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SYNTHESIS AND DEAMINATION OF 9-AMINOIMADAZO[1,2-*a*]BENZIMIDAZOLES

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The reaction between 1,2-diaminobenzimidazole and α-halocarbonyl compounds has given some novel 9-aminoimidazo[1,2-a]benzimidazoles. On treatment with nitrous acid or potassium hydroxide in DMSO, these compounds give, in addition to the deaminated compounds, 3-nitroso-derivatives of the deamination products. In the system DMSO–KOH, 9-benzylideneaminoimidazobenzimidazoles are converted smoothly into 1(9H)-imidazobenzimidazoles. It is shown that 3-nitroso-derivatives which are unsubstituted in the NH group exist predominantly in the hydroxyimino form.

Significant numbers of 9-substituted imidazo[1,2-*a*]benzimidazoles have shown high pharmacological activity [1, 2]. It was therefore of interest to develop a method of synthesis for the hitherto unknown 9-aminoimidazo[1,2-*a*]benzimidazoles. These could clearly be obtained by the reaction between 1,2-diaminobenzimidazole [3] and α-halocarbonyl compounds.

We have found that the diamine (I) reacts readily with α-haloketones to give the salts (II), which on boiling in 2% sodium bicarbonate solution cyclize in 75-80% yields to 9-aminoimidazo[1,2-*a*]benzimidazoles (III). The imines (IV) are undoubtedly intermediates in this reaction, and some of these (IVa, b) were isolated and characterized. On cyclization of the salts (IIc, d), in addition to (IIIc, d) there were obtained 10-12% yields of 1-amino-3-acetonyl- (Vc) and 1-amino-3-pivaloylmethylbenzimidaz-2-one (Vd). On heating in acid, the method normally used for the preparation of 9-alkylimidazo[1,2-*a*]benzimidazoles [4], (II) were unaffected. It is noteworthy that under the conditions of formation of the salts (II), the reaction of 1,2-diaminobenzimidazole with α-bromopropiophenone results in spontaneous cyclization to the imidazobenzimidazole (IIIe), half of the starting diamine binding the hydrogen bromide liberated.

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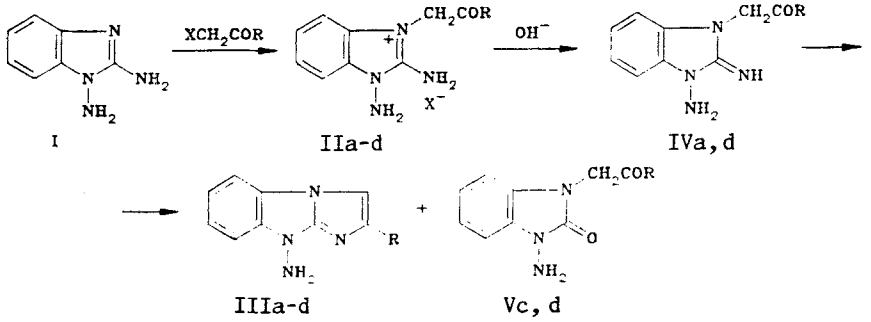
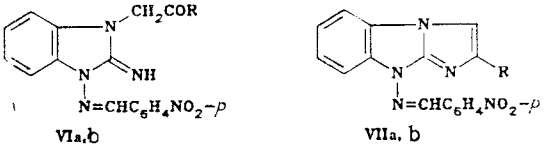


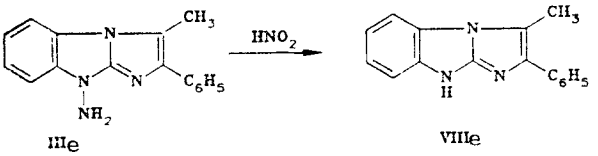
II—IV a $R=C_6H_5$, $X=Br$; b $R=C_6H_4OCH_3$-*p*, $X=Br$; c $R=CH_3$, $X=Cl$; d $R=C(CH_3)_3$, $X=Br$; V c $R=CH_3$, d $R=C(CH_3)_3$

The structures of the benzimidazoles (III) were confirmed by the absence from their PMR spectra of signals for methylene protons, and of carbonyl absorption in the IR spectra. As compared with the iminamines (IV), which give Schiff's bases (VI) on brief heating with p-nitrobenzaldehyde in alcohol, the N-amino group in (III) is less reactive, formation of the azomethines (VII) requiring the use of piperidine as a catalyst. On heating the imines (IV) with p-nitrobenzaldehyde in DMF, the cyclic azomethines (VII) were formed immediately.



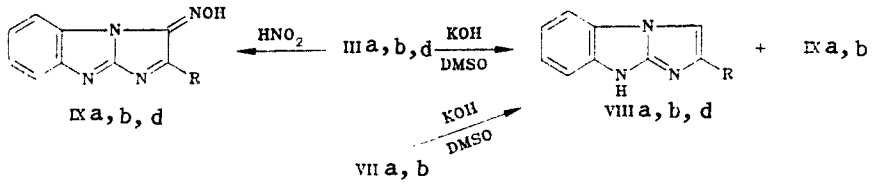
VI, VII a $R=C_6H_5$; b $R=C_6H_4OCH_3$-*p*

Since the N-amino group may be readily eliminated [5], the synthesis of the amines (III) opens up a route to N-unsubstituted imidazo[1,2-*a*]benzimidazoles (VIII), the usual methods of preparation of which are somewhat inconvenient [2, 6-8], or difficult to repeat [9]. In fact, treatment of a solution of 9-amino-3-methyl-2-phenylimidazo[1,2-*a*]benzimidazole (IIIe) in acetic acid with sodium nitrite (1 mole) at 5-10°C gave the 1(9H)-imidazobenzimidazole (VIIIe) in 82% yield.



However, treatment of the benzimidazole (IIIa) (in which the 3-position of the heterocycle is unsubstituted) with nitrous acid (1 mole) gave only the hitherto unknown 3-hydroxyimino-2-phenyl-3H-imidazo[1,2-*a*]benzimidazole (IXa) (46% yield), 42% of starting material being recovered. Structure (IXa) is supported by its physicochemical data (orange color, IR and PMR spectra), and by direct synthesis by nitrosation of 2-phenylimidazobenzimidazole (VIIIa)* under the same conditions. The reaction may be taken almost completely toward the formation of the oxime (IXa) by treating (IIIa) with 2 moles of nitrous acid. Similar behavior is seen on deamination of (IIIb). It was not possible to avoid nitrosation by introducing a bulky tert-butyl substituent into the 2-position of the imidazobenzimidazole, although the yield of the corresponding isonitroso compound (IXd) on reaction with 2 moles of nitrous acid fell to 20%. Reaction of the benzimidazole (IIIc) with nitrous acid afforded a mixture of compounds which it was not possible to separate. It appears that the previously noted instability of 1(9H)-2-methylimidazobenzimidazole [7] comes into play here, together with the known cleavage of the imidazole ring on nitrosation of 9-R-2-methylimidazobenzimidazoles [10].

*It has been reported [10] that 9-R-2-phenylimidazobenzimidazoles are readily nitrosated to give the green 3-nitroso-derivatives, which on treatment with acid are converted into red cations, which clearly exist, like (IXa), in the isonitroso form.

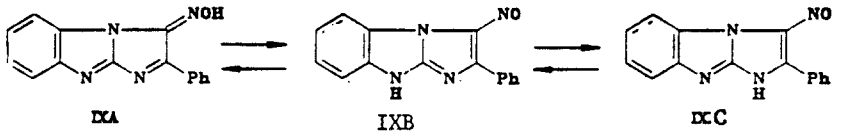


VIII, IX a R=C_6H_5; b R=$C_6H_4OCH_3$-*p*; d R=$C(CH_3)_3$

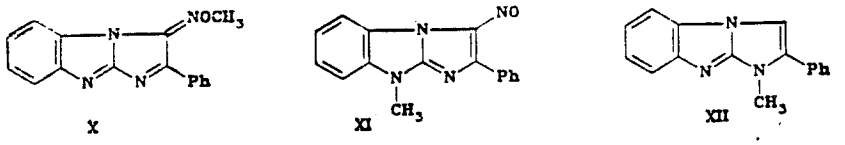
It therefore appears that the impossibility of smoothly deaminating these compounds (IIIa, b, d) with nitrous acid is due to nitrosation of nitrogen-unsubstituted imidazobenzimidazoles taking place more rapidly than deamination. For this reason, we attempted to deaminate the amines (III) with KOH in DMSO, as described for 1-aminoindole [11]. On brief heating of solutions of (IIIa, b, d) in dry DMSO with powdered KOH at 65-70°C, the imidazobenzimidazoles (VIIIa, b, d) were obtained in 70-75% yields. With compounds (IIIa, b), however, there were unexpectedly obtained as by-products (12-15%) the oximes (IXa, b). We initially believed that these compounds arose by electrophilic amination of the imidazobenzimidazoles (VIIIa, b) by the hydroxylamine formed under the reaction conditions (cf., for example, the reaction of 3,4-dimethylpyrrole with hydroxylamine in alkali [12]). Separate experiments showed, however, that (VIIIa) failed to react with hydroxylamine in alkaline DMSO. It only remained to assume that the aminating agent is the starting N-amino compound, reaction of which with the ambident anion of (VIII) gives the 3-aminoimidazobenzimidazole, which is then readily oxidized to the oxime (IX). We did in fact find that authentic 1(9H)-3-amino-2-phenylimidazobenzimidazole was rapidly converted into the hydroxyimino compound (IXa) in 88% yield under the conditions of deamination in the system DMSO–KOH. The use of the DMSO–KOH system with (IIId) enabled the novel 1(9H)-2-tert-butylimidazobenzimidazole (VIIId) to be obtained. This compound, like the corresponding 2-methylimidazobenzimidazole [7], was found to be unstable, which is probably a general property of 2-alkylimidazobenzimidazoles with a free NH group.

N-Amino-derivatives of azines [13] and azoles [14] are known to be readily deaminated by cleavage of the N–N bond in their azomethines (a nitrile is eliminated during the reaction). We tried out this method for the conversion of the Schiff bases (VIIa, b) into (VIII), but it transpired that on boiling in nitrobenzene they merely underwent resinification. On heating in DMSO in the presence of KOH, however, they were readily converted into the imidazobenzimidazoles (VIIIa, b).

Since the novel 3-nitrosoimidazo[1,2-*a*]benzimidazoles obtained during this investigation, which are unsubstituted at NH, could theoretically exist in several tautomeric forms (IXA-C), the question arose as to which of these predominated.



The bright orange color of (IXa) had already suggested that it had the hydroxyimino structure (IXA). In fact, a fixed, model form of this tautomer (X) had the same color. However, a fixed form of tautomer (IXB) (compound (XI), obtained previously [10]) is green in color. The UV-VIS spectra of (IXa) and (X) are also very similar, differing from that of (XI) in the presence of an additional absorption band at 270 nm (log ε 3.80) for (X), and 268 nm (3.82) for (IXa).



Indirect support for structure (IXA) is provided by the results of methylation of this compound. It is known that, in the absence of obvious steric hindrance, methylation of the anions of heterocyclic compounds (except for mercapto derivatives) takes place at the atom to which a proton also adds [15]. The anion of (IXa) is methylated by methyl iodide to form exclusively compound (X). Structure (X) is supported by the already-mentioned UV-VIS spectral features, and by the position of the signal for the protons of the methyl group (4.34 ppm), which is at much lower field than the signals for the CH_3 group in (XI) (3.94 ppm) and 1-methyl-2-phenylimidazobenzimidazole (XII) (3.55 ppm).

Clearly, in neutral media (IX) will be methylated differently, most likely at the endocyclic pyridine nitrogens ($N_{(1)}$ or $N_{(9)}$). In fact, on heating (IXa) with dimethyl sulfate at 130°C, 48% of (XI) was obtained.

TABLE 1. Properties of Compounds Obtained

Compound	Empirical formula	mp, °C*	Yield, %	Compound	Empirical formula	mp, °C*	Yield, %
IIa	$C_{15}H_{15}BrN_4O$	257 ... 258	93	Vd	$C_{13}H_{17}N_3O_2$	164 ... 165	12
IIb	$C_{16}H_{17}BrN_4O$	279 ... 280	92	VIa	$C_{22}H_{17}N_5O_3$	258 ... 260	87
IIc	$C_{10}H_{13}ClN_4O$	198 ... 200	76	VIb	$C_{23}H_{19}N_5O_4$	269 ... 270	89
IId	$C_{13}H_{19}BrN_4O$	247 ... 248	82	VIIa	$C_{22}H_{15}N_5O_2$	283 ... 284	78
IIIa	$C_{15}H_{12}N_4$	220 ... 221	80	VIIb	$C_{23}H_{17}N_5O_3$	274 ... 275	81
IIIb	$C_{16}H_{14}N_4O$	219 ... 220	76	VIIId	$C_{13}H_{15}N_3$	172 ... 174	54
IIIc	$C_{10}H_{10}N_4$	205 ... 207	75	VIIIe	$C_{16}H_{13}N_3$	279 ... 280	82
IIId	$C_{13}H_{16}N_4$	209 ... 210	77	IXa	$C_{15}H_{10}N_4O$	254 ... 255	—
IIIe	$C_{16}H_{14}N_4$	186 ... 187	76	IXb	$C_{16}H_{12}N_4O_2$	274 ... 275	85
IVa	$C_{15}H_{14}N_4O$	175 ... 176	95	IXd	$C_{13}H_{14}N_4O$	273 ... 274	20
IVb	$C_{16}H_{16}N_4O_2$	180 ... 182	94	X	$C_{16}H_{12}N_4O$	171 ... 172	91
Vc	$C_{10}H_{11}N_3O_2$	155 ... 156	10				

*Compounds (IIb), (IIIb), (VIa), and (VIb) were recrystallized from butanol, (IIc) from a mixture of alcohol and ether (3:1), (IIId) from ethyl acetate, (VIIa), (VIIb), and (IXb) from DMF, (VIIIe) from xylene, and the remaining compounds from alcohol.

Unfortunately, we have been unable to obtain a fixed model form of the tautomer (IXC), so that its absence from the mixture cannot be rigorously confirmed. Nevertheless, the occurrence of this form is unlikely. Alkylation of the anion of imidazo[1,2-*a*]benzimidazole at $N_{(9)}$ [2] shows that the electron density at this heteroatom is greater than at $N_{(1)}$. A further reduction in the electron density at $N_{(1)}$ should result on introducing a nitroso group into the 3-position. For these reasons, the possibility of addition of a proton to $N_{(1)}$ can probably be discounted.

EXPERIMENTAL

The IR spectra were measured on a UR-20 in Vaseline grease, and UV spectra on a Specord 40M spectrophotometer in methanol. The PMR spectra of (IIIa, c), (VIIId), and (XII) were obtained on a Tesla BS-487 (80 MHz) instrument, and of (IXa), (X), and (XI) on a Varian XL (100 MHz) spectrometer, internal standard HMDS. The reactions were followed and the purities of the products established by TLC on plates of alumina (activity grade III), eluent chloroform, visualized with iodine vapor.

The properties of the compounds obtained are shown in Table 1. The elemental analyses were in agreement with he calculated values.

1,2-Diamino-3-phenacylbenzimidazolium Bromide (IIa). To a solution of 0.74 g (5 mmoles) of 1,2-diaminobenzimidazole in 10 ml of DMF was added at 70°C 0.99 g (5 mmoles) of phenacyl bromide. After spontaneous cooling of the mixture (~30 min), the solid which separated was filtered off and washed with acetone. IR spectrum: 3370, 3250, 3050 (NH, NH_2), 1700 cm^{-1} (CO).

The **quaternary salts (IIb-d)** were obtained similarly.

1-Amino-3-phenacylbenzimidazolin-2-imine (IVa). A suspension of 0.69 g (2 mmoles) of the salt (IIa) in 20 ml of 2% sodium bicarbonate solution was boiled for 10 min. After cooling, the solid was filtered off and washed with water. IR spectrum: 3450, 3320, 3200 (NH, NH_2), 1680 cm^{-1} (CO).

Imine (IVb) was obtained similarly.

9-Amino-2-phenylimidazo[1,2-*a*]benzimidazole (IIIa). A suspension of 0.69 g (2 mmoles) of the salt (IIa) in 70 ml of 2% sodium bicarbonate solution was boiled for 5 h. On cooling, the colorless solid was filtered off and washed with water. IR spectrum: 3280, 3135 (NH_2), 1620, 1600, 1580 cm^{-1}. PMR spectrum (DMSO–D_6): 5.88 (2H, s, NH_2, disappears on deuteration); 6.93-7.76 ppm (10H, m, aromatic protons).

Compound (IIIb) was obtained similarly.

Cyclization of 3-Acetonyl-1,2-diaminobenzimidazolium Chloride (IIc). A solution of 2.40 g (10 mmoles) of the salt (IIc) in 100 ml of 2% sodium bicarbonate solution was boiled for 1 h. The **9-amino-3-methylimidazo[1,2-*a*]benzimidazole (IIIc)** which separated on cooling was filtered off and washed with water. Weight 1.2 g. PMR spectrum (DMSO–D_6): 2.23 (3H, s, CH_3), 5.85 (2H, br.s, NH_2; disappears on deuteration), 6.92-7.71 ppm (5H, m, aromatic protons). The mother liquors were extracted with 50 ml of chloroform, and the chloroform extract evaporated and

chromatographed on a column of alumina (15 × 300 mm), eluent chloroform. From the first fraction (R_f 0.4) there was obtained 0.2 g of the imidobenzimidazole (IIIc), and from the second (R_f 0.3), 0.25 g of **1-amino-3-acetonylbenzimidazol-2-one (Vc).** IR spectrum: 3300, 3190 (NH_2): 1705, 1690 cm^{-1} (C=O).

Compounds (IIId) and (Vd) were obtained similarly.

9-Amino-3-methyl-2-phenylimidazo[1,2-*a*]benzimidazole (IIIe). To a solution of 1.48 g (10 mmoles) of 1,2-diaminobenzimidazole in 20 ml of DMF at 70°C was added 1.08 g (5 mmoles) of α-bromopropiophenone, whereupon the color of the solution deepened and heat was liberated. After 30 min, the solvent was removed under reduced pressure, and the dry residue treated with 30 ml of chloroform. The precipitated hydrochloride of the starting diamine was filtered off, and the mother liquors chromatographed on a column of alumina (15 × 150 mm), eluent chloroform, the fraction R_f 0.4 being collected.

1-(p-Nitrobenzylidene)amino-3-phenacylbenzimidazolin-2-imine (VIa). A solution of 0.53 g (2 mmoles) of the imine (IVa) and 0.3 g (2 mmoles) of p-nitrobenzaldehyde in 10 ml of alcohol was boiled for 30 min. The orange-colored solid which separated on cooling was filtered off. IR spectrum: 3320 (NH), 1680 (C=O), 1650 cm^{-1} (C=N).

Compound (VIb) was obtained similarly.

9-(p-Nitrobenzylidene)amino-2-phenylimidazo[1,2-*a*]benzimidazole (VIIa). A. A solution of 0.4 g (1 mmole) of the imine (VIa) in 3 ml of DMF was boiled for 1 h. The red solid which separated on cooling was filtered off and washed with alcohol, to give 0.3 g (79%) of product. IR spectrum: 1600, 1580, 1575 cm^{-1}.

B. A solution of 0.25 g (1 mmole) of (IIIa) and 0.15 g (1 mmole) of p-nitrobenzaldehyde in 10 ml of propanol was boiled with 1-2 drops of piperidine for 1 h. The solid which separated on cooling was filtered off, and washed with alcohol to give 0.32 g (84%) of product. The compound was identical with that obtained by method **A.**

Compound (VIIb) was obtained similarly.

1(9H)-3-Methyl-2-phenylimidazo[1,2-*a*]benzimidazole (VIIIe). To a solution of 0.52 g (2 mmoles) of (IIIe) in 10 ml of glacial acetic acid was added dropwise with stirring at 5-10°C a solution of 0.14 g (2 mmoles) of sodium nitrite in 3 ml of water. The mixture was stirred at this temperature for 1 h, then diluted with 20 ml of water and neutralized with concentrated ammonia. The solid was filtered off and washed with water. IR spectrum: 1630, 1610 cm^{-1}.

3-Hydroxyimino-2-phenyl-3H-imidazo[1,2-*a*]benzimidazole (IXa). A. To a solution of 0.5 g (2 mmoles) of (IIIa) in 10 ml of glacial acetic acid was added slowly with stirring at 5-10°C a solution of 0.14 g (2 mmoles) of sodium nitrite in 3 ml of water. The solution immediately turned yellow in color, and an orange-colored precipitate began to separate. After 1 h at 5-10°C, the solid was filtered off and washed with water, yield 0.24 g (46%). IR spectrum: 2800-2100, 1605, 1555 cm^{-1}. UV spectrum, λ_{max} (log ε): 242 (4.02), 250 (4.02), 268 (3.82), 400 nm (3.53). PMR spectrum (DMSO–D_6): 7.33 (2H, m, 3'-H), 7.70 (4H, m, 5-H–8-H), 8.0 (1H, m, 4'-H), 8.44 (2H, m, 2'-H), 13.66 ppm (1H, br.s, OH).

Treatment of the mother liquors with water gave 0.21 g (42%) of the starting material (IIIa).

B. Using the above method, from the imidazobenzimidazole (IIIa), but using 2 moles of sodium nitrite (IXa) was obtained in 87% yield.

Compounds (IXb) and (IXd) were obtained similarly.

C. To a solution of 0.7 g (3 mmoles) of (VIIIa) in 10 ml of glacial acetic acid was added at 5-10°C a solution of 0.21 g (3 mmoles) of sodium nitrite in 3 ml of water. The mixture was kept for 20 min, then the orange-colored solid which had separated was filtered off, yield 0.72 g (97%). The compound obtained in this way gave no depression of melting point with material obtained by methods **A** and **D.**

D. To a suspension of 0.3 g (5.3 mmoles) of powdered KOH in 4 ml of dry DMSO was added 0.25 g (1 mmole) of 1(9H)-3-amino-2-phenylimidazo[1,2-*a*]benzimidazole, and the mixture stirred for 1 h at 50-60°C, cooled, diluted with 20 ml of water, and acidified with concentrated HCl to pH 3. The orange-colored solid which separated was filtered off and washed with water and alcohol, yield 0.23 g (88%).

Reaction of 9-Amino-2-arylimidazo[1,2-*a*]benzimidazoles (IIIa, b) with KOH in DMSO. To a suspension of 1.68 g (30 mmoles) of powdered KOH in 5 ml of dry DMSO was added 1 mmole of the 9-amino-2-arylimidazobenzimidazole, and the mixture stirred for 1 h at 50-60°C. It was then cooled poured into 20 ml of water, and neutralized with concentrated HCl. The colorless 1(9H)-2-arylimidazo[1,2-*a*]benzimidazole which separated was filtered off and washed with water to give 1(9H)-2-phenylimidazo[1,2-*a*]benzimidazole (VIIIa) [yield 70-75%, mp 310°C (from DMF); the literature [6] gives mp 310°C] and 1(9H)-2-(p-methoxyphenyl)imidazo[1,2-*a*]benzimidazole (VIIIb) mp 305-307°C (from DMF), the literature [9] gives mp 295-297°C].

Acidification of the mother liquors to pH 4-5 precipitated the red 3-hydroxyimino compounds (IXa) and (IXb), in 10-12% yields. These compounds gave no depression of melting point with authentic samples of the oximes (IXa) and (IXb).

1(9H)-2-(tert-Butyl)imidazo[1,2-*a*]benzimidazole (VIIId). To a suspension of 1.68 g (30 mmoles) of powdered KOH in 5 ml of dry DMSO was added 0.23 g (1 mmole) for the amine (IIId). The mixture was stirred for 1 h at 70-80°C, cooled, poured into 20 ml of water, and neutralized with concentrated HCl. The colorless solid which separated was filtered off and washed with water. The product was purified by chromatography on a column (15 × 100 mm) of alumina, eluent chloroform, R_f 0.25. PMR spectrum ($CDCl_3$): 1.45 [9H, s, $C(CH_3)_3$], 6.9 (1H, s, 3-H), 7.1 (2H, m, aromatic protons), 7.43 ppm (2H, m, aromatic protons).

Reaction of 2-Aryl-1-(p-nitrobenzylideneamino)imidazo[1,2-*a*]benzimidazoles (VIIa, b) with KOH in DMSO. To a suspension of 1.68 g (30 mmoles) of powdered KOH in 5 ml of dry DMSO was added 1 mmole of (VIIa) or (VIIb), and the mixture stirred for 1 h at 60-70°C. The solution was then cooled, poured into 20 ml of water, and neutralized with concentrated HCl. The colorless solid which separated was filtered off, washed with water, and recrystallized from DMF, yield 75-80%. The physicochemical characteristics of the compounds obtained were in agreement with those of the imidazobenzimidazoles (VIIIa) and (VIIIb) described above.

1(9H)-3-(Acetamido)-2-phenylimidazo[1,2-*a*]benzimidazole ($C_{17}H_{14}N_4O$). To a suspension of 1.3 g (5 mmoles) of the oxime (IXa) and Raney nickel (obtained from 0.5 g of the alloy) was added 1 ml of hydrazine hydrate. Evolution of gas then commenced, and the solution gradually became colorless. When gas evolution had ceased, the mixture was treated with a further 20 ml of methanol, boiled for 30 min, and filtered. The solid which separated on cooling the filtrate (3-amino-2-phenylimidazobenzimidazole) was isolated and washed with methanol. Weight 0.74 g. The compound oxidized readily in air, so that it was used in the reaction with KOH in DMSO without purification. It was characterized as its acetyl derivative, obtained by boiling 0.49 g (2 mmoles) of the amine in 5 ml of acetic anhydride for 10 min. The solid which separated on cooling the mixture was filtered off and washed with ether. Yield 0.5 g (86%), colorless prisms, mp 266-267°C (from DMF). IR spectrum: 3250 (NH), 1705 (CO), 1660, 1600, 1585 cm^{-1}.

3-Methoxyimino-2-phenyl-3H-imidazo[1,2-*a*]benzimidazole (X). To a suspension of 0.52 g (2 mmoles) of the oxime (IXa) in 4 ml of DMSO was added with stirring 0.2 g (3.6 mmoles) of powdered KOH. The solid (IXa) then dissolved, and to the resulting solution was added 0.2 ml (3.2 mmoles) of methyl iodide. After 15 min, a red solid separated. After stirring for a further 15 min, 10 ml of water was added, and the solid filtered off and washed with water. UV spectrum, λ_{max} (log ε): 246 (3.88), 270 (3.80), 390 nm (3.52). PMR spectrum (DMSO-D_6): 4.34 (3H, s OCH_3), 7.34 (2H, m, m-H, C_6H_5), 7.58-7.84 (5H, m, p-H, C_6H_5 and 5-H–8-H), 8.42 ppm (2H, m, o-H, C_6H_5).

9-Methyl-3-nitroso-2-phenylimidazo[1,2-*a*]benzimidazole (XI). A mixture of 0.2 g (0.76 mmole) of (IXa) and 0.1 ml (1.1 mmoles) of dimethyl sulfate was heated for 10 min at 130°C. After cooling, the mixture was treated with 3 ml of concentrated ammonia, and extracted with 20 ml of chloroform. Purification was effected by column chromatography (15 × 200 mm) on alumina, eluent chloroform, the fraction R_f 0.9 being collected. Yield 0.1 g (48%), bright green crystals, mp 245-246°C (the literature [10] gives mp 247°C). UV spectrum: λ_{max} (log ε): 240 (3.96), 246 (3.96), 391 (3.72). PMR spectrum (DMSO-D_6): 3.94 (3H, s, CH_3), 7.35-7.83 (6H, m, m-H, C_6H_5, 5-H–8-H), 8.03 (1H, m, p-H, C_6H_5), 8.62 ppm (2H, m, o-H, C_6H_5).

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"ENE" ADDUCTS OF N-SUBSTITUTED TRIAZOLINEDIONES.

3.* SYNTHESIS OF NOVEL TYPES OF IMIDOURAZOLES FROM N-SUBSTITUTED cis-CYCLOHEX-4-ENE-1,2-DICARBOXIMIDES

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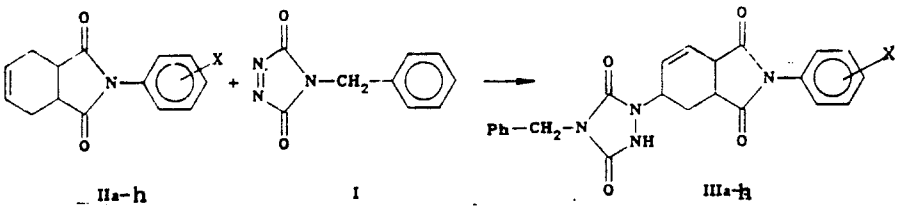
Some novel "ene" adducts of N-aryl-cis-cyclohex-4-ene-1,2-dicarboximides (N-Ar-cis-4-CHDI), and its cis,cis-3-methyl- and cis-4-methyl derivatives, to 4-benzyl-1,2,4-triazoline-3,5-dione (4-benzyl-TAD) have been prepared and characterized.

The "ene" reaction of 4-substituted TAD with olefins has been studied extensively [3-6]. Also reported has been the reaction of 4-phenyl-TAD with cyclohexene and 1-methylcyclohexene [5]. There have, however, been no reports of the reaction of 4-R-TAD with di- and trisubstituted cyclohexenes. Attempts to use N-substituted cis-4-CHDI in this reaction are of particular interest for the preparation of individual stereoisomeric compounds, and could precede a study of the mechanism of this reaction. The presence of functional groups in the adducts obtained would enable them to be used as reactive monomers in polycondensation reactions for the preparation of highly thermally stable polymers with known steric structures [7].

In earlier communications [1, 2] we referred to the reaction of 4-R-TAD with the N-arylimides of unsaturated cyclic dicarboxylic acids.

The object of the present investigation was to synthesize and establish the structures of ene-adducts of 4-benzyl-TAD (I) with N-aryl-cis-4-CHDI (IIa-h) and their 3- (IV) and 4- (VI) methyl derivatives.



IIa-h I IIIa-h

II, III a X=H, b X=*p*-CH_3, c X=*m*-CH_3, d X=*o*-CH_3, e X=*p*-OCH_3, f X=*p*-Br, g X=*p*-Cl, h X=*m*-Cl

*See [1] and [2], respectively, for Communications 1 and 2.

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