

COMPOUNDS RELATED TO ACRIDINE. XI.<sup>1</sup>  
REACTION OF 1,3-DI(9-ACRIDINYL)PROPANE  
WITH p-NITROSO-N,N-DIMETHYLANILINE

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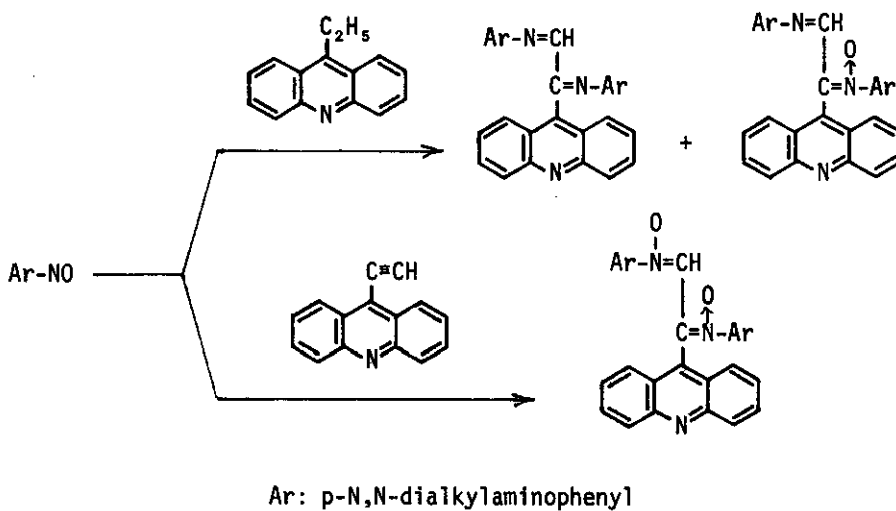
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Although 9-propylacridine (II) did not react with p-nitroso-N,N-dimethylaniline (I) under various conditions, 1,3-di(9-acridinyl)propane (III) reacted with I under the influence of HCl to give the mono-nitrone compound (IV) and cleaved products V-VII, whose relative yields were greatly affected by the reaction conditions.

Previously,<sup>2</sup> we have reported that hydrochloric acid (HCl) is an extremely effective catalyst for the condensation of acridine having an active methyl group with p-substituted nitrosobenzenes, and that the total yield of nitrone and anil as condensation products is fairly good compared with that in the presence of a basic catalyst which is usually employed in the Ehrlich-Sachs re-

action.<sup>3</sup> Moreover, even 9-ethylacridine<sup>4</sup> and 9-ethynylacridine<sup>5</sup> react with two moles of *p*-nitroso-*N,N*-dialkylaniline under the influence of HCl to yield a mixture of 1-(9-acridinyl)-1,2-bis(*p*-*N,N*-dialkylaminophenylimino)ethane and its *N*<sup>1</sup>-oxide, and *N*<sup>1</sup>,*N*<sup>2</sup>-dioxide, respectively, as depicted below.

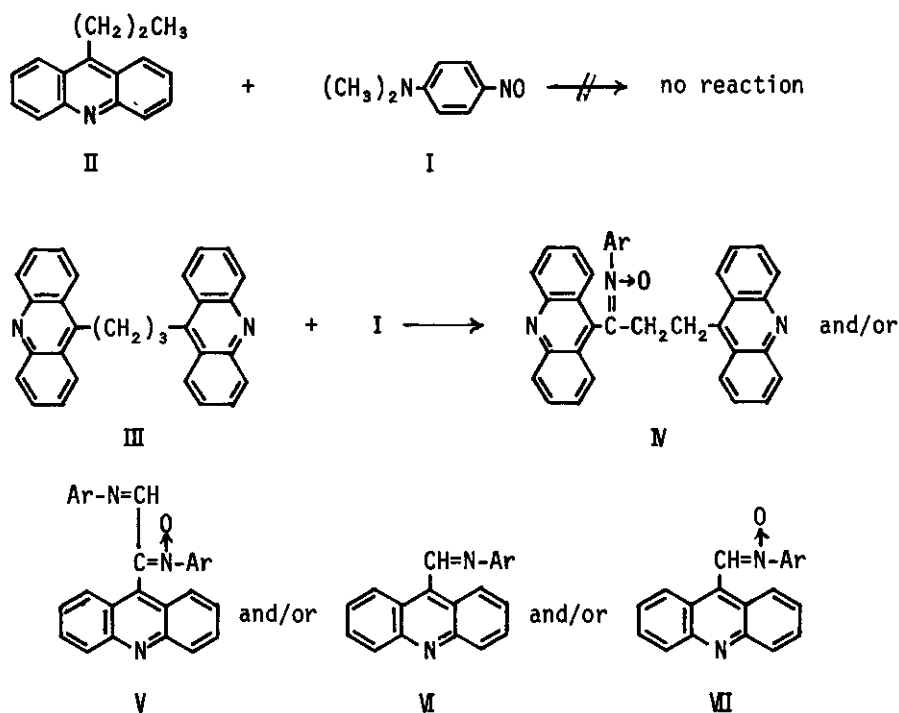


Therefore, it appeared of interest to investigate further the scope of the above reaction. In this communication we wish to report the reaction of the 9-propylacridine system with *p*-nitroso-*N,N*-dimethylaniline (I). In view of the result of reaction of 9-ethylacridine with I, 9-propylacridine (II) might be expected to react with three moles of I. Contrary to expectation, the reaction of II with I did not take place in the presence of HCl as well as of a basic catalyst under various conditions. However, we found that 1,3-di(9-acridinyl)propane (III)<sup>6</sup> having methylene groups activated by two acridinyl groups, reacted with three moles of I under the influence of HCl to afford several products: whose relative yields depended on the reaction conditions as shown in Table 1. In the reaction in refluxing ethanol, products, IV-VII, were formed together with tarry materials, and the yield of IV increased with the decrease in the amount

of HCl. At lower reaction temperatures, the compound IV was the predominant product.

The molecular formula of IV [ $C_{37}H_{30}N_4O$ , mp  $225^{\circ}C$  dec., orange prisms] was consistent with that of a mono-nitrone compound, and the nmr spectrum in  $CF_3COOH$  displayed signals at  $\delta$  3.3 (6H, s,  $NCH_3$ ), 3.5 (4H, m,  $CH_2CH_2$ ), and 7.1-9.0 ppm (20H, aromatic protons). Although 1,3-di(9-acridinyl)-1-(p-N,N-dimethylamino-phenylimino)propane N-oxide and its 2-isomer are possible for the structure of mono-nitrone compound, the mass spectrum supports strongly that IV is 1-isomer [ $m/e$  546 ( $M^+$ ), 530 ( $M^+ - O$ ), 528 ( $530^+ - H_2$ ), 324 (9-acridinyl- $C=N^+-C_6H_4NMe_2$ , base peak)].

By the identification with authentic samples, the structures of other products obtained as all red prisms were confirmed to be 1-(9-acridinyl)-1,2-



Ar: p-N,N-dimethylaminophenyl

bis(p-N,N-dimethylaminophenylimino)ethane N<sup>1</sup>-oxide (V) [mp 265°C dec.],<sup>4</sup> (9-acridinylmethylene)-p-N,N-dimethylaminoaniline (VI) [mp 248°C],<sup>2</sup> and its N-oxide (VII) [mp 243°C dec.],<sup>2</sup> respectively.

Table 1

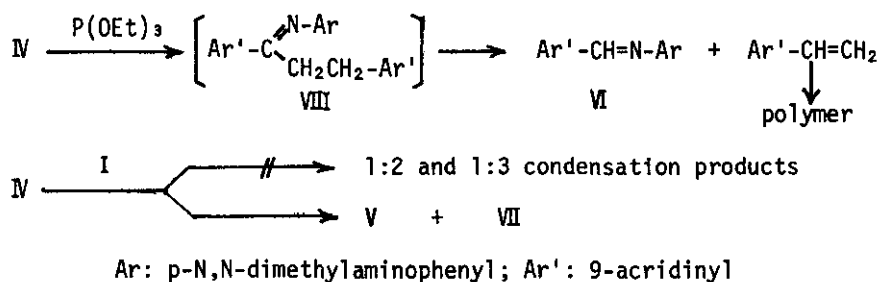
Reaction conditions <sup>a)</sup>			Product, %			
Time, h	Temp. °C	HCl, ml	IV	V	VI	VII
4	reflux	0.1	—	5.7	25.6	—
1.5	reflux	0.05	10	5	+ <sup>b)</sup>	17
1.5	reflux	0.03	25.5	—	—	—
15	50	0.03	36.5	+	—	—
15	60	0.03	51	1.1	—	—
15	70	0.03	65.6	4.9	—	+

a) A mixture of I (1.1 g), III (1.0 g), and the specified amount of HCl (d<sup>27</sup> 1.1748) in ethanol (20 ml) was heated under the reaction conditions described in the Table. b) A sign, +, means a trace amount.

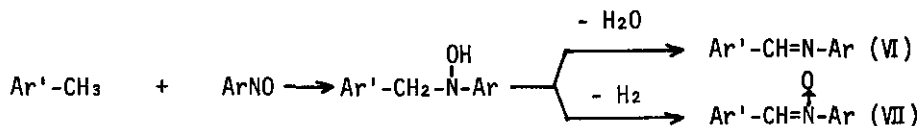
It is known that anil and nitron compounds are difficult to separate. The yields shown in Table 1 are those of pure products obtained by several recrystallizations of the respective reaction mixture. As shown in Table 1, no 1:2 and 1:3 condensation products of III and I were formed, and the cleaved products, V—VII, were obtained under forcing conditions.

Attempts to obtain 1,3-di(9-acridinyl)-1-(p-N,N-dimethylaminophenylimino)-propane (VIII) by deoxygenation of IV with triethylphosphite were unsuccessful; IV (1.0 g) was heated with triethylphosphite (10 ml) under reflux for 5 h, giving 0.31 g (52%) of the anil VI along with resinous materials. This fact suggests that the mono-anil VIII undergoes thermal decomposition to form VI and 9-vinylacridine which polymerizes to resinous material. The reaction of the

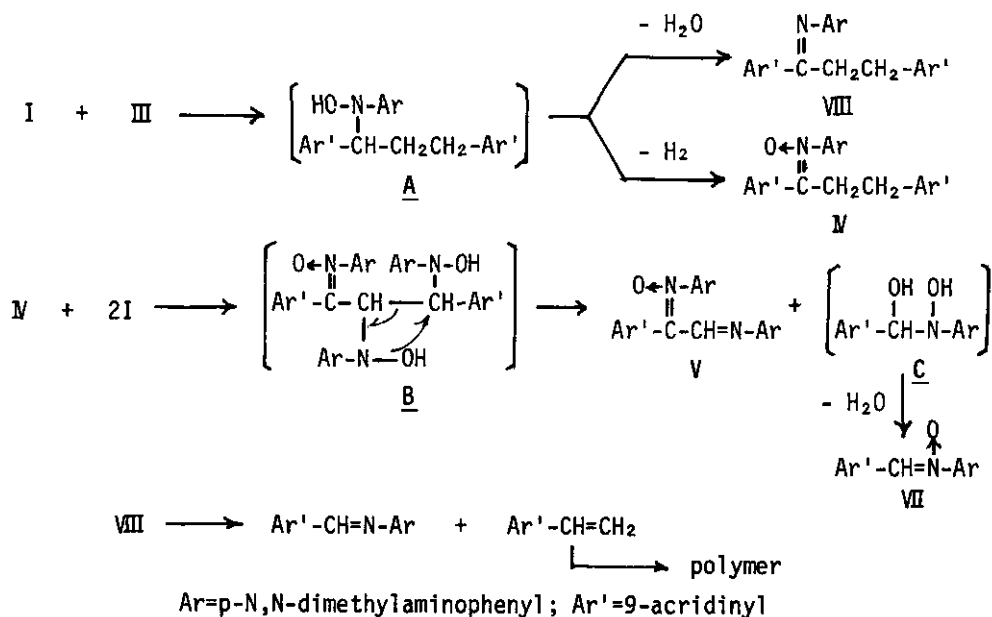
mono-nitrone **IV** with two or three moles of **I** in the presence of HCl did not give 1:2 and 1:3 condensation products, but the cleaved products, **V** and **VII**, were obtained in small quantities, besides the recovery of **IV**. For example, when a mixture of **IV** (1.0 g) and **I** (0.82 g) in ethanol (20 ml) was heated with HCl (0.04 ml) at 70°C for 15 h, **V** (22 mg, 2.5%) and **VII** (26 mg, 4%) were obtained together with recovery of **IV** (57.5%).



Kröhnke and his co-workers<sup>7,8</sup> suggested the mechanism via the aldol-type intermediate for the formation of the anil **VI** and nitrone **VII** in the reaction of 9-methylacridine (Ar'-CH<sub>3</sub>) with **I** (ArNO) under the influence of a basic catalyst:



Although the exact pathway for the formation of products in the reaction of **III** with **I** is not clear, we viewed the following pathway on the basis of above considerations. The compound **III** reacts with one mole of **I** to give the aldol-type intermediate **A**, followed by dehydrogenation or dehydration to form the nitrone **IV** or anil **VIII**. As described above, the anil **VIII** undergoes thermal decomposition to give **VI** and 9-vinylacridine. Since the nitrone **IV** is stable under the reaction conditions, a further reaction of **IV** with two moles of **I** takes place under forcing conditions, forming the aldol-type intermediate **B**.



The intermediate B decomposes into V and diol C, which gives VII by dehydration.

#### References

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