319. *The Reactivity of Groups in Substituted Acridones. Part II. Cationoid Activity at Position 4 in Acridones.*

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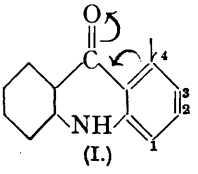
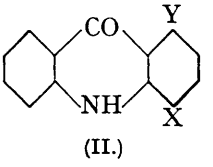
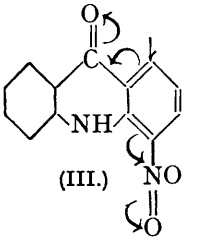
THE cationoid activity previously found (J., 1932, 2772) in acridones (I) at position 4 has now been confirmed by the demonstration that halogen substituted there is readily replaced by anionoid reagents: from 1 : 4-dihalogenoacridones (II; X and Y = Cl or Br) the halogen (Y) is removed by piperidine, 1-halogeno-4-piperidinoacridones being produced identical with the compounds already obtained by the removal of the nitro-group from 1-halogeno-4-nitroacridones (*loc. cit.*) and in better yield than by the latter method.


(I.)


(II.)


(III.)

4-Chloro-1-methylacridone (II; X = CH_3, Y = Cl) is unchanged even on heating for a long time with piperidine. This is in agreement with the effect of a methyl group on substitution and replacement in the benzene ring, *i.e.*, facilitating cationoid and retarding anionoid attack.

Bradley and Robinson (J., 1932, 1255) have shown that even hydrogen may be replaced by piperidino in such compounds as nitrobenzene, which yields *p*-piperidinonitrobenzene. The somewhat similar case of 1-nitroacridone, where the cationoid effects of the nitro- and the carbonyl group will be cumulative (III), might be expected to yield 1-nitro-4-piperidinoacridone. No such reaction took place on heating with excess of piperidine in the presence of sodamide. 1-Nitro-4-piperidinoacridone is readily obtained, however, by treating 4-chloro-1-nitroacridone with piperidine.

EXPERIMENTAL.

The following substituted diphenylamine-6′-carboxylic acids have been prepared from the requisite substituted aniline and potassium *o*-bromobenzoate, and converted into the undernoted corresponding acridones by the methods already described (*loc. cit.*).

2 : 5-*Dichlorodiphenylamine-6′-carboxylic acid* formed greyish-white needles (yield, 48%), m. p. 232° (Found : Cl, 24·4. $C_{13}H_9O_2NCl_2$ requires Cl, 25·1%), 2 : 5-*dibromodiphenylamine-6′-carboxylic acid* greyish-white needles (yield, 36%), m. p. 229—230° (Found : Br, 42·8. $C_{13}H_9O_2NBr_2$ requires Br, 43·1%), and 5-*chloro-2-methyldiphenylamine-6′-carboxylic acid* lemon-coloured needles (yield, 60%), m. p. 180—181° (Found : Cl, 13·0. $C_{14}H_{12}O_2NCl$ requires Cl, 13·1%).

5-*Chloro-2-nitrodiphenylamine-6′-carboxylic acid*, which was best prepared from potassium anthranilate and 2 : 4-dichloronitrobenzene, was found to be dimorphous—yellow needles and reddish cubic plates, both m. p. 228°. The reddish cubic plates, when crystallised quickly from glacial acetic acid, were converted into the yellow needle form (Found : Cl, 11·9. $C_{13}H_9O_4N_2Cl$ requires Cl, 12·1%).

1 : 4-*Dichloroacridone* formed microcrystalline yellowish needles (yield, 64%), m. p. 268° (Found : Cl, 26·4. $C_{13}H_7ONCl_2$ requires Cl, 26·9%), 1 : 4-*dibromoacridone* pale yellow needles (yield, 55%), m. p. 232—233° (Found : Br, 44·8. $C_{13}H_7ONBr_2$ requires Br, 45·3%), and 4-*chloro-1-methylacridone* small, pale yellow needles (yield, 75%), m. p. 298° (Found : Cl, 14·5. $C_{14}H_{10}ONCl$ requires Cl, 14·5%). 4-*Chloro-1-nitroacridone* crystallised from nitrobenzene in reddish tabular plates, m. p. 240° (Found : Cl, 13·2. $C_{13}H_7O_3N_2Cl$ requires Cl, 13·0%).

By the action of piperidine on the above acridones under the conditions given in the previous communication the following 4-piperidinoacridones have been obtained: 1-chloro-4-piperidinoacridone (yield, 77%), 1-bromo-4-piperidinoacridone (yield, 89%),and 1-*nitro-4-piperidinoacridone*, which formed fine orange-yellow needles (yield, almost theoretical), m. p. 192° (Found :

N, 13·3. $C_{18}H_{17}O_3N_3$ requires N, 13·0%). The first two showed no depression in m. p. in admixture with those already described.

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