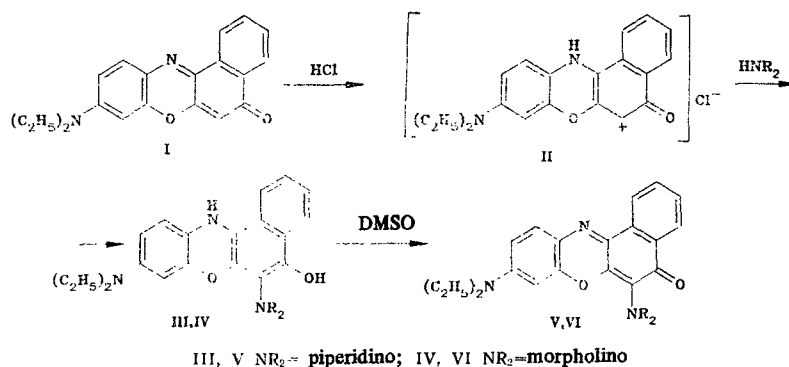


NUCLEOPHILIC ADDITION OF MORPHOLINE AND PIPERIDINE
TO 9-DIETHYLAMINO BENZO[a]PHENOXAZIN-5-ONE

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Although nucleophilic addition to phenoxazines and benzo[a]phenoxazines have been known for a long time [1-3], the addition of nucleophiles to an annealed quinonimine nucleus has not been described. On investigating this reaction with the known laser dyestuff oxazine-17 (I) it was discovered by us that the latter reacted readily in DMSO with piperidine and morpholine in the presence of their hydrochlorides forming the corresponding 6-amino derivatives (V) and (VI) which fluoresced at 610-660 nm and were active agents for lasers based on organic compounds.



Seemingly, protonation of the endocyclic nitrogen atom occurs first with the formation of carbocation (II), which is transformed on interaction with nucleophilic reagents into leuco bases (III) and (IV) oxidized in the DMSO medium to quinonimines (V) and (VI).

The characteristic singlet of the olefinic proton at 6.3 ppm was absent from the PMR spectra of compounds (V) and (VI) but was present in starting material (I), which indicates the addition of the nucleophile at position 6 and corresponds with the data of [4].

Compounds (V) and (VI) were synthesized by boiling benzophenoxazine (I) (10 mmoles) and piperidine or morpholine (0.1 mole) in the presence of their hydrochlorides (50 mmoles) in DMSO (50 ml) for 4 h. The reaction products were isolated by column chromatography on silica gel, eluent was hexane-dioxane (1:2). Yield of compound (V) was 73%, mp 180-181°C, M⁺ 401. Yield of compound (VI) was 51%, mp 177-178°C, M⁺ 403.

The data of elemental analysis corresponded to those calculated.

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