PYRIMIDO[2,1-*a*]ISOQUINOLINIUM SALTS

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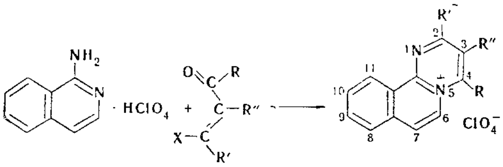
1-Aminoisoquinolinium perchlorate reacts with β-diketones and β-chlorovinyl ketones to give pyrimido[2,1-*a*]isoquinolinium salts that form polymethine dyes.

Just as protic salts of α-aminoazaheterocycles react with β-chlorovinyl ketones to give condensed pyrimidinium salts with a quaternary-bridge nitrogen atom [1, 2], 1-aminoisoquinolinium perchlorate (I) reacts with β-diketones and β-chlorovinyl ketones to give the previously unknown pyrimido[2,1-*a*]isoquinolinium salts (II, Table 1).



I

II

X = OH, Cl

While isoquinoline I reacts with β-chlorovinyl ketones under mild conditions, the reaction with β-diketones proceeds only when the components are heated to 260°C.

The PMR spectra confirm the formation of a condensed ring with a quaternary-bridge nitrogen atom. Thus, the signal of an aromatic proton at 7.5 ppm is observed in the PMR spectra when R″ = H. The methyl groups in the 2- and 4-positions of IIa-c have chemical shifts of 2.6 and 2.7 ppm, respectively, while those in the 3-position have chemical shifts of 3−2.3 ppm. The 6-H proton gives a doublet at 8.2 ppm with J = 7.5 Hz, while the 7-H doublet is superimposed on the multiplet of phenylene protons at 7.7-7.9 ppm. The multiplet at 9.0-9.1 ppm, which is related to 11-H, is also a confirmation of structure II; the strong 11-H paramagnetic shift is explained by coupling with the electron pair of $N_{(1)}$, which is rigidly fixed by the pyrimidine ring.

Benzoylacetone reacts with aminoisoquinoline I to give one isomer, the structure of which (IId) is confirmed mainly by the character of the phenyl signal, which appears as a singlet at 7.31 ppm; this corresponds to a phenyl group in the α-position relative to the bridge nitrogen atom [3-5]. Methyl and phenyl β-chlorovinyl ketones react with I to give one isomer (IIe and IIf), the structures of which are confirmed by the PMR spectra. The chief factor in the spectrum of IIe that confirms its structure is $J_{2,3} = 5$ Hz [4, 5] (δ 9.00, 2-H; 7.64, 3-H; 2.78 ppm, 4-CH_3); in the case of IIf, not only this factor ($J_{2,3} = 5$ Hz) but also the phenyl singlet at 7.32 ppm serves as a confirmation of its structure.

All salts II, except for IIf, give polymethine dyes under the usual conditions. Thus, red styryl IIg was obtained from IId and p-dimethylaminobenzaldehyde in acetic anhydride; IIa reacts with p-dimethylaminobenzaldehyde at both methyl groups and gives a mixture of styryl derivatives (according to the PMR spectrum, in which both unchanged methyl groups are observed).

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TABLE 1. Pyrimido[2,1-*a*]isoquinolinium Salts

Compound	R	R′	R″	mp, °C	Empirical formula	Cl, %		Yield, %
						found	calc.	
IIa	CH_3	CH_3	H	240	$C_{14}H_{13}ClN_2O_4$	11,6	11,5	54
IIb	CH_3	CH_3	CH_3	246	$C_{15}H_{15}ClN_2O_4$	11,1	10,9	41
IIc	CH_3	CH_3	C_2H_5	241	$C_{16}H_{17}ClN_2O_4$	10,7	10,7	24
IId	C_6H_5	CH_3	H	232	$C_{19}H_{15}ClN_2O_4$	9,5	9,6	40
IIe	CH_3	H	H	210	$C_{13}H_{11}ClN_2O_4$	12,0	12,0	70
IIf	C_6H_5	H	H	251	$C_{18}H_{13}ClN_2O_4$	10,0	9,9	63
IIg	C_6H_5	A*	H	>300	$C_{28}H_{24}ClN_3O_4$	7,0	7,1	85

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*A $=CH=CH-C_6H_4-N(CH_3)_2$-p.

EXPERIMENTAL

The PMR spectra of 15-20% solutions of the compounds in trifluoroacetic acid were recorded with a Tesla BS487B spectrometer (80 MHz) with hexamethyldisiloxane as the standard. The spectrum of an alcohol solution of the dye was recorded with an SF-10 spectrophotometer.

Condensation of 1-Aminoisoquinoline with β-Diketones. A mixture of 0.005 mole of I, 0.008-0.01 mole of the β-diketone, and 2 ml of acetic acid was heated in a sealed ampul at a bath temperature of 260° for 2 h (3 h for benzoylacetone). The mixture was then cooled and washed with ether, and II were recrystallized from water (IIa, d), ethanol (IIc), or acetic acid (IIb) with the addition of activated charcoal (see Table 1).

Condensation of 1-Aminoisoquinoline with β-Chlorovinyl Ketones. A 0.005-mole sample of I, 0.008 mole of methyl or phenyl β-chlorovinyl ketone, and 5 ml of acetic acid were heated on a water bath for 5-10 min, after which it was allowed to stand at room temperature for 24 h. The resulting precipitate was separated and recrystallized from methanol.

4-(4-Dimethylaminostyryl)-2-phenylpyrimido[2,1-*a*]isoquinolinium Perchlorate (IIg). A mixture of 0.30 g (0.0008 mole) of IId, 0.17 g (0.015 mole) of p-dimethylaminobenzaldehyde, and 2 ml of acetic anhydride was heated at 120-125° for 10 min. It was then cooled, and the dye crystals were separated and recrystallized from ethanol. UV spectrum: λ_{max} 558 nm (log ε 4.71).

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