The Condensation of 9-Ethylacridine and p-Nitosodimethylaniline¹⁾

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It has previously been reported²⁾ that the condensation of the 9-methylacridine derivative and the aromatic nitroso compound in the presence of a catalytic amount of hydrochloric acid affords the condensation products, an anil and a nitrone, in a fairly good yield compared with the yield when a basic catalyst is used.

From this result, it may be concluded that hydrochloric acid can noticeably activate the active methyl group at the 9-position of the acridine ring in the reaction with the aromatic nitroso compound.

Accordingly, it appeared of interest to investigate whether 9-ethylacridine (I) can be condensed with the aromatic nitroso compound in the presence of hydrochloric acid.

The reaction of I with p-nitrosodimethylaniline (II) did not take place in the presence of potassium carbonate, and p, p'-bis(dimethylamino)azoxybenzene (III) (m. p. $240\sim241^{\circ}$ C (reported, $241\sim242^{\circ}$ C³⁾)) was formed in only a small amount. In the presence of hydro-

chloric acid, however, I reacted with II to give the condensation products. For example, when a solution of 1.0 g. of I, 1.4 g. of II and 0.20 ml. of concentrated hydrochloric acid in 25 ml. of ethanol was refluxed for 5 hrs., 1.29 g. of reddish brown crystals (IV) (m. p. 261~263°C (decomp.)) was obtained. Found: C, 77.51, 77.74; H, 6.04, 6.10; N, 14.11, 14.36%.

The hydrolysis of 1.0 g. of IV with 10 ml. of 12% aqueous hydrochloric acid afforded 0.30 g. of acridine-9-carboxaldehyde (VII) (m.p. 147° C (reported, 147° C⁴))). The treatment of 0.5 g. of IV with 10 ml. of cold 10% aqueous sulfuric acid gave the α -nitrone- β -formyl compound (V) as orange prisms (m. p. 208°C (decomp.)). Found: C, 74.85; H, 5.18; N, 11.13. Calcd. for $C_{23}H_{19}O_2N_3$: C, 74.78; H, 5.18; N, 11.37%. IR (Nujol): 1662 cm^{-1} (C=O).

From the condensation of V and p-amino-dimethylaniline, the α -nitrone- β -anil compound (IVa) was obtained as reddish brown prisms (m. p. 265°C (decomp.)). Found: C, 76.67; H, 6.24; N, 14.10. Calcd. for $C_{31}H_{29}ON_5$: C, 76.36; H, 6.00; N, 14.36%. The infrared spectrum of IVa showed the characteristic bands at 1212, 1119, 818 and 758 cm⁻¹. Furthermore, 0.26 g. of V was oxidized with silver oxide to give 0.10 g. of the nitrone (VI), which was prepared by the condensation of 9-methylacridine (X) and II and which was easily hydrolyzed to VII. V was also easily hydrolyzed with dilute hydrochloric acid to afford VII.

On the other hand, the dianil compound (IVb) was obtained as red prisms (m.p. 283°C (decomp.)) by several fractional recrystallizations of IV from pyridine. Found: C, 78.87; H, 6.19; N, 14.65. Calcd. for C₃₁H₂₉N₅: C, 78.95; H, 6.20; N, 14.85%. Its infrared spectrum exhibited the distinctive bands at 1228, 1158, 819 and 742 cm⁻¹.

From the results of the infrared spectrum of IV, which revealed all the distinctive bands of IVa and IVb, and from the results of the elemental analysis, IV seems to be a mixture of the two compounds. However, the ratio of these two compounds in IV has not been established.

¹⁾ Presented at the General Meeting of the Kyushu, Chugoku and Shikoku Districts of the Chemical Society of Japan, Kagoshima, December, 1963.

²⁾ O. Tsuge, M. Nishinohara and M. Tashiro, This Bulletin, 36, 1477 (1963).

³⁾ H. von Pechmann and W. Schmitz, Ber., 31, 295 (1898).

⁴⁾ L. Chardonnens and P. Heinrich, Helv. Chim. Acta, 32, 635 (1949).

The compounds VIII and IX could not be separated, but it seems most reasonable to conclude from the above results that the hydrolysis of IV to VII proceeds successively through the course depicted in Chart 1.

Further investigation is in progress; details

of this work will be published in the near future.

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