UNUSUAL REACTION OF ACRIDINIUM METHIODIDE

FORMATION OF TRIIODIDES ON REACTION

WITH DIALKYLANILINES

O. N. Chupakhin, V. N. Charushin, and I. Ya. Postovskii

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We have found that dialkylanilines containing amino groups with bulky substituents undergo reaction with acridinium methiodide (I) in dimethyl sulfoxide at room temperature in 80 h or in dimethylformamide at 120° with bubbling in air or in the course of 3 h to give deeply colored crystalline II, containing three iodine atoms, instead of the expected 9-[p-(N, N-dialkylamino)phenyl]acridinium iodides [1].

In contrast to the usual products of nucleophilic substitution of hydrogen in iodide I by aniline and dimethyl- and diethylanilines and their derivatives [1], triiodides II are soluble in benzene and chloroform. The electronic spectra of alcohol solutions of triiodides II contain a maximum at 286-289 nm (alcohol solutions of iodine and the I_3^- ion absorb at $\lambda_{\rm max}$ 294 nm [2]) in addition to the absorption bands at 260 and 360 nm typical for acridinium salts. The PMR spectra correspond to structure II. The percentage of I⁻ ions determined by potentiometric titration with AgNO₃ solution was close to the calculated value (14.8%) for IId (14.2%). The results of analysis for C, H, and N (and the determination of the total iodine for IIb and IIc) are in good agreement with the calculated values.

TABLE 1. Iodine Complexes with Acridinium Salts

Compound	R	mp, °C	Electronic spectrum, λ_{max} , nm (log ϵ)	Yield with respect to iodine, %
IIa	C₃H ₇	183—185	260 (5,02), 289 (4,73),	35
IIb	C_4H_9	155—156	360 (4,61), 592 (4,11) 260 (5,01), 288 (4,72), 360 (4,59), 594 (4,13)	52
Ilc	C5H11	156—157	259 (4,92), 288 (4,60), 360 (4,67), 593 (4,18)	37
IId	$CH_2C_6H_5$	137—139	260 (5,05), 286 (4,69), 360 (4,62), 560 (4,16)	90

LITERATURE CITED

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