example, instead of the expected N-benzoylpyrazole (III), 2,6-diphenyl-4-(1-benzyl-3-indolyl)pyrylium perchlorate (II) gives a compound to which we assign the 1,5-diphenyl-3-(1-benzyl-3-indolyl)-2-pentene-1,5-dione mono(benzoylhydrazone) (IV) structure. Intense amide absorption bands at 3400-3500, 1640, and 1340 cm^{-1} are observed in its IR spectrum. A band of lower intensity at 1600 cm^{-1} is characteristic for the C=C bond in α,β-unsaturated ketones with a trans configuration [5]. Substances of the IV type were also obtained by the reaction of isonicotinic acid hydrazide with 2,6-diphenyl-4-(1-methyl-3-indolyl)pyrylium, 2,4,6-triphenylpyrylium, and 2-methyl-4,6-diphenylpyrylium perchlorates.

When hydrazone IV is refluxed in acetic acid, benzhydrazide is cleaved to give an unsaturated 1,5-diketone (V), the structure of which was proved by the IR spectrum and by comparison with a sample of known structure obtained from perchlorate II and sodium acetate in aqueous alcohol.

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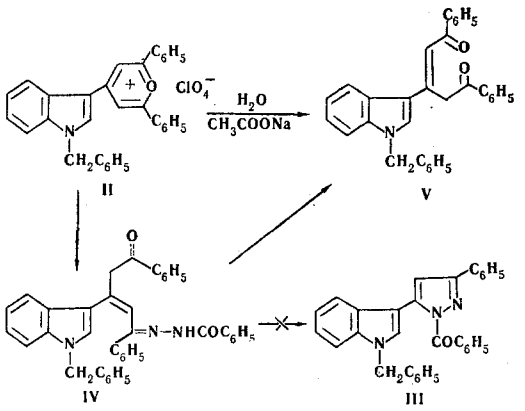

EXPERIMENTAL

5-(3-Indolyl)pyrazoles. A 0.45 g sample of phenylhydrazine was added to a suspension of 0.01 mole of indolylpyrylium perchlorate in 50-100 ml of alcohol, and the mixture was refluxed for 30-60 min until the solids had dissolved. The solution was cooled to give a crystalline precipitate, which was removed by filtration and dissolved in benzene. The benzene solution was washed several times with water, dried with sodium sulfate, and concentrated to a small volume. The solution was cooled to give a precipitate of the corresponding pyrazole derivative.

1,3-Diphenyl-5-(1-benzyl-3-indolyl)pyrazole. This compound was obtained in 61% yield and had mp 164°C. UV spectrum(in alcohol): λ_{max} 226, 240, and 285 nm, log ε 4.48, 4.45, and 4.09. Found: C 84.4; H 5.5; N 9.6%. $C_{30}H_{23}N_3$. Calculated: C 84.7; H 5.4; N 9.9%.

1,3-Diphenyl-5-(1-methyl-3-indolyl)pyrazole. This compound was obtained in 50% yield and had mp 97°. UV spectrum (in alcohol); λ_{max} 229, 240, and 288 nm, log ε 4.32, 4.33, and 3.89. Found: C 78.5; H 5.9; N 11.9%. $C_{24}H_{19}N_3 \cdot H_2O$. Calculated: C 78.5; H 5.7; N 11.4%.

1,3-Diphenyl-5-(1,2-dimethyl-3-indolyl)pyrazole. This compound was obtained in 78% yield and had mp 145°. UV spectrum (in alcohol): λ_{max} 205 and 291 nm, log ε 5.02 and 4.38. Found: C 81.0; H 6.1; N 11.6%. $C_{25}H_{21}N_3 \cdot 1/2\,H_2O$. Calculated: C 80.6; H 5.9; N 11.3%.

1,3-Diphenyl-5-(2-methyl-3-indolyl)pyrazole. This compound was obtained in 62% yield and had mp 186°. UV spectrum (in alcohol); λ_{max} 229, 288, and 337 nm, log ε 4.40, 4.05, and 4.11. Found: C 80.5; H 5.8; N 11.8%. $C_{24}H_{19}N_3 \cdot 1/2H_2O$. Calculated: C 80.4; H 5.6; N 11.7%.

1,5-Diphenyl-3-(1-benzyl-3-indolyl)-2-pentene-1,5-dione Mono(benzoylhydrazone) (IV). A mixture of 0.001 mole of 2,6-diphenyl-4-(1-benzyl-3-indolyl)pyrylium perchlorate and 0.002 mole of benzhydrazine in a small volume of purified dimethylformamide was refluxed gently for 1 h, cooled, and poured into water. The reaction product was isolated in the usual way and crystallized from benzene. The characteristics of these compounds and other arylhydrazones obtained by the same route are presented in Table 1.

TABLE 1. $C_6H_5C(=NNHCOR)CH=CR''CH_2COR'$

R	R′	R″	Mp, °C	IR spectrum (ν_{max}), cm^{-1}	Empirical formula	N, % found	N, % calc.	Yield, %
Phenyl	Phenyl	1-Benzyl-3-indolyl	215	3500—3400, 1640, 1600, 1550, 1420, 1340	$C_{39}H_{31}N_3O_2$	7,5	7,3	50
4-Pyridyl	Phenyl	1-Methyl-3-indolyl	239	3500—3400, 1620, 1600, 1540, 1420, 1340	$C_{32}H_{26}N_4O_2$	11,5	11,2	48
4-Pyridyl	Phenyl	Phenyl	204	3500—3400, 1640, 1600, 1550, 1430, 1345	$C_{29}H_{23}N_3O_2$	9,8	9,4	58
4-Pyridyl	Methyl	Phenyl	151	3500—3400, 1625, 1600, 1545, 1410, 1355	$C_{24}H_{21}N_3O_2$	11,3	11,0	52

1,5-Diphenyl-3-(1-benzyl-3-indolyl)-2-pentene-1,5-dione (V). A) A solution of 0.3 g of IV in 10 ml of acetic acid was refluxed for 5 h, cooled, and poured into water. The reaction product was isolated in the usual way to give 74% of a product with mp 195° (from benzene). Found: C 83.5; H 5.5; N 2.9%. $C_{32}H_{25}NO_2$. Calculated: C 84.4; H 5.4; N 3.1%.

B) 2,6-Diphenyl-4-(1-benzyl-3-indolyl)pyrylium perchlorate was refluxed for 1 h in a small volume of aqueous alcohol with excess sodium acetate to give 84% of V.

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