

A NOVEL ONE-STEP SYNTHESIS OF DIBENZO-1,4-DIAZEPINES  
FROM ACRIDINE DERIVATIVES

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During the course of studies on the new synthesis of heterocyclic compounds we found a novel one-step synthesis of dibenzo[b,e]-1,4-diazepines involving a ring expansion from acridine derivatives by their reaction with hydroxylamine-0-sulfonic acid.

We wish to show some typical cases of this reaction in this paper. Substances having a benzodiazepine ring are used as psychotropic drugs and many synthetic methods for them are known. We obtained 5-methyl-dibenzo[b,e]-1,4-diazepine derivatives(II) by the reaction of N-methylacridinium derivatives(I) with hydroxylamine-0-sulfonic acid in absolute methanol containing 30% ammonia for 3 - 4 hours at room temperature. Results of this reaction in typical compounds (Ia-c) are shown in Table I. In the case of Ia, 9-amino-10-methylacridinium iodide (III) was obtained as a by-product in several percent yield.

The structure of II was determined by the alternative four-step synthesis of IIa from 2-chloronitrobenzene and methylaniline as reported in the literature.<sup>1</sup> Structures of IIb and IIc were confirmed from their NMR spectral data and elemental analysis.

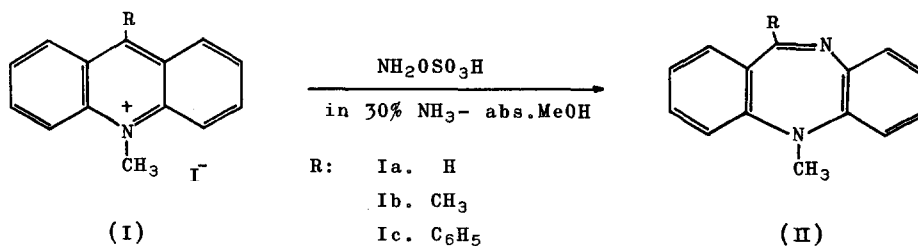

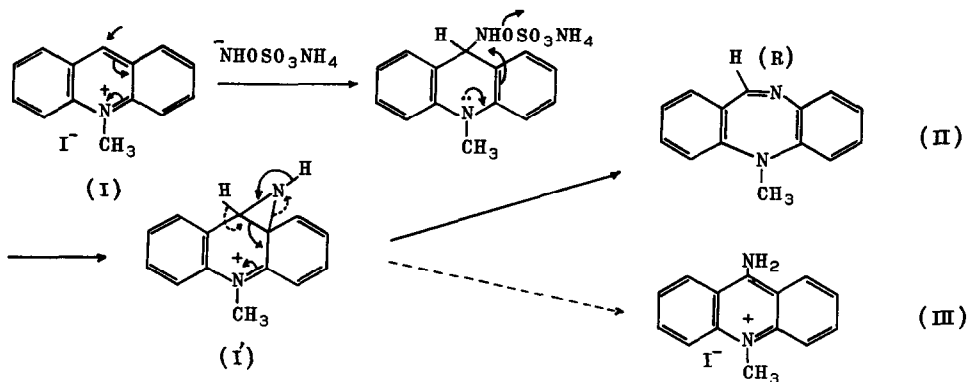


Table I

Compd. No.	R	Appearance	m.p. (°C)	Yield (%)	NMR ( $\tau$ ) in CDCl <sub>3</sub>		
					H—N—	CH <sub>3</sub> —N—	Aromatic ring H
IIa:	H	yellow needles	96 (rept. <sup>1</sup> : 96)	71.5	1.60 (1H, s)	6.80 (3H, s)	2.7-3.4 (8H, m)
IIb:	CH <sub>3</sub>	hygroscopic substance	203-204 (picrate)	17.0		7.40 (3H, s) 6.85 (3H, s)	2.7-3.3 (8H, m)
IIc:		yellow prisms	142 (rept. <sup>2</sup> : 137-138)	18.8		6.78 (3H, s)	2.6-3.1 (11H, m) 2.2-2.4 (2H, m)

The mechanism of this reaction is presumed to be as follows: As the first step, a nucleophilic attack of hydroxylamine-O-sulfonic acid takes place on the 9-position of I and would be followed by formation of an aziridine ring (I') which is converted to II by the ring expansion. Formation of III is elucidated as a result of prototropy different from that to II.

Details on the effect of various ring substituents on this ring expansion and its application will be reported in the near future.



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## REFERENCES

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