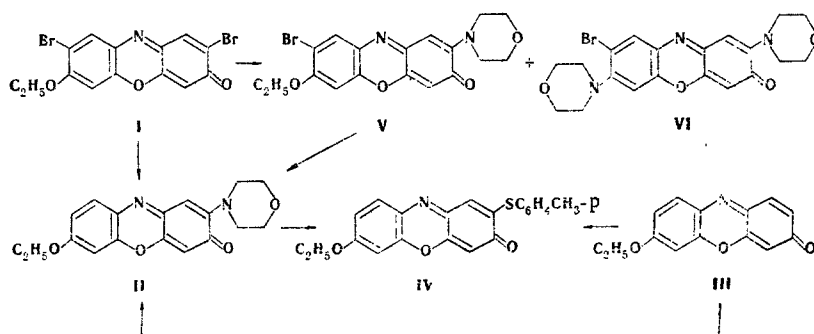


ELIMINATION OF BROMINE DURING THE REACTION OF 2,8-DIBROMO-7-ETHOXY-3-PHENOXAZINONE WITH MORPHOLINE*

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We have established that the reaction of 2,8-dibromo-7-ethoxy-3-phenoxazinone (I) with morpholine without a solvent leads not only to replacement of the bromine in the quinoid ring but also to simultaneous elimination of the second bromine atom in the 8 position to give 2-morpholino-7-ethoxy-3-phenoxazinone (II). The structure of the latter was proved by synthesis from 7-ethoxy-3-phenoxazinone and conversion of II to the known [2] 2-(p-tolylthio) derivative (IV).



The reaction of I with morpholine and morpholine hydrochloride in alcohol does not lead to elimination but rather to nucleophilic substitution of the bromine atom in the quinoid ring to give 2-morpholino-8-bromo-7-ethoxy-3-phenoxazinone (V) and also to replacement of the ethoxy group by a morpholine residue to give small amounts of 2,7-dimorpholino-8-bromo-3-phenoxazinone (VI).

N-Methylmorpholine also reacts with I to give V. Piperidine and aniline react like morpholine. The mechanism of the reaction is being studied.

EXPERIMENTAL

2-Morpholino-7-ethoxy-3-phenoxazinone (II). A 15-ml sample of morpholine was added to 1 g (2.5 mmole) of I, and the mixture was refluxed for 3 h. It was then cooled, and the resulting precipitate was removed by filtration, washed with alcohol, dried, and chromatographed with a column filled with activity III aluminum oxide (elution with chloroform) to give 0.45 g (55%) of orange needles with mp 223-225° (from butanol). Found: C 66.1; H 5.6; N 8.9%. C₁₈H₁₈N₂O₄. Calculated: C 66.3; H 5.6; N 8.6%.

2-Morpholino-8-bromo-7-ethoxy-3-phenoxazinone (V) and 2,7-Dimorpholino-8-bromo-3-phenoxazinone (VI). A 1-g (2.5 mmole) sample of I, 1.9 g (14.4 mmole) of morpholine hydrochloride, and 15 ml of morpholine were suspended in 50 ml of ethanol, and the mixture was refluxed for 3 h. It was then cooled

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and the resulting precipitate was removed by filtration, washed with alcohol, and chromatographed with a column filled with activity III aluminum oxide (elution with chloroform). Evaporation of the first (yellow) fraction gave 0.6 g (60%) of V with mp 240–242° (from butanol). Found: C 53.5; H 4.3; Br 19.7; N 7.1%. $C_{18}H_7BrN_2O_4$. Calculated: C 53.4; H 4.2; Br 19.7; N 6.9%.

Evaporation of the second (brown) fraction gave 0.15 g (15%) of VI. Found: C 53.8; H 4.3; N 9.3%. $C_{20}H_{10}N_3O_4$. Calculated: C 53.8; H 4.5; N 9.5%.

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