

REACTION OF PYRYLIUM SALTS WITH INDOLINE

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It is well known that N,N-disubstituted aromatic amines are formed by the reaction of 2-methylpyrylium salts with secondary amines [1, 2]. We have shown that indoline also enters into this reaction to form N-arylindolines that are difficult to synthesize by other paths. The reaction proceeds by 2-h refluxing of a mixture of 1 mole of 2-methylpyrylium salt with 2 moles of indoline in benzene with stirring and subsequent removal of the solvent and crystallization of the product from acetone. We have isolated the products of the reaction of indoline with 2-methyl-4,6-diphenyl-, 2-methyl-4,6-di(p-tolyl)-, and 2-methyl-4,6-di(α -thienyl)pyrylium perchlorates (Table 1). The IR spectra of these compounds contain all the gamma frequencies of the benzene ring, but the intense absorption band of the NH group, which appears at 3400 cm^{-1} in the spectrum of the starting indoline, is absent. The corresponding N-arylindoles can be obtained by dehydrogenation of these compounds. For example, N-(3,5-diphenylphenyl)indole with mp 144-146° was obtained in 57% yield by dehydrogenation of diphenyl derivative I with chloroaniline in xylene. Found %: C 89.95; H 5.38; N 4.05. $\text{C}_{26}\text{H}_{19}\text{N}$. Calculated %: C 89.91; H 5.47; N 4.03.

Products of reaction of indoline with 2,4,6-trimethyl- and 2-methyl-4,6-di(p-anisyl)pyrylium perchlorates could not, however, be obtained. It is likely that in the 2 position of the pyrylium ring of these salts the necessary "concentration" of positive charge sufficient for attack by a base of such strength as indoline is not created, for it is precisely this position that is necessary for subsequent cyclization.

Indoline reacts differently with alkoxyppyrylium salts. For example, it forms 2,6-dimethyl-4-(1-indolinyl)pyrylium perchlorate with mp 247° in 92% yield on reaction with 2,6-dimethyl-4-methoxyppyrylium perchlorate. The IR spectrum of this compound does not contain absorption bands from carbonyl and secondary amino groups but does contain the absorption bands of the ClO_4^- anion at 1100 cm^{-1} and of the $\text{C}=\text{C}$ group at 1660 cm^{-1} . This salt is converted to 2,6-dimethyl-4-(1-indolinyl)pyridine (IV) by refluxing with excess ammonium carbonate in alcohol or excess ammonium acetate in acetic acid. The IR spectrum does not contain absorption bands of secondary amino and carbonyl groups but does contain a band at 1590 cm^{-1}

TABLE 1.

Comp.	R	X	mp	Empirical formula	N, %	
					found	calc.
I	Phenyl	CH	171—172	$\text{C}_{26}\text{H}_{21}\text{N}$	4.03	4.20
II	p-Tolyl	CH	156—158	$\text{C}_{26}\text{H}_{25}\text{N}$	3.63	3.73
III	α -Thienyl	CH	146—148	$\text{C}_{22}\text{H}_{17}\text{NS}_2$	3.78	3.90
IV	Methyl	N	117	$\text{C}_{18}\text{H}_{16}\text{N}_2$	12.31	12.50

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