LETTERS TO THE EDITOR

REACTION OF 9-(AMINOARYL)ACRIDINIUM SALTS WITH HYDRAZINES

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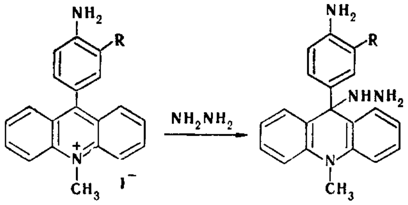
It is known that hydrazine reduces acridinium salts, giving 9,9'-bi(9,10-dihydroacridinyl)s [1]. We have found that 9-(aminoaryl)acridinium salts (Ia-d) are not reduced under these conditions. Instead, the addition of hydrazine takes place with the formation of 9-(aminoaryl)-9-hydrazino-10-methyl-9,10-dihydroacridines (IIa-d).



I a-d II a-d

I,II a R=H; b R=CH_3, c R=NH_2; d R=OH

The absorption spectra of compounds (II) in chloroform have the broad band with λ_{max} 290 nm that is characteristic for dihydroacridines. In proton-donating solvents (C_2H_5OH, i-C_3H_7OH, CH_3COOH), compounds (II) dissociate with the cleavage of the C_9-N bond, the splitting off of the hydrazine residue, and the formation of the aromatic structure of an acridinium cation. Thus, in ethanol substance (II) exists predominantly in the form of acridinium cations (λ_{max} 255, 355, 560 nm) and in chloroform in the dihydroacridine form (λ_{max} 290 nm). On dissociation, the hydrazine residue that splits off apparently captures a proton from the ethanol with the formation of hydrazine and ethoxide ion. A confirmation of this is the fact that compounds (II) are not cleaved in aprotic solvents (chloroform, benzene, DMFA). The dissociation of dihydroacridines (products of the addition of substances with active methylene groups to acridinium salts) under the action of ethanol is known [2].

Amines such as morpholine, piperidine, butylamine, etc., react with (I) in the same way as hydrazine. A similar case of the addition of ammonia to quaternary salts of 9-alkyl- and 9-arylacridines has been described previously [3].

9-(4-Aminoaryl)-9-hydrazino-10-methyl-9,10-dihydroacridines (II, Table 1). A mixture of 0.005 mole of a compound (I) and 0.1 mole of hydrazine was boiled for 5 min. Then it was cooled and was poured into 30 ml of water, and the precipitate that deposited was filtered off and crystallized from benzene (IIa) or xylene (IIb-d).

TABLE 1. 9-Hydrazino-9,10-dihydroacridines (II)

Compound	mp, °C	Empirical formula*	Yield, %
IIa	160	$C_{20}H_{20}N_4$	96
IIb	168	$C_{21}H_{22}N_4$	97
IIc	155	$C_{20}H_{21}N_5$	98
IId	273–275	$C_{20}H_{20}N_4O$	59

*All the compounds had satisfactory elementary analyses.

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9-(4-Dimethylaminophenyl)-10-methyl-9-morpholino-9,10-dihydroacridine. A mixture of 0.5 g (0.0012 mole) of (I) and 2 ml (0.023 mole) of morpholine was stirred at room temperature for 5 min. Then 30 ml of heptane was added and the mixture was filtered. Yield 0.45 g (96%), mp 220°C (from heptane). Found, %: C 77.9; H 7.3; N 10.4. $C_{26}H_{29}N_3O$. Calculated, %: C 78.2; H 7.3; N 10.5.

LITERATURE CITED

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2. F. Kröhnke and L. Honig, Ber., 90, 2215 (1957).
3. H. Decker and P. Becker, Ber., 46, 696 (1913).