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CERTAIN AZOMETHINES IN THE 3a-AZAINDOL-2-ONE SERIES

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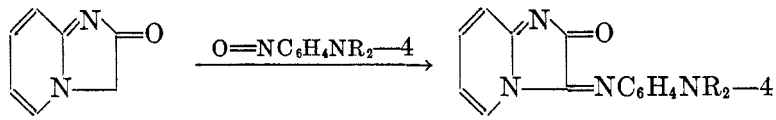
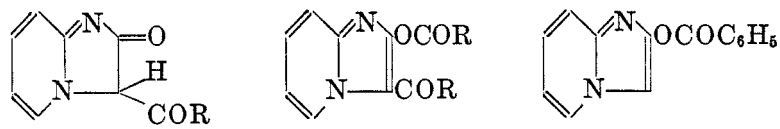
The reaction between several 2-acylacetaminopyridines and certain aromatic nitrosoamines, which gave magenta-colored azomethine dyes (I) in the 3a-azaindol-2-one series,[1] was described in a previous paper. It was shown that the same product resulted from a given nitrosoamine and any of the 2-acylated aminopyridines, and that the substance was readily synthesized from the base (II) or its hydrochloride.



II I

It was also shown that the magenta dyes gave bluish salts.

Analogous azomethines have been prepared from the 4-, 5-, and 6-methyl-2-aminopyridines. Of considerably more interest, however, is the observation that the mono- and di-acetylazaindolones (III, IV; R = CH_3) (3) give the same magenta dye as the unsubstituted heterocycle (II), the acetyl groups being eliminated in the process.



III IV V

It was shown long ago (3, 4) that the O-acyl group in an azaindolone is extremely easily hydrolyzed off in alkaline solution—this would account for the loss of one acetyl group and formation of the monoacetylazaindolone from the diacetyl derivative. The remaining acetyl group then "couples out" during the reaction with the nitrosoamine; such an elimination of a group is known to occur in color photography.

3,3-Dibromo-3a-azaindol-2-one (5) likewise gives the same magenta dye with coupling out of the halogens. The simple acid salts, such as the hydrochloride, lose the acid when treated with sodium acetate and give the same magenta dye (1).

The important point is, that a given 3a-azaindolone, its simple salts, and its mono- or di-acyl derivatives, all give the same dye, and that dye has the structure shown in I.

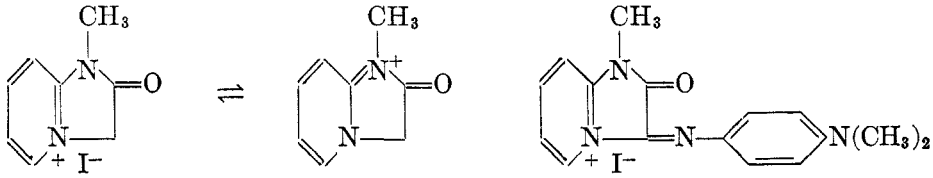
[1] In the previous paper (1) these substances were named as derivatives of pyrimidazole. However, the name pyrimidazole is not sufficiently specific, being used for several ring systems [Ring Index numbers 755, 756 and 765 (2)].

Other mono- and di-acyl derivatives would be expected to resemble the acetylated base. Thus, both O- (V) and C-benzoyl (III; R = C_6H_5) (3, 4) and distearoyl (IV; R = $C_{17}H_{35}$) (6) derivatives do not give dyes containing the acyl radicals, but the same magenta dye (I) already mentioned. The identity of the dye was determined by its isolation, observation of melting point, mixed melting point, and spectrophotometric data.[2] 3-Benzal-3a-azaindol-2-one likewise gives the same dye, but at a much slower rate.

From these facts it appears that the only variation that can be made in 3a-azaindolone couplers is to introduce substituents into the 6-membered ring (by use of substituted 2-aminopyridines) or to use benzologs (*e.g.*, 2-aminoquinolines).

The structures of 3a-azaindolone salts are difficult to represent by an unequivocal formula. As a monoacidic base, 3a-azaindol-2-one forms a monohydrochloride (7), a monohydriodide (7), and picrate (8), and a monomethiodide of the dye (I) has been reported (1).

We have found that 3a-azaindol-2-one (II) forms a monomethiodide and a perchlorate (VII). When the methiodide is treated with nitrosodimethylaniline, a bluish dye is formed; this substance appeared to be identical with the methiodide formed from the dye (I) (R = CH_3), and previously described (1). The structure ascribed earlier to this salt must therefore be in error; the methyl group must be on one of the heterocyclic nitrogen atoms. The methyl group is placed on the lactim nitrogen atom, which is in accordance with the ideas of Brooker (9); and also conforms with Chichibabin's hydriodide (VI) (8). The cation of the salt (VIII) so formed is one of several resonance forms, of which VIII is preferred since it contains an aromatic system. The methiodide of the dye is now assigned the structure shown in X.



VIII IX X

EXPERIMENTAL

The 2-acetoacetamidopyridines were prepared as before (1); the 4-methyl derivative (XII) had the melting point 118–119°; the 5-methyl (XIII), 135°; and the 6-methyl (XIV), 98°. When these substances were treated with oxidized developer (unsymm.-diethyl-*p*-toluylenediamine), they gave yellow dyes which soon changed to magenta. The λ_{max} for the magenta dye from XII is at 554; from XIII, at 564; and from XIV, at 560. The analyses are collected in Table I.

Diacetyl-3a-azaindol-2-one (XV) was obtained by refluxing a mixture of 5 g. of 3a-azaindol-2-one hydrochloride and 35 ml. of acetic anhydride until solution was complete; the yield, after cooling was 4.9 g.; m.p. 198°. Reindel and Rauch (3) started with pyridylglycine; the yield and melting point were the same. The distearoyl derivative (XI) was

[2] We are indebted to Dr. P. W. Vittum and Mr. G. H. Brown of these Laboratories for the last data.

prepared in a similar manner, using 11 g. of stearic anhydride per 1.4 g. of 3a-azaindol-2-one hydrochloride, and heating at 120° for one-half hour; at the end, the mixture was heated at 200° for ten minutes. After recrystallization from xylene, the yield was 3 g. The other 3a-azaindol-2-ones were obtained following the literature procedures.

The dye (I) was prepared from all the substituted 3a-azaindol-2-ones by the same general procedure (1). Equivalent amounts of *p*-nitrosodiethyl-*m*-toluidine, the heterocyclic substance, and a catalytic amount of potassium carbonate, in alcohol, were refluxed three to four hours. Usually, the dye separated in a reasonably pure condition; the yields were 50–60%. After recrystallization from butanol, the melting point was 203°; there was no depression on admixture with an authentic specimen (1). Spectrophotometric curves were also identical (2).

3a-Azaindol-2-one methiodide (VIII) was prepared from the hydrochloride as follows: 8 g. of the latter salt, 4.3 g. of sodium acetate, and 40 ml. of absolute ethanol were heated to boiling, treated with 3 g. of Norit, and filtered. To the red filtrate was added 40 ml. of methyl iodide and the solution left overnight in a closed bottle; 6.2 g. of bright red crystals separated. Even after recrystallization from ethanol, the product, m.p. 168–170°, was not

TABLE I

ANALYSES

NO.	SUBSTANCE	EMPIRICAL FORMULA	ANALYSES	
			Calc'd %, N	Found %, N
XII	4-Methyl amide	$C_{10}H_{12}N_2O_2$	14.6	14.4
XIII	5-Methyl amide	$C_{10}H_{12}N_2O_2$	14.6	14.4
XIV	6-Methyl amide	$C_{10}H_{12}N_2O_2$	14.6	14.7
XI	Distearoyl derivative	$C_{43}H_{74}N_2O_3$	4.2	4.3
VII	Perchlorate	$C_8H_9ClN_2O_5$	11.3	11.2
X	Dye	$C_{16}H_{17}IN_4O$	13.8	14.0
XVII	Dye perchlorate	$C_{16}H_{17}ClN_4O_5$	14.7	14.6

analytically pure, so it was transformed into the *perchlorate* (VII), m.p. 174–175°, by mixing 1.3 g. in 5 ml. of water with a warm solution of 1 g. of sodium perchlorate in an equal volume of water.

The methiodide (X) of the dye (I) was obtained by warming for three hours a mixture of 2.7 g. of 3a-azaindol-2-one methiodide, 1.4 g. of *p*-nitrosodimethylaniline, and 40 ml. of absolute ethanol. The yield was 3.7 g., 91%. It may be recrystallized from water, but a better product results if it is precipitated from its solution in nitrobenzene by ether; the melting point, 236–237°, is not depressed[3] on admixture with an authentic specimen prepared in the earlier work (1). This dye was likewise converted into a *perchlorate* (XVII), m.p. 230°; it deflagrates like most perchlorates.

The dye base (I) gives a yellow solution in concentrated sulfuric acid.

When an alkaline solution of the dye or its methiodide (X) is boiled, an odor of an isocyanide is noticed and the deep bluish-red color changes to a dirty purple.

[3] The melting point of the original sample was 240°; the mixed melting point with the 237–238° specimen was 238–239°, from which it may be concluded that the methiodides are identical. However, the behavior of the aqueous solution, on making alkaline with a few drops of sodium carbonate solution, is somewhat different. The difference is detected by shaking the straw-colored alkaline solution with butyl acetate. The specimen, m.p. 240°, gives a yellowish-orange ester layer, while the lower-melting isomer gives a magenta layer.

SUMMARY

The same azomethine dye, a derivative of 3a-azaindol-2-one, results when a variety of 3a-azaindol-2-ones, substituted in the 5-membered ring, are treated with aromatic nitrosoamines. Isomeric dyes are formed with alkyl groups in the 6-membered ring. Two methiodides and perchlorates are described and a type structure for such salts is proposed.

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