418. *The Reactivity of Groups in Substituted Acridones. Part I. Replacement of Nitro-groups by Piperidyl and Piperazyl.*

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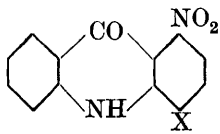
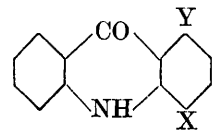
NUMEROUS cases, *e.g.*, *o*- and *p*-dinitrobenzenes, 4-chloro-1 : 2-dinitrobenzene, are known in which one of two cationoid groups in an aromatic nucleus, ortho or para to each other, is replaced when attacked by an anionoid reagent.

That the carbonyl group in anthraquinone acts as a cationoid group is shown by the facts that 1-chloroanthraquinone gives 1-piperidylanthraquinone when heated with piperidine (D.R.-P. 136777), the nitro-group in 1-nitroanthraquinone may be replaced by the methylamino- (D.R.-P. 144634), dimethylamino-, or piperidyl group (D.R.-P. 136777), and in 4-chloro-1-nitroanthraquinone both the nitro-group and the chlorine atom are replaced on heating with *p*-toluidine (D.R.-P. 126803).

It has now been found that in the reaction between piperidine or piperazine and 1-halogeno-4-nitroacridones (I) the *p*-nitro-group,



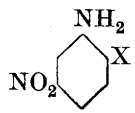
(I; X = Cl or Br)



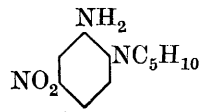
(II; Y = piperidyl or piperazyl)

instead of activating the halogen atom and facilitating its replacement by the negative reagent, is itself replaced, the product being (II).

The activating influence of the *o*-carbonyl group on the nitro-group in the acridone ring may be inferred from the similarity to the reactions in the anthraquinone series. Further, that the removal of the heterogeneous polarity caused by the two cationoid groups (CO and NO_2) ortho to one another proceeds more readily than the replacement of activated halogen may be inferred, since such reaction takes place in this case, whereas in 2-halogeno-5-nitroanilines (III), in the absence of heterogeneous polarity, the removal of halogen by piperidyl to give 5-nitro-2-piperidylaniline (IV) proceeds normally on heating in a sealed tube.



(III; X = Cl or Br.)



(IV.)

EXPERIMENTAL.

Nitration of o-*Chloro*(or *Bromo*)*aniline.*—KNO_3 (1 mol.; 1 part) in H_2SO_4 (*d* 1·84; 37 parts) was added to the base (1 mol.) in H_2SO_4 (30—37 parts) at 0—2° during ½ hr. The mixture was poured on ice (60 parts) and then into H_2O (800 parts). 2-Chloro- and 2-bromo-5-nitroaniline were obtained from spirit in yellow needles, m. p. 117° (yield, 52%) and 138° (yield, 70%) respectively.

Acridone Formation.—The above 2-halogeno-5-nitroanilines (1/50 g. mol.), K *o*-bromobenzoate (1/50 g.-mol.), amyl alcohol (10 c.c.), and Cu powder (0·1 g.) were heated under reflux for 4 hr., the mixture made alkaline with NaOH, the alcohol distilled in steam, the residue cooled, and the filtered solution acidified with dil. HCl. The yellow ppt., cryst. from AcOH, gave the 2-halogeno-5-nitrodiphenylamine-6′-carboxylic acids. These were heated on a steam-bath with H_2SO_4 (*d* 1·84; 12—14 parts) for 15—20 min., the solution poured into H_2O, and the solid which separated boiled with H_2O, then with dil. Na_2CO_3 aq., and again with H_2O, and crystallised from much AcOH.

2-*Chloro*-5-*nitrodiphenylamine*-6′-*carboxylic acid* formed golden-yellow needles (yield, 40%), m. p. 260—261° (Found: N, 9·8. $C_{13}H_9O_4N_2Cl$ requires N, 9·6%), and 2-*bromo*-5-*nitrodiphenylamine*-6′-*carboxylic acid* brownish-orange needles (yield, 34%), m. p. 252° (Found: Br, 24·2. $C_{13}H_9O_4N_2Br$ requires Br, 23·7%).

1-*Chloro*-4-*nitroacridone* (I; X=Cl) formed yellow needles (yield, 64%), m. p. 320° (Found: N, 10·0. $C_{13}H_7O_3N_2Cl$ requires N, 10·2%), and 1-*bromo*-4-*nitroacridone*, lemon-yellow needles (yield, 55%), m. p. 305° (Found: Br, 24·9. $C_{13}H_7O_3N_2Br$ requires Br, 25·1%).

Action of Piperidine or Piperazine on 1-*Halogeno*-4-*nitroacridones.*—The acridone (1 part) was gently refluxed with piperidine (approx. 5 parts) or piperazine (approx. 2½ parts) until it dissolved (about 1 hr.), the solution poured into cold H_2O, and the ppt. crystallised from dil. EtOH.

1-*Chloro*-4-*piperidylacridone* (II; X = Cl, Y = $C_5H_{10}N$) formed yellow needles, m. p. 110° (Found: N, 8·9; Cl, 11·1. $C_{18}H_{17}ON_2Cl$ requires N, 9·0; Cl, 11·3%); the hydrochloride, pptd. by dry HCl from $CHCl_3$, crystallised from H_2O in yellow needles, m. p. 168—169°.

1-*Bromo*-4-*piperidylacridone* formed bright yellow needles, m. p. 112° (decomp.) after softening at 98—102° (Found: Br, 21·6. $C_{18}H_{17}ON_2Br$ requires Br, 22·4%); the hydrochloride had m. p. 164—165°.

1-*Chloro*-4-*piperazylacridone* formed brownish-yellow needles, m. p. 197—198° (Found: N, 13·8; Cl, 10·3. $C_{17}H_{16}ON_3Cl$ requires N, 13·4; Cl, 11·3%).

Action of Piperidine on 2-*Halogeno*-5-*nitroanilines.*—Piperidine at its b. p. had little action on the halogenonitroanilines. 2-Chloro-5-nitroaniline (6·88 g.) and piperidine (7 c.c.) were heated in a sealed tube at 180° for 6 hr., and the product poured into H_2O (400 c.c.). The oil obtained, after solidifying, was crystallised twice from spirit, giving 2-*piperidyl*-5-*nitroaniline* in chocolate-brown needles (3·3 g.), m. p. 79—81° (Found: N, 19·4. $C_{11}H_{15}O_2N_3$ requires N, 19·0%).

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