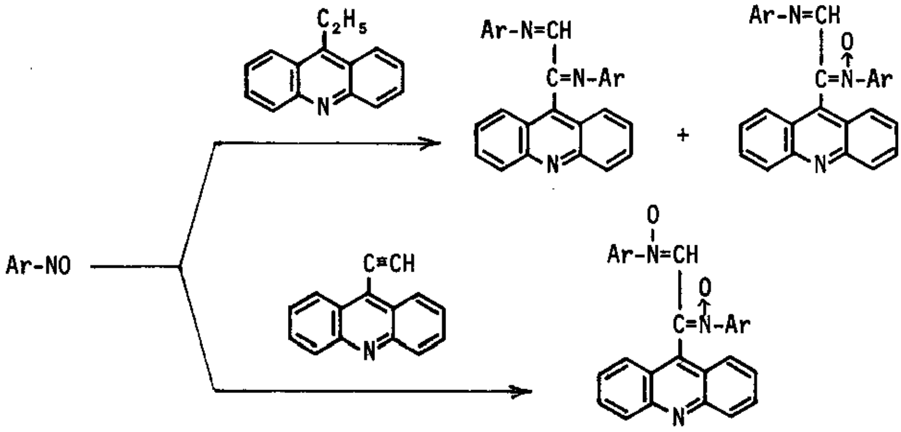
HETEROCYCLES, Vol. 2, No. 5, 1974

COMPOUNDS RELATED TO ACRIDINE. XI.[1]
REACTION OF 1,3-DI(9-ACRIDINYL)PROPANE WITH P-NITROSO-N,N-DIMETHYLANILINE

Akiyoshi Torii and Hideki Higashiuchi
Department of Industrial Chemistry, Kurume Technical College,
Komorino, Kurume 830, Japan
Otohiko Tsuge*
Research Institute of Industrial Science, Kyushu University,
Hakozaki, Higashi-ku, Fukuoka 812, Japan

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,[2] 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 reaction.[3] Moreover, even 9-ethylacridine[4] and 9-ethynylacridine[5] 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^1-oxide, and N^1,N^2-dioxide, respectively, as depicted below.

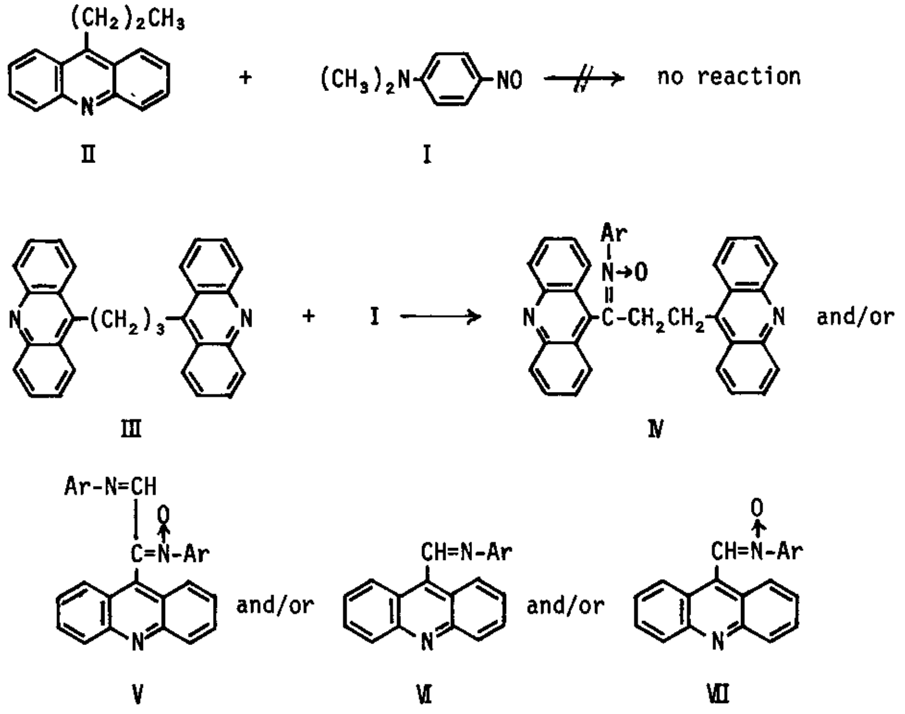


Ar: p-N,N-dialkylaminophenyl

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)[6] 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°C dec., orange prisms] was consistent with that of a mono-nitrone compound, and the nmr spectrum in CF_3COOH displayed signals at δ 3.3 (6H, s, $NC\underline{H}_3$), 3.5 (4H, m, $C\underline{H}_2C\underline{H}_2$), and 7.1-9.0 ppm (20H, aromatic protons). Although 1,3-di(9-acridinyl)-1-(p-N,N-dimethylaminophenylimino)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-$C\equiv\overset{+}{N}$-$C_6H_4NMe_2$, 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^1-oxide (V) [mp 265°C dec.],[4] (9-acridinylmethylene)-p-N,N-dimethylaminoaniline (VI) [mp 248°C],[2] and its N-oxide (VII) [mp 243°C dec.],[2] respectively.

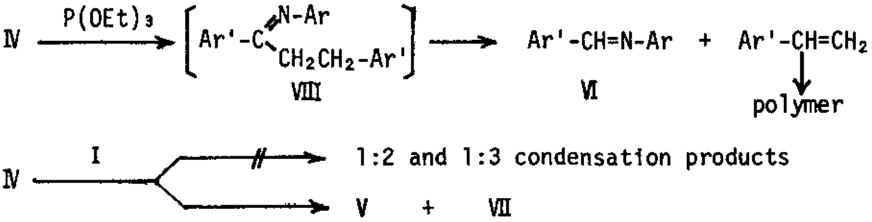
Table 1

Reaction conditions a)			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	+b)	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^{27} 1.1748) in ethanol (20 ml) was heated under the reaction conditions described in the Table. b) A sign, +, means a trace amount.

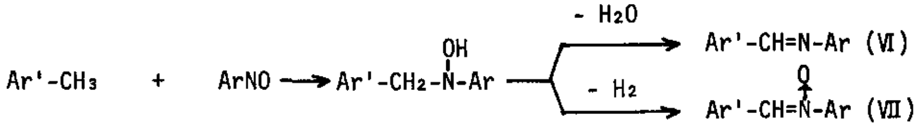
It is known that anil and nitrone compounds are difficult to separate. The yields shown in Table 1 are those of pure products obtained by several recrystallizations of the respective reaction mixture. As shown in Table 1, no 1:2 and 1:3 condensation products of III and I were formed, and the cleaved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

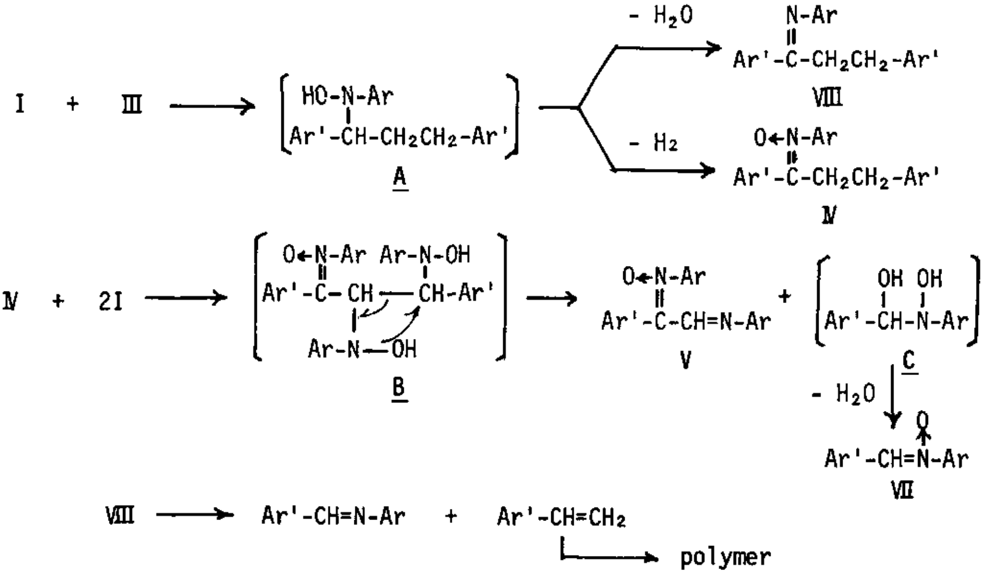


Ar: p-N,N-dimethylaminophenyl; Ar': 9-acridinyl

Kröhnke and his co-workers[7,8] suggested the mechanism via the aldol-type intermediate for the formation of the anil VI and nitrone VII in the reaction of 9-methylacridine ($Ar'-CH_3$) 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 bais 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.



Ar=*p*-N,N-dimethylaminophenyl; Ar'=9-acridinyl

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

References

1 Part X of this series: O. Tsuge and A. Torii, Bull. Chem. Soc. Japan, 1973, 46, 283.

2 O. Tsuge, M. Nishinohara, and M. Tashiro, ibid., 1963, 36, 1477.

3 P. Ehrlich and F. Sachs, Chem. Ber., 1899, 32, 2341.

4 O. Tsuge, M. Nishinohara, and K. Sadano, Bull. Chem. Soc. Japan, 1965, 38, 2037

5 O. Tsuge and A. Torii, ibid., 1970, 43, 2920.

6 O. Tsuge and A. Torii, ibid., 1972, 45, 3187.

7 F. Kröhnke, Chem. Ber., 1938, 71, 2583.

8 F. Kröhnke, H. Leister, and I. Vogt, ibid., 1959, 90, 2792.

Received, 13th August, 1974