REACTION OF DI(1'-IMINOISOINDOLIN-3-YLIDENEAMINO)ARENES WITH HYDRAZINE HYDROCHLORIDE

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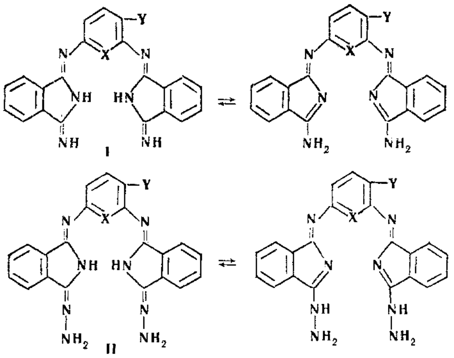
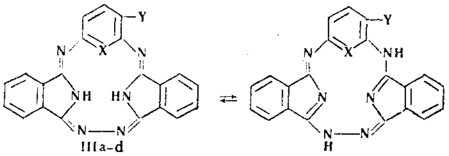
It has been shown that the reaction of 1,3-di(1'-iminoisoindolin-3'-ylideneamino)benzene and its derivatives and compounds related to them with hydrazine hydrate in dimethylformamide gives heterocyclic compounds. The structure of these compounds has been established, and their properties have been studied.

We have previously shown that the reaction of di(1'-iminoisoindolin-3-ylideneamino)arenes having the general formula I with hydrazine hydrate gives the corresponding hydrazino derivatives II [1].



X=CH, N; Y=H, CH_3, Cl

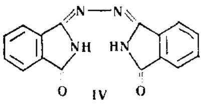
The replacement of hydrazine hydrate by hydrazine hydrochloride should not, one would think, have an appreciable influence on the nature of the products formed. However, this is not in fact the case. When 2,6-di(1'-iminoisoindolin-3-ylideneamino)pyridine, 1,3-di(1'-iminoisoindolin-3-ylideneamino)benzene, and their substituted derivatives are heated with hydrazine hydrate in dimethylformamide solution, heterocyclic compounds are formed which consist of two isoindole residues and one residue of pyridine or benzene or their derivatives, with the general formula III. The pH of the medium apparently plays a part in the formation of the macrocyclic compound, since at a low temperature heterocyclic compounds are still formed with hydrazine hydrochloride, although slowly.



IIIa-d

a X=CH, Y=H; b X=CH, Y=CH_3; c X=CH, Y=Cl; d X=N, Y=H

In comparison with the products formed on heating with hydrazine hydrate, these are red and not yellow, have a higher melting point, and do not react with a acetic anhydride, benzaldehyde, and benzyl chloride, which shows the absence of amino groups and the low reactivity of the exocyclic imino group. In addition, the new compounds are far more difficult to hydrolyze than the di(1'-iminoisoindolin-3-ylideneamino)arenes of the compound obtained from 2,6-di(1'-iminoisoindolin-3-ylideneamino)pyridine yielded 2,6-diaminopyridine and product IV, while complete hydrolysis gave the same 2,6-diaminopyridine and phthalic acid. Product IV was also obtained by heating iminooxoisoindoline (iminophthalimide) with hydrazine hydrochloride. Its hydrolysis with 25% hydrochloric acid gave phthalic acid.



The IR spectrum of the heterocyclic compound consisting of two isoindole residues and one pyridine residue contained an absorption band at 3430 cm^{-1}, characteristic for the stretching vibrations of the imino group [2]. The absorption band at 3290 cm^{-1} found in 2,6-di(1'-iminoisoindolin-3-ylindeneamino)-pyridine must also be ascribed to the stretching vibrations of the imino group, since there is no supplementary absorption band close to 1650 cm^{-1} due to the deformation vibrations of NH_2 groups. The absorption band at 3430 cm^{-1} must be ascribed to the stretching vibrations of the imino group. Moreover, only in the IR spectrum of the heterocyclic compound are there strong absorption bands at 1605 and 625 cm^{-1} that can be ascribed to the stretching vibrations of an N—N group [3].

The presence of substituents in the benzene residue of the heterocyclic compounds displaces the absorption maximum towards the long-wave region of the spectrum.

EXPERIMENTAL

"5,21:8,13-Diimino-15,19-methino- (or -nitrilo-) -6,7,14,20-tetraazadibenzo[d,o]cycloheptadecynes" (III) [3,10:19,24-Diimino-12,16-methino-(or -nitrilo-)-1,2,11,17-tetraazadibenzo[d,o]cycloheptadeca-2,4,10,13,15,17,19,25-octaene]. A solution of 0.01 mole of the appropriate di(1'-iminoisoindolin-3'-ylideneamino)aryl and 0.015 mole of hydrazine hydrochloride in 50 ml of dimethylformamide was heated in the boiling water bath for 8–10 hr and cooled, after which the contents of the flask were poured into 200 ml of water and 15–20 ml of 24% ammonia added. The precipitate that deposited was filtered off, and washed first with water and then with hot ethanol until the melting point was constant (table). For this purpose, the precipitate was boiled with 20–30 ml of ethanol for 3 min and the mixture was filtered hot. The operation was repeated three to five times. The macrocyclic compounds III obtained were red, had high melting points, and were insoluble in water, ether, acetone, benzene and its homologs, and carbon tetrachloride. They dissolved in benzyl alcohol, chlorobenzene, nitrobenzene, and dimethylformamide. They were stable to the action of alkalis, to sulfuric and hydrochloric acids in the cold, and to acetic acid on heating. They dissolved in concen-

5, 21:8, 13-Diimino-15, 19-methino- (or -nitrilo-) -6, 7, 14, 20-tetraazadibenzo[d, o]-cyclopentadecynes (IIIa–d).

Compound	X	Y	Mp, °C	λ_{max}, nm	Empirical formula	Found, %				Calculated, %				Yield, %
						C	H	N	Cl	C	H	N	Cl	
IIIa	CH	H	330—333	445	$C_{22}H_{14}N_6 \cdot 2H_2O$	63.3	4.5	21.1	—	65.9	4.5	21.2	—	46
IIIb	CH	CH_3	342—345	470	$C_{23}H_{16}N_6 \cdot 2H_2O$	67.0	4.8	20.4	—	66.5	4.7	21.4	—	40
IIIc	CH	Cl	334—336	475	$C_{22}H_{13}N_6Cl \cdot \cdot 2H_2O$	60.2	3.9	19.9	8.0	61.4	4.0	19.4	8.2	40
IIId	N	H	336—337	485	$C_{21}H_{13}N_7 \cdot 2H_2O$	62.9	4.1	24.4	—	62.8	4.3	24.4	—	40

trated sulfuric acid in the cold. When their acid solution was diluted with water, they precipitated in unchanged form. On being heated with sulfuric and hydrochloric acids, they hydrolyzed to the corresponding amines and phthalic acid.

Hydrolysis of compounds III. A mixture of 1 mM of a compound III and 10 ml of 25% hydrochloric acid was boiled until the dark red color had disappeared. When the solution was cooled with ice, colorless crystals of phthalic acid deposited (1.5–1.8 mM, mp 198° C). The filtrate was neutralized with caustic soda, and the aromatic diamine was extracted with ether. Elimination of the ether yielded 0.9 mM of 2, 6-diaminopyridine and 0.8 mM of m-phenylenediamine or 0.9 mM of 4-m-toluylenediamine, with melting points close to those given in the literature.

1, 1''-Azinodi(isoindolin-3-one) (IV). A mixture of 2.92 g (0.02 mole) of iminooxoindoline and 1.05 g (0.01 mole) of hydrazine hydrochloride in 50 ml of dimethylformamide was heated in the boiling water bath for 6 hr and cooled, after which the reaction mixture was poured into water and the precipitate that deposited was filtered off and was washed with water and ethanol. Yield 2.3 G (80%), mp 324–325° C (from dioxane). Found, %: C 65.9; H 3.49; N 19.14; mol. wt. 283 (Rast). Calculated for ($C_{16}H_{10}N_4O_2$), %: C 66.2; H 3.45; N 19.3; mol. wt. 290.

The absorption spectra in the visible region were taken on an SFD-1 instrument in dimethylformamide and the IR spectra on a UR-10 instrument with LiF and NaCl prisms in the form of tablets with potassium bromide.

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