A 60-mg (0.01 mmole) sample of orthoboric acid and 150 ml of xylene were added to 2.5 g (0.01 mmole) of Ic, and 1.7 g (67%) of IIc, with M^+ 255 (I_{rel} 42%) and mp 241°C, was synthesized as described for IIa. $C_{18}H_{25}N \cdot HClO_4$.

The authors thank N. N. Chichelova for the 1,5-diketones, which were synthesized in the department of organic chemistry of Vladivostok State University.

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OXIDATION OF 1-AMINOBENZIMIDAZOLES. SYNTHESIS AND PROPERTIES OF 1,1'-AZOBENZIMIDAZOLES*

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UDC 547.873'785.5.04:542.943:541.124:543.51'422

1-Amino-2-R-benzimidazoles are oxidized by lead tetraacetate to give, depending on the substituent in the 2-position, either to 1,1'-azobenzimidazoles (R = H, CH_3, C_6H_5, Cl, $N(CH_3)_2$) or 3-R-benzo-1,2,4-triazines (R = NH_2, $NHCH_3$, NHC_6H_5, OH). The factors affecting the course of the reaction are discussed. The physicochemical properties of the 1,1'-azobenzimidiazoles obtained have been examined.

1,2-Diaminobenzimidazole (Ia) is oxidized by lead tetraacetate [2] or manganese dioxide [3] to give good yields of 3-aminobenzo-1,2,4-triazine (IIa) as the sole product. By analogy with other, similar reactions of N-aminoazoles, this reaction is assumed to involve the intermediate formation of a highly reactive N_1-nitrene, which intramolecularly attacks atom $C_{(2)}$ of the imidazole ring. If this reaction does in fact occur, other 1-aminobenzimidazoles should react similarly, thus providing a route to the highly inaccessible 3-R-benzo-1,2,4-triazines. In order to test this hypothesis, we have examined the oxidation of 1-aminobenzimidazole (Ib) and its 2-substituted derivatives (Ic-h), together with some other compounds.

The oxidation of 1-aminobenzimidazoles with lead tetraacetate is extremely complex, often giving difficultly-separable mixtures and unstable compounds. The products are highly dependent on the substituent present in the 2-position. For example, oxidation of the parent benzimidazole (Ib) with a small excess of lead tetraacetate in dichloromethane at 20°C gives, instead of the expected benzotriazine (II) (R = H), 32% of 1-acetylbenzimidazole (IVa), and 5% of the hitherto unknown 1,1'-azobenzimidazole (IIIb). When this reaction was carried out in the presence of calcium oxide (to bind the acetic acid liberated), in addition to the tetrazine (IIIb) (5%), the second reaction product was benzimidazole (perhaps as a result of hydrolytic cleavage of (IVa) under these conditions [6, p. 38]). Oxidation of 1-amino-5,6-dimethylbenzimidazole with lead tetraacetate gave 10% of 1-acetyl-5,6-dimethylbenzimidazole (IVb) only. The yield of the tetrazene (IIIb) was increased to 25% when the oxidation of (Ib) was carried out with bromine water.† Under similar conditions, 1-amino-5,6-dimethylbenzimidazole was oxidized to the tetrazene (V) (10%) and 5,6-dimethylbenzimidazole (55%).

*For preliminary communication, see [1].

†Attempts to obtain the tetrazene (IIIb) by oxidation of 1-aminobenzimidazole with mercuric oxide were unsuccessful [7].

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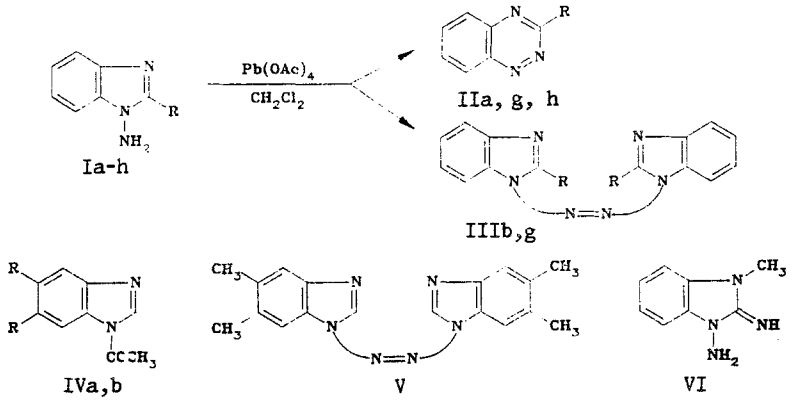
0009-3122/89/2511-1241$12.50

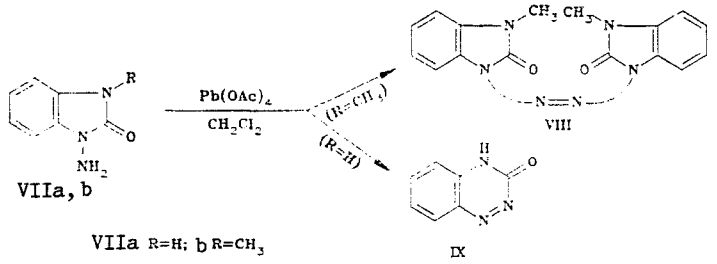
Oxidation of 1-amino-2-methyl- (Ic), 1-amino-2-phenyl- (Id), and 1-amino-2-chlorobenzimidazole (Ie) with lead tetraacetate to the tetrazenes is more successful. In this instance, (IIIc-e) were isolated in yields of 40, 43, and 58% respectively. Oxidation of 1-amino-2-dimethylamino- (If) and 1-amino-2-methylaminobenzimidazole (Ig) under the same conditions resulted in considerable resinification, and the formation of complex mixtures of unstable products from which the tetrazenes (IIIf) and (IIIg) were isolated in yields of 4 and 7.5%. In addition, oxidation of (Ig) gave 3-methylaminobenzo-1,2,4-triazine (IIg) in 5% yield. Only 3-phenylaminobenzotriazine (IIb) (25%) could be isolated on oxidation of the amine (Ih).



I, II a $R=NH_2$, I, III b R=H, c $R=CH_3$, d $R=C_6H_5$, e R=Cl, f $R=N(CH_3)_2$; I—III g $R=NHCH_3$, I, II h $R=NHC_6H_5$; IV a R=H, b $R=CH_3$

These findings prompt the questions: 1) why is the formation of tetrazenes on oxidation of 1-aminobenzimidazoles the rule, while benzo-1,2,4-triazines are formed in relatively few instances? 2) what is the reason for the improved yields of tetrazenes when substituents such as methyl, phenyl, or chloro are present in the 2-position of 1-aminobenzimidazole?, and 3) what is the mechanism of formation of the 1-acetylbenzimidazoles (IV)? These questions will be considered in order.

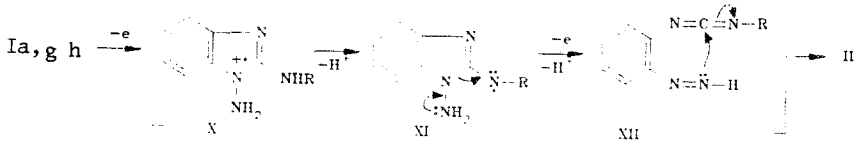
It is noteworthy that benzotriazines are only formed from 1-aminobenzimidazoles bearing in the 2-position a substituent with at least one N—H bond. In fact, apart from compounds (Ia, g, h), benzotriazines are formed from 1,2-diaminobenzotriazoles containing substituents in the benzene ring [2], and also from 1-amino-2-benzylaminobenzimidazole [8]. This leads to the conclusion that ring enlargement occurs either via the tautomeric imino-form,* or that at some stage it requires the elimination of a proton from the N—H bond in the 2-position. To test these hypotheses, we oxidized the recently-synthesized imine (VI) [8], together with the 1-aminobenzimidazolone (VIIa) and its 3-methyl derivative (VIIb).



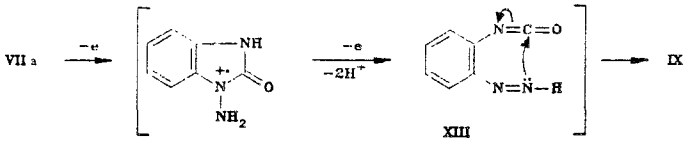
VIIa R=H; b $R=CH_3$

Unfortunately, treatment of the imine (VI) with lead tetraacetate resulted in considerable resinification and degradation. Under the same conditions, 1-amino-3-methylbenzimidazolone (VIIb) gave 49% of the tetrazene (VIII), and the benzimidazolone (VIIa) gave 48% of benzo-1,2,4-triazin-2-one (IX). Since both these compounds (VII) exist in the oxo-form, equivalent to the imino-form (VI), but give totally different results on oxidation, it may be assumed that the formation of benzotriazines results from elimination of a proton from the N—H group, rather than as a result of tautomerism. In our view, the formation of benzotriazines (II) probably occurs without the intermediate formation of a nitrene, by the mechanism:

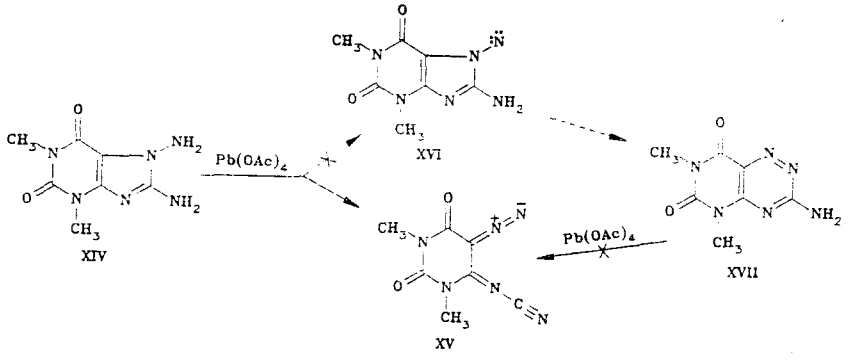
*Although the tautomeric equilibrium in 20 aminobenzimidazoles is strongly shifted towards the amino-forms [9], the possibility cannot be excluded that in the N-nitrene (where this is formed) the position of the equilibrium could differ considerably.



Electrochemical measurements have shown [10] that the first step in the oxidation of 1-aminobenzimidazoles involves detachment of an electron from the π-orbital of the molecule, rather than from the N-amino group. The cation-radical (X) thus formed must be stabilized by loss of a proton. Since the N-amino group has a lower NH-acidity than the 2-amino group [10], the proton will in the first instance be cleaved from the 2-position to give the radical (XI). Subsequent oxidation and stabilization will then occur with participation of the N-amino group to give, first, the carbodiimide (XII), followed by closure of the triazine ring. The conversion of (VIIa) into (IX) can, in principle, be depicted similarly as proceeding via the isocyanate (XIII).



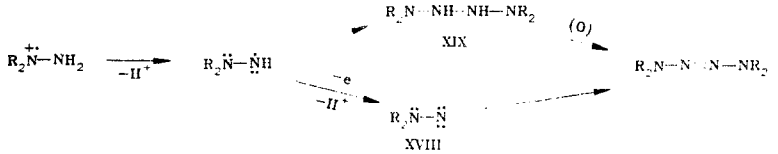
Indirect, but weighty support for this mechanism for the formation of benzotriazines is provided by the oxidation of 7,8-diaminotheophylline (XIV), recently obtained by the authors [11]. Like the diamine (Ia), it behaves anomalously in comparison with 7-amino- and 7-amino-8-methyltheophylline. Although the latter are converted by treatment with lead tetraacetate into pyrimido[4,5-e]-1,2,4-triazine-6,8-diones [12, 13], the diamine (XIV) under these conditions gives the hitherto unreported 1,3-dimethyl-5-diazo-6-cyanoiminohexahydropyrimidine-2,4-dione (XV). If the N-nitrene (XVI) were formed as an intermediate in this reaction, it would probably undergo conversion into the known [14] amine (XVII). We have, however, found that the latter compound is unaffected by treatment with lead tetraacetate. It follows that modification of the 8-amino group in the early stages is involved in the formation of (XV).



In principle (XV) is the oxidation product of an intermediate (XII). The fact that, like its hydrogenated precursor, it does not undergo cyclization to the amine (VI) could be due to the reduced aromaticity of the uracil nucleus [15, p. 48], which, in contrast to the benzene ring, is readily stabilized in the orthoquinonoid form [13].

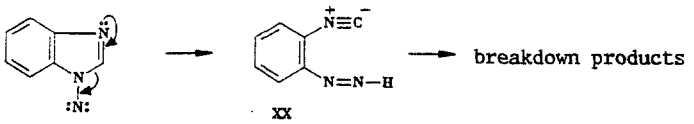
We now turn to the possible reasons for the marked variability of the yields of tetrazenes with respect to the substituent present in the 2-position. The key question is this: are nitrenes involved in the formation of tetrazenes, or not? Oxidation of 2-alkyl-1-aminobenzimidazoles in the presence of olefins has previously been reported [16] to give good yields if 2-alkyl-1-aziridinylbenzimidazoles, the reaction being highly stereospecific. This reaction is considered to be evidence for the formation of the N-nitrene, and it may therefore be concluded that in the present case also, i.e., in the absence of an olefin, the tetrazenes (III) are formed by dimerization of the nitrenes (XVIII), as follows:*

*Another mode of formation of tetrazenes is possible, involving the formation of the tettrazanes (XIX), these being subsequently oxidized. In a few instances, tetrazanes have been isolated [17], but they were found to be highly unstable compounds which decomposed with the liberation of a molecule of nitrogen. There appears to be no reports of the oxidation of heterocyclic tetrazanes to tetrazenes.

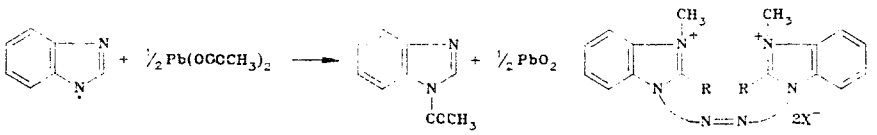


Why then do the N-nitrenes formed from compounds Ib-f not transform into benzonitrazenes? The reason undoubtedly lies in the high electron deficiency of position 2 in the benzimidazole molecule [15, p. 48]. Nitrenes, then, being the most electron deficient particles, have a tendency to attack atoms with higher electron density. Because of this the N-nitrene rings of indazole [18], theophylline [12, 13], and a series of other compounds are particularly easily enlarged.

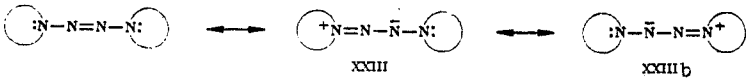
When enlargement of the ring is impossible, in addition to dimerization into tetrazenes, N-nitrene of nitrogen, etc. [4, 5, 18]. It can be hypothesized that, for example, in the absence of a substituent at position 2, N-nitrenes of benzimidazole have a tendency to break the ring to form unstable compounds of type XX. Actually, during the oxidation of amine Ib the reaction mixture has a strong isonitryl odor. If position 2 has a substituent (amines Ic-e, IVa) the breaking of the ring is hindered and consequently the yield of tetrazene is increased, with the exception of tetrazene IIIe whose low yield can be explained by its high instability (see below).



As far as we are aware, the formation of N-acetyl compounds (IV) on oxidation of N-aminoheterocycles with lead tetraacetate has not been reported. The mechanism of this reaction must be homolytic, since it is difficult to postulate the presence, in a mixture containing lead acetates and acetic acid, of sufficiently reactive electrophilic acetylating agents. It is likely that the decomposition of one of the intermediate oxidation products (the nitrene or tetrazane, for example) gives the N-benzimidazolyl radical (XXI), which cleaves an acetyl radical from one of the lead acetates, for example from the diacetate:



Since the 1,1'-azobenzimidazoles (III) have not previously been reported as the free bases,* it was of interest to examine their physicochemical properties. The molecular structures of the tetrazenes suggest that they should readily decompose with liberation of a molecule of nitrogen. In fact, most of these compounds, like the salts (XXII), are amazingly stable. For example, the tetrazene (IIIb) withstands heating at 200°C, and may be recrystallized from such aggressive solvents as acetic acid and dimethylformamide. The other tetrazenes (IIIc-e) are nearly as stable. This could be due to conjugation of the azo-group with the π-system of the heterocycle, thereby increasing the contribution of structures (XXIIa) and (XXIIIb) to the resonance hybrid, and increasing the order of the bonds between the ring nitrogens and the azo-group.



*The only report is of the preparation of the 1,1'-azobenzimidazolium salts (XXII) by oxidation of 1-amino-2-R-3-methylbenzimidazolium salts with bromine water [19]. No physicochemical properties of the salts (XXII) were however determined.

TABLE 1. UV Spectra of Compounds Synthesized (in methanol)

Compound	λ_{max}, nm (log ε)	Compound	λ_{max}, nm (log ε)
IIg	245 (3,46), 305 (2,49), 406 (2,51)	IIIf	214 (3,44), 275 (3,44), 340 (3,10)
IIh	273 (4,48), 421 (3,50)	IIIg	275 (3,45), 340 (3,18)
IIIb	262 (3,18), 343 (3,07)	V	271 (4,47), 350 (4,36)
IIIc	269 (3,69), 351 (2,18)	VIII*	265 (4,51), 337 (4,20)
IIId	238 (3,89), 270 (4,08), 350 (3,78)	IX	231 (4,07), 297 (3,14), 390 (3,15)
IIIe	264 (3,63), 344 (3,45)		

*Spectrum obtained in chloroform solution.

TABLE 2. Mass Spectra of Compounds Obtained

Compound	Recording temperature, °C	m/z (I>5)
IIIb	150	50 (13,4), 55 (10,6), 56 (5,9), 57 (27,5), 63 (17,5), 64 (13,9), 67 (18,6), 69 (8,7), 71 (15,1), 76 (17,8), 83 (12,3), 84 (8,9), 85 (9,7), 90 (100), 91 (12,0), 103 (6,6), 110 (7,8), 111 (5,1), 117 (55,6), 118 (68,5), 119 (5,7), 196 (29,1), 233 (5,2), 234 (2,3), 262 (52,9, M+), 263 (9,0)
IIIc	150	43 (9,3), 44 (6,3), 50 (10,1), 55 (6,1), 57 (13,2), 63 (17,6), 64 (12,0), 69 (5,8), 71 (7,2), 76 (17,3), 77 (14,1), 83 (5,4), 90 (100), 91 (10,9), 117 (20,2), 131 (83,0), 132 (18,7), 159 (9,5), 290 (68,8, M+), 291 (13,3)
IIId	150	50 (12,0), 51 (11,9), 63 (27,8), 64 (17,1), 76 (13,7), 77,2 (13,3), 90 (100), 91 (11,4), 97 (6,2), 166 (7,5), 179 (6,0), 192 (6,7), 193 (99,8), 194 (89,3), 195 (10,2), 221 (10,8), 414 (22,9, M+), 415 (6,5)
IIIe	150	50 (8,9), 63 (20,1), 64 (15,5), 76 (8,7), 90 (100), 91 (6,8), 151 (39,5), 152 (11,7), 153 (12,1), 330 (6,4, M+), 332 (3,6)
IIIf	190	51 (8,7), 52 (8,0), 57 (6,0), 63 (7,9), 64 (6,6), 65 (10,1), 77 (8,8), 78 (7,7), 90 (12,1), 91 (15,5), 92 (15,8), 118 (68,1), 119 (32,2), 131 (9,4), 132 (50,7), 133 (8,3), 146 (94,9), 147 (9,6), 160 (36,8), 161 (100), 162 (10,2), 348 (1,8, M+)
V	180	51 (9,7), 52 (5,2), 53 (6,2), 55 (12,3), 57 (9,6), 59 (9,6), 63 (5,6), 65 (15,8), 69 (6,9), 72 (5,1), 73 (6,5), 77 (10,8), 78 (10,2), 91 (37,3), 92 (5,3), 102 (7,1), 103 (10,4), 104 (12,1), 105 (6,5), 116 (25,9), 117 (9,8), 118 (51,2), 119 (7,8), 129 (6,2), 131 (20,2), 144 (6,9), 145 (70,0), 146 (83,7), 147 (8,9), 174 (6,4), 275 (6,9), 289 (12,1), 290 (6,6), 318 (100, M+), 319 (24,3)
VIII	235	44 (15,8), 51 (10,4), 65 (14,6), 77 (20,5), 78 (13,6), 90 (8,7), 92 (22,2), 119 (73,9), 120 (11,9), 147 (100), 148 (19,1), 294 (8,1), 322 (21,4, M+)
IX	95	41 (12,4), 43 (7,3), 50 (78,8), 51 (16,6), 52 (20,7), 62 (10,8), 63 (37,8), 64 (60,2), 65 (16,6), 74 (16,6), 75 (20,7), 76 (64,3), 77 (9,3), 90 (22,8), 91 (39,8), 92 (87,8), 93 (10,4), 119 (100), 120 (8,3), 147 (72,6, M+), 148 (10,8)

The tetrazene (IIIf) is, however, much less stable, decomposing gradually on storage, and on attempted recrystallization. All the tetrazenes decompose with deflagration in the flame of a burner, which enables them readily to be distinguished from the original benzimidazoles and benzo-1,2,4-triazines.

The conjugation in the tetrazenes is readily apparent from their UV spectra (Table 1). For example, while the spectra of benzimidazole and its 1-alkyl and 1-amino-derivatives show two peaks at 250-260 and 275-280 nm [10, 20], the spectra of (III) show, in addition to the peak at 260 nm, a band at 340-350 nm, which is undoubtedly due to $\pi \rightarrow \pi^*$ electron transfer involving both the heterocycle and the azo-group. For the tetrazenes (IIIe-g) and (XXII) (R = H), the terminal absorption from this band extends to nearly 400 nm, and they are therefore yellow in color, in contrast to the colorless compounds (IIIb-d). The 1,1'-azobenzimidazoles are readily distinguishable from the bright yellow benzotriazines (II) and (IX) in their color and UV spectra, those of the latter having long wavelength absorption at 395-405 nm.

TABLE 3. PMR Spectra of 1-Substituted Benzimidazoles

Compound	Solvent	Species	Chemical shift, ppm					
			2-H, m	4-H	5-H, m	6-H, m	7-H	Substituent
XXIVa	$CDCl_3$	Base	7,85	7,80 d.d	7,34	7,34	7,34 m	3,83 (s, CH_3)
	$CDCl_3$+ CF_3CO_2D	Cation	9,42	7,93 d.d	7,56	7,56	7,56 m	4,11 (s, CH_3)
	DMSO-D_6	Base	8,16	7,59 m	7,23	7,23	7,59 m	3,84 (s, CH_3)
XXIVb	$CDCl_3$	Base	7,95	7,76 d.d	7,35	7,35	7,35 m	4,84 (br, NH_2)
	$CDCl_3$+ CF_3CO_2D	Cation	9,15	7,76 m	7,76	7,76	7,76 m	—
XXIVc	$CDCl_3$	Base	7,75	7,60 d	—	7,15	7,15 m	3,75 (s, 1-CH_3); 2,45 (s, 5-CH_3)
IIIb	$CDCl_3$	Base	8,58	7,90 d.d	7,48	7,48	8,18 d.d	
	$CDCl_3$+ CF_3CO_2D	Cation	10,48	8,13 d.d	7,93	7,93	8,66 d.d	
	DMSO-D_6	Base	9,16	7,85 d.d	7,51	7,51	8,42 d.d	
	DMSO-D_6+ CF_3CO_2D	Cation	9,55	7,93 d.d	7,55	7,55	8,52 d.d	
IIId	$CDCl_3$	Base	—	7,1 ... 7,9 m	7,1 ... 7,9	7,1 ... 7,9	8,07 d.d	7,1 ... 7,9 (m, $2C_6H_5$)
V	$CDCl_3$	Base	8,47	7,62 s	—	—	7,94 s	2,43 (s, $2CH_3$); 2,48 (s, $2CH_3$)
	$CDCl_3$+ CF_3CO_2D	Cation	10,14	7,83 s	—	—	8,25 s	2,54 (s, 5- and 6-CH_3)
VIII	DMSO-D_6	Base	—	7,34 m	7,34	7,34	7,34 m	3,27 (s, 2N—CH_3)
XXII*	DMSO-D_6	Cation	9,58	7,65 d.d	7,40	7,40	8,0 m	4,08 (s, 2N—CH_3)
XXVIIa	$CDCl_3$	Base	8,35	7,85 m	7,40	7,40	7,85 m	7,40 (m, *m*- and *p*-C_6H_5); 7,85 (m, *o*-C_6H_5); 8,74 (s, CH=N)
	$CDCl_3$+ CF_3CO_2D	Cation	9,93	7,98 m	7,65	7,65	7,98 m	7,65 (m, *m*- and *p*-C_6H_5); 7,98 (m, *o*-C_6H_5); 9,16 (s, CH=N)
XXVIIb	$CDCl_3$	Base	—	7,89 m	7,28	7,28	7,89 m	2,74 (s, 2-CH_3); 7,53 (m, *m*- and *p*-C_6H_5); 7,67 (s, *o*-C_6H_5); 8,96 (s CH=N)
	$CDCl_3$+ CF_3CO_2D	Cation	—	7,98 m	7,64	7,64	7,98 m	2,97 (s, 2-CH_3); 7,64 (m, C_6H_5); 9,01 (s, CH=N)

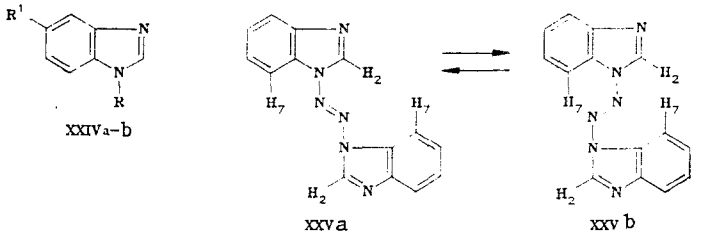
*R = H, X = Br^-.

The electron acceptor properties of the azo-group result in a considerable decrease in the basicity of the imidazole nuclei at which protonation occurs (see below). For example, the first and second protonation constants pK'_a and pK''_a for (IIIb) (in acetonitrile) are 9.05 and 6.00, whereas the pK_a of 1-aminobenzimidazole under the same conditions is 12.83 [10].

The mass spectra of all the tetrazenes show the molecular ion peaks (Table 2). The $M^{+\cdot}$ peak is most intense (100%) for the tetrazene (V), and least intense for (IIIf) (1.8%), which, as noted above, is less stable. The principal mode of fragmentation of the molecular ions $[Bzm{-}N{=}N{-}Bzm]^{+\cdot}$ is by dissociative fission of the N–N bond between the heterocycle and the azo-group, resulting in the formation of the species Bzm·. In addition, concurrent rearrangement with loss of a hydrogen atom gives strong peaks for the pseudomolecular ion $BzmH^{+\cdot}$ (the intensity of this peak for (IIIf) is 100%). Further breakdown of the species Bzm· and $BzmH^{+\cdot}$ takes place in the usual way for benzimidazoles [21, 22], in particular giving ions with m/z 90 and 91, the first of these being the strongest in the mass spectra of (IIIb, c, e). It is interesting that the mass spectra of the tetrazenes (IIIb), (V), and (VIII) show fragmentation of the molecular ion due to elimination of a molecule of nitrogen and the formation of pseudomolecular ions of the dimers $[Bzm{-}Bzm]^{+\cdot}$ (m/z 234, 290, and 294 respectively). The intensities of these peaks are however small, especially in the case of the tetrazene (IIIb).

Useful information on the preferred conformations of the tetrazenes in solution is provided by their PMR spectra (Table 3). We first consider the assignments of the spectral signals. It is well known that protons $H_{(4)}$ and $H_{(7)}$ (ortho) are magnetically equivalent as a result of rapid tautomerism, the same being true of $H_{(5)}$ and $H_{(6)}$, the two latter signals being seen as a doublet at higher field [23]. In the case of 1-substituted benzimidazoles such as (XXIVa) and (XXIVb), protons $H_{(5)}$ and $H_{(6)}$, though no longer equivalent, give as in the previous case a combined multiplet at high field. However, the signal for one of the two ortho-protons is shifted to lower field, where a separated doublet of doublets is seen.* It is difficult to resolve theoretically the question of whether this signal is for proton $H_{(4)}$ (as a result of the anisotropic effect of the lone pair on the pyridine nitrogen), or for $H_{(7)}$ (as a result of the descreening effect of the more electronegative pyrrole nitrogen), and no firm conclusion on this score has been reached in the literature [24]. We have found that the PMR spectrum of 1,5-dimethylbenzimidazole (XXIVc) shows at low field (apart from the signal for proton $H_{(2)}$), a weakly split signal (J = 1.2 Hz) which may unambiguously be assigned to proton $H_{(4)}$ (Table 3). The signals for the other compounds examined were assigned on the same basis, bearing in mind that the position of the signal for $H_{(4)}$ in the PMR spectra of the tetrazenes should change to a comparatively small extent, whereas the signal for $H_{(7)}$, as a result of the proximity of the azo-group, will undergo a large shift. This assumption has been confirmed.

In the PMR spectra of the tetrazenes (IIIb) and (V), protons $H_{(2)}$ and $H_{(7)}$ are shifted to much lower field. For example, the chemical shifts of these protons in the tetrazene (IIIb) are 8.58 and 8.18 ppm, whereas in the 1-methylbenzimidazole (XXIVa) they are 7.84 and 7.34 ppm, and in the 1-aminobenzimidazole (XXIVb) they are 7.95 and 7.35 ppm respectively.

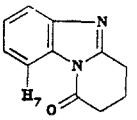


XXIV a, c R=CH_3, b R=NH_2; a, b R^1=H, c R=CH_3

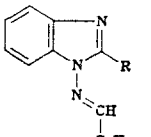
This shift could be the consequence of either the electron acceptor influence or the screening effect of the azo-group. The lone pairs of the nitrogens of the azo-group clearly descreen the $H_{(2)}$ and $H_{(7)}$ protons, but in conformation (XXVa) this effect will be more marked on the $H_{(2)}$ atoms, and in conformation (XXVb), on $H_{(7)}$. In our view, conformation

*Such separation is characteristic of solutions of 1-R-benzimidazoles in $CDCl_3$. In DMSO-D_6, as will be seen from the example of 1-methylbenzimidazole (XXIVa) (Table 3), the signals for protons $H_{(4)}$ and $H_{(7)}$ appear together.

(XXVb) is preferred, since the chemical shift of the $H_{(7)}$ proton in the PMR spectrum of the tetrazene (IIIb) is almost identical with that for the same proton (8.21) ppm) in the spectrum of (XXVI) [25], which may be regarded as a model of this conformation. In addition, the hydrazones (XXVII), for which the existence of a conformation of type (XXVb) is not possible, show a signal for $H_{(7)}$ at higher field (7.85 ppm).



XXVI



XXVII a R=H; b R=CH_3

The only tetrazene which does not show a shift of the $H_{(7)}$ proton to lower field is (VIII). Ths is probably due partly to the π-excess of the imidazole ring, and partly to the considerable disruption of the planarity of the molecule resulting from repulsion between the lone pairs of the oxygen atom and the azo-group.

When the neutral 1-methylbenzimidazole (XXIVa) is converted into its cation, the signal for $H_{(2)}$ is shifted to lower field by ∿1.6 ppm (Table 3). Approximately the same shift is seen in the case of the hydrazone (XXVIIa), indicating protonation of the imidazole ring rather than the azomethine group.* Although in the case of the amine (XXIVb) a change from a neutral to an acid medium results in a smaller shift (1.2 ppm) in the $H_{(2)}$ signal, as we have shown previously [10], this is also protonated at the intramolecular nitrogen atom. With this in mind, the especially marked shift of the $H_{(2)}$ signal (1.9 and 1.7 ppm) seen for the tetrazenes (IIIb) and (V) on adding deuteroacetic acid to their solutions in $CDCl_3$ is noteworthy. Since all the other signals in the PMR spectra of acid solutions of (IIIb) and (V) undergo a slightly greater diamagnetic shift than with (XXIVa) and (XXIVb), this finding can only be due to the formation of dictations by protonation of both imidazole rings. This observation does not apply to acidic solutions of tetrazenes in DMSO, in which the shift of the $H_{(2)}$ signal is much smaller (0.4 ppm). Since the chemical shifts of the $H_{(2)}$ proton in the PMR spectra of the cation (IIIb) and the bismethobromide (XXII) in DMSO-D_6 are almost identical, it maybe assumed that this situation is due, not to deprotonation of the protonic salts of (IIIb) and (V), but to their specific and very strong solvation, which in some way contributes to the paramagnetic shift of the signals.

EXPERIMENTAL

PMR spectra were recorded on a Bruker WH-90 spectrometer (90 MHz) at 30°C. Chemical shifts were measured on the δ-scale, internal standard TMS (for solutions in $CDCl_3$ and DMSO-D_6) or dioxane (for solutions in CF_3COOD). When measuring the PMR spectra of the cations, to a solution of 1 mg of the compound in 0.5 ml of $CDCl_3$ were added successively 12, 24, 36, 48, and 60 mg of CF_3COOD. The spectrum usually ceased to change (shift in the signals to lower field) after the addition of 48-60 mg of the acid. This spectrum was taken to be that of the cation (or dication in the case of tetrazenes). Mass spectra were obtained on an MAT-311A spectrometer, with direct introduction of the sample into the ion source) accelerating voltage 3.0 kV, ionizing voltage 70 eV, cathode emission current 1.0 mA. UV spectra were obtained on a Specord-M40 spectrophotometer, in methanol, and IR spectra on a UR-20 spectrometer. The progress of the reactions was followed, and the purity of the products checked, by TLC on Brockman grade IV alumina. Melting points were measured on a PTP apparatus in a sealed glass capillary. Melting points were uncorrected.

The N-aminobenzimidazoles (Ib, e, f) were obtained as described in [10], and 1-amino-5,6-dimethylbenzimidazole and amines (Ic, g) as in [26, 28] respectively.

The elemental analyses for C, H, and N of compounds (Id, h), (IIg, h), (IIIb-g), (IVb), (V), (VIIb), (VIII), and (XV) were in agreement with the calculated values.

1-Amino-2-phenylbenzimidazole (Id, $C_{20}H_{15}N_3$). In a three-necked, one liter flask fitted with a stirrer and thermometer were placed 12 g (62 mmole) of 2-phenylbenzimidazole, 8.4 g

*Assignment of the signals for the imidazole ring and azomethine protons in the PMR spectrum (XXVIIa) was made by comparison with the PMR spectrum of the hydrazone (XXVIIb).

(138 mmole) of 85% KOH, 300 ml of ethanol, and 450 ml of water. The mixture was stirred with heating until a solution was obtained, and a soltuion of sodium hydroxylamine-O-sulfonate (27 g, 240 mmole) in 50 ml of water added with stirring at 35-40°C over five minutes. The mixture was stirred for a further hour at this temperature (after this time, the hydroxylaminesulfonate had either reacted with the compound, or been decomposed by the alkali. The alcohol was removed completely from the solution by distillation, and the solid which separated (12.2 g) filtered off, and washed with 50 ml of water. The filtrate was neutralized with acetic acid to give 1.1 g of recovered 2-phenylbenzimidazole. The solid (12.2 g) consisted of 2-phenylbenzimidazole (R_f 0.43) and 1-amino-2-phenylbenzimidazole (R_f 0.5), which chould not be separated either by chromatography or fractional crystallization. In order to effect separation, the amine was converted into the hydrazone by boiling with 6.1 ml (57 mmole) of benzaldehyde in 50 ml of glacial acetic acid for one hour. On cooling, 7.8 g of crystalline solid separated and was filtered off and washed with 10 ml of chloroform. It was nearly pure 2-phenylbenzimidazole. The filtrate was evaporated to dryness in a rotary evaporator, and the residue (4.12 g) purified by chromatography on a column of alumina, eluent chloroform. First eluted was 1-benzylideneamino-2-phenylbenzimidazole (R_f 0.8), yield 3.96 g (23%), colorless crystals, mp 118.5-119.5°C (from alcohol), IR spectrum (Vaseline grease): 1568, 1590, 1600 cm^{-1}. Next eluted was a small amount of 2-phenylbenzimidazole. The overall recovery of 2-phenylbenzimidazole was 9.0 g (75%).

To isolate the amine (Id), 3.96 g (13 mmole) of 1-benzylideneamino-2-phenylbenzimidazole was boiled with 80 ml of 10% HCl, with simultaneous distillation of the benzaldehyde (∿1 h). After cooling, the mixture was basified with ammonia, and the precipitated amine filtered off and washed with water to give 2.8 g of product (22% calculated on 2-phenylbenzimidazole, or 97% calculated on 1-benzylideneamino-2-phenylbenzimidazole). The 1-amino-2-phenylbenzimidazole was obtained as colorless cyrstals (from water) or plates (from benzene), mp 203-204°C, in agreement with the literature value [29]. IR spectrum (Vaseline grease): 3147, 3325 cm^{-1} (NH_2). UV spectrum, λ_{max} (log ε): 236 (3.95), 293 nm (4.03). The compound has been obtained previously by a complex route from o-nitrophenylhydrazine [29].

1-Amino-2-phenylaminobenzimidazole (Ih, $C_{13}H_{12}N_4$). A mixture of 6.4 g (30 mmole) of 1-aminobenzimidazole-2-sulfonic acid and 10 ml (110 mmole) of aniline was boiled for 1 h. When the reaction was complete, the excess aniline was removed by steam distillation, and the resulting solid amine (Ih) filtered off, washed with 50 ml of water and 20 ml of alcohol. and dried at 120°C to give 4.5 g (67%) of colorless crystals, mp 226-228°C (from alcohol). IR spectrum (Vaseline grease): 1520, 1560, 1600, 1640 (ring), 3160, 3300, 3330 cm^{-1} (NH_2, NH).

Oxidation of 1-Aminobenzimidazole (Ib). A. To a suspension of 0.67 g (5 mmole) of the amine (Ib) in 25 ml of dry dichloromethane was added in portions with stirring over five minutes 2.65 g (6 mmole) of lead tetraacetate. The mixture, which quickly turned yellow, then red-brown, was stirred for 1 h at 20°C. Ethylene glycol (5 ml) was then added, followed after 10 min by 50 ml of water. The layers were separated, and the aqueous layer extracted with dichloromethane (2 × 25 ml). The organic solutions were combined, dried over anhydrous sodium sulfate, and evaporated. The residue (0.34 g) consisted of a mixture of (IVa) and the tetrazene (IIIb). The former was extracted with hot isooctane, to give 0.3 g (37%) of colorless crystals, mp 113°C, in agreement with [6]. IR spectrum (chloroform): 1745 cm^{-1} (C=O). The isooctane-insoluble resinous material was triturated with 5 ml of acetone, to give 0.032 g (5%) of 1,1'-azobenzimidazole (IIIb, $C_{14}H_{10}N_6$) as colorless crystals, mp 270-272°C (decomp., from DMF). The IR spectrum showed no characteristic absorptions.

B. To a suspension of 2.66 g (20 mmole) of the amine (Ib) and 3.1 g (55 mmole) of CaO in 50 ml of dry dichloromethane was added in portions 9.75 g (22 mmole) of lead tetraacetate. Heat was liberated, and the mixture turned red, then light brown. After stirring for 1 h at 20-25°C, the solid was filtered off and treated with 3 ml of ethylene glycol to give 2.1 g (85%) of benzimidazole, mp 170-172°C. From the dichloromethane layer there was obtained 0.13 g (5%) of the tetrazene (IIIb), identical with the material obtained by method A.

C. To a solution of 0.4 g (3 mmole) of the amine (Ib) and 0.86 g (3 mmole) of $Na_2CO_3 \cdot 10H_2O$ in 35 ml of water was added with vigorous stirring over 20 min 47 ml (9 mmole) of a saturated aqueous solution of bromine. The mixture was stirred at room temperature for 1 h 20 min, and the solid which separated filtered off and washed with alcohol and ether. There was obtained 0.1 g (25%) of the tetrazene (IIIb), which gave no depression of melting point on admixture with the material obtained by method A.

2,2'-Dimethyl-1,1'-azobenzimidazole (IIIc, $C_{16}H_{14}N_6$). To a solution of 1.47 g (10 mmole) of the amine (Ic) in 50 ml of dry dichloromethane was added in portions with stirring 6.65 g (15 mmole) of lead tetraacetate. The mixture was then stirred for 1 h 30 min at room temperature, and 5 ml of ethylene glycol added, followed after 10 min by 100 ml of water. The precipitated tetrazene (IIIc) was filtered off, washed with water (5 ml) and ether(5 ml) to give 0.63 g (43%) of colorless, fibrous needles, mp 260-262°C (decomp., from DMF), R_f 0.66 (eluent, chloroform). IR spectrum (Vaseline grease): 1570, 1628 cm^{-1} (ring).

2,2'-Diphenyl-1,1'azobenzimidazole (IIId, $C_{26}H_{18}N_6$). To a suspension of 0.5 g (2.7 mmole) of the amine (Id) in 25 ml of dry dichloromethane was added over 3 min 1.3 g (2.9 mmole) of lead tetraacetate. The mixture was stirred at room temperature for 30 min (some resinification occurred), then 0.5 ml of ethylene glycol was added, followed after a further ten minutes by water (10 ml). The solvent was removed from the organic layer by distillation, and the residue (0.51 g) dissolved in chloroform and passed through a column of alumina. The fraction with R_f 0.9 was collected, this being the tetrazene (IIId). Yield 0.2 g (40%), colorless, fibrous needles, mp 227°C (decomp., from alcohol).

2,2'-Dichloro-1,1'-azobenzimidazole (IIIe, $C_{14}H_8Cl_2N_6$). To a solution of 1 g (6 mmole) of the amine (Ie) in 50 ml of dry dichloromethane was added over 3 min 4 g (9 mmole) of lead tetraacetate. The mixture was stirred at 20°C for 50 min, 2 ml of ethylene glycol added, and then after a further 10 min, 200 ml of water. The solid which separated (0.53 g) was filtered off, and the aqueous layer extracted with dichloromethane (2 × 25 ml) to give a further 0.35 g of product. The solids were combined, dissolved in the minimum amount of chloroform, and passed through a column of alumina (eluent, chloroform). The first fraction, R_f 0.85, was collected. Yield 0.58 g (58%), colorless needles, mp 238-239°C (decomp., from DMF).

2,2'-Bis(dimethylamino)-1,1'-azobenzimidazole (IIIf, $C_{16}H_{16}N_8$). To a solution of 0.88 g (5 mmole) of the amine (If) in 25 ml of dry dichloromethane was added 3.3 g (7.5 mmole) of lead tetraacetate, over 5 min. The deep brown mixture was stirred for 30 min at room temperature, and 2 ml of ethylene glycol added, followed after 10 min by 50 ml of water. The aqueous layer was separated from the organic layer, and the tetrazene (IIIf) extracted with dichloromethane (2 × 25 ml). The organic solutions were combined, dried over anhydrous sodium sulfate, and the solvent removed to a volume of 15 ml. The solution was then chromatographed on a column of alumina (eluent, chloroform), the fraction with R_f 0.73 being collected. Yield 0.035 g (4%). Pale yellow crystals, mp 120°C (decomp.) IR spectrum (Vaseline grease): 1570, 1590, 1612 cm^{-1} (ring).

Oxidation of 1-Amino-2-methylaminobenzimidazole (Ig). To a suspension of 0.8 g (5 mmole) of the amine (Ig) in 50 ml of dry dichloromethane was added with stirring over 10 min at 0-5°C in portions 2.44 g (5.5 mmole) of lead tetraacetate. After 50 min, 2 ml of ethylene glycol was added, followed after a further 10 min by 50 ml of water. The mixture was stirred for 10 min, the organic layer separated, and the aqueous layer extracted with dichloromethane (3 × 70 ml). The organic layers were combined, dried over anhydrous sodium sulfate, the solvent distilled off to a volume of 20 ml, and the reaction products separated on a column of alumina (chloroform), two fractions being collected. The first compound eluted was 3-methylaminobenzo-1,2,4-triazine (IIg, $C_8H_8N_4$), R_f 0.49, yield 0.4 g (5%). Yellowish-green crystals, mp 173-174°C (from benzene and hexane). IR spectrum (chloroform): 1580 (ring), 3460 cm^{-1} (NH).

The second fraction (R_f 0.33) contained the tetrazene (IIIg), $C_{16}H_{16}N_8$, yield 0.06 (7.5%), colorless crystals, mp 190°C (decomp., from benzene and methanol). IR spectrum (Vaseline grease): 1590, 1650 (ring), 3250, 3425 cm^{-1} (NH).

3-Phenylaminobenzo-1,2,4-triazine (IIh, $C_{13}H_{10}N_4$). In a three-necked 50 ml flask fitted with a stirrer and thermometer were placed 0.45 g (2 mmole) of the amine (Ih) and 25 ml of dry dichloromethane. To the stirred mixture was added in portions 0.97 g (2.2 mmole) of lead tetraacetate over 5 min, when resinifcation occurred. After stirring for 15 min at 20°C, the solution was treated with 0.5 ml of ethylene glycol, followed after 10 min by 25 ml of water. The aqueous layer was separated, and extracted with chloform (30 ml). The organic layers were combined, dried over anhydrous sodium sulfate, concentrated to a volume of 15 ml, and chromatographed on a column of alumina (chloroform). The fraction with R_f 0.6 was collected, to give 0.11 g (25%) of organge crystals (from alcohol), mp 197°C, in agreement with the literature value [30]. IR spectrum (Vaseline grease): 1597 (ring), 3190, 3250 cm^{-1} (NH).

Oxidation of 1-Amino-5,6-dimethylbenzimidazole. A. To a suspension of 0.81 g (5 mmole) of 1-amino-5,6-dimethylbenzimidazole in 25 ml of dry dichloromethane was added 2.5 g (5.6 mmole) of lead tetraacetate. The mixture was stirred for 15 min, then 2 ml of ethylene glycol was added, followed after 10 min by 50 ml of water. The organic layer was separated, dried over sodium sulfate, and evaporated to give 0.094 g (10%) of 1-acetyl-5,6-dimethylbenzimidazole (IVb, $C_{11}H_{12}N_2O$) as colorless crystals, mp 138-139°C (from isooctane), in agreement with the value reported in [31]. IR spectrum (chloroform): 1745 cm^{-1} (C=O). PMR spectrum ($CDCl_3$): 2.33 (6H, s, $2CH_3$); 2.65 (3H, s, $COCH_3$); 7.50 (1H, s, 4-H); 7.93 (1H, s, 7-H); 8.08 (1H, s, 2-H).

B. To a suspension of 0.81 g (5 mmole) of 1-amino-5,6-dimethylbenzimidazole and 4.3 g (15 mmole) of $Na_2CO_3 \cdot 10H_2O$ in 50 ml of water was added 78 ml (15 mmole) of a saturated aqueous solution of bromine over 10 min with vigorous stirring and cooling (0-5°C). The mixture was stirred at this temperature for 1 h, and the solid which separated was then filtered off, and washed with 4 ml of cold alcohol and 10 ml of ether to give 0.08 g (10%) of the tetrazene (V) ($C_{18}H_{18}N_6$) as colorless crystals, mp 290-291°C (decomp., from DMF), R_f 0.57 (eluent chloroform).

The mother liquors were neutralized and evaporated to dryness. The residue was suspended in 40 ml of chloroform, and passed through a short (1 × 2 cm) column of alumina (chloroform) to give 0.4 g (55%) of 5,6-dimethylbenzimidazole, mp 201-205°C, in agreement with the literature value [32].

1-Aminobenzimidazolone (VIIa). A solution of 10.7 g (50 mmole) of 1-aminobenzimidazole-2-sulfonic acid and 19.3 g (300 mmole) of 85% KOH in 100 ml of water was boiled for 5 h. The mixture was cooled, filtered, and the filtrate neutralized with acetic acid. The solid which separated was filtered off, washed with 50 ml of 1% ammonia and 20 ml of cold water, and recrystallized from 100 ml of water to give 7.2 g (95%) of colorless needles, mp 245-246°C, in agreement with the literature value [33]. IR spectrum (Vaseline grease): 1725 (C=O), 3200, 3320 cm^{-1} (NH_2).

1-Amino-3-methylbenzimidazol-2-one (VIIb, $C_8H_9N_3O$). In a three-necked 100 ml flask fitted with a stirrer and thermometer were placed 7.4 g (50 mmole) of 1-methylbenzimidazolone and 14 g (200 mmole) of 85% KOH in 50 ml of water. To the solution obtained was added with stirring over 3-4 min at 35-40°C a solution of sodium hydroxylamine-O-sulfonate, obtained by neutralizing 20 g (160 mmole) of the 90% acid with sodium bicarbonate in 30 ml of water. The mixture was stirred for 30 min, and the solid amine (VIIb) which separated was filtered off, washed with 30 ml of cold water, dried, and recrystallized from 30 ml of benzene, to give 8 g (82%) of colorless needles, mp 131-132°C. IR spectrum (Vaseline grease): 1695, 1717 (C=O); 3205, 3285 cm^{-1} (NH_2).

3,3'-Dimethyl-1,1'-azobenzimidazoline-2,2'-dione (VIII, $C_{16}H_{14}N_6O_2$). In a three-necked 50 ml flask fitted with a stirrer and thermometer were placed 0.5 g (3 mmole) of the amine (VIIb) and 15 ml of dry dichloromethane. To the resulting solution was added with stirring over 5 min in portions 1.55 g (3.5 mmole) of lead tetraacetate. After 30 min, 0.5 ml of ethylene glycol was added, followed after 10 min by 10 ml of water. The precipitate (0.09 g) of the tetrazene was filtered off, and washed with 10 ml of cold alcohol. Evaporation of the organic layer, and trituration of the residue with 10 ml of alcohol gave a further 0.15 g of the tetrazene (VIII). Overall yield, 0.24 g (49%), colorless, fibrous needles, mp 231-232°C (decomp., from alcohol), R_f 0.89 (chloroform). IR spectrum (Vaseline grease): 1610 (ring), 1720 cm^{-1} (C=O).

Benzo-1,2,4-triazin-3-one (IX). To a suspension of 5 g (33 mmole) of the amine (VIIa) in 200 ml of dry dichloromethane was added in portions 16.8 g (38 mmole) of lead tetraacetate over 5 min, whereupon a yellow solid separated. After 30 min, 5 ml of ethylene glycol was added, followed after a further 10 min by 100 ml of water. The solid was separated, acidified with 50% acetic acid, and extracted with 200 ml of chloroform. The organic solutions were combined, dried over anhydrous sodium sulfate, and the solvent distilled off to give 2.4 g (46%) of crude (IX). This was triturated with 50 ml of ethyl acetate, filtered, and recrystallized from alcohol with activated charcoal to give 0.4 g (8%) of (IX) as orange crystals, mp 208°C (decomp., from ethanol), in agreement with the value given in [30]. IR spectrum (Vaseline grease): 1590, 1610 (ring), 1665 (C=O), 2000-3200 cm^{-1} (broad NH band). PMR spectrum (DMSO-D_6): 7.39 (1H, m, $J_{6,7} = J_{7,8} = 8.1$, $J_{5,7} = 1.5$ Hz, 7-H); 7.51 (1H, m, $J_{5,6} = 7.3$, $J_{5,7} = 1.5$ Hz, 5-H); 7.84 (1H, m, $J_{5,6} = 7.3$, $J_{6,7} = 8.1$, $J_{6,8} = 1.5$ Hz, 6-H); 8.34 (1H, d, $J_{7,8} = 8.1$, $J_{6,8} = 1.5$ Hz, 8-H); 12.70 ppm (br, NH).

1,3-Dimethyl-5-diazo-6-cyanoiminohexahydropyrimidin-2,4-dione (XV, $C_7H_6N_6O_2$). To a suspension of 1.05 g (5 mmole) of the finely-ground amine (XIV) in 50 ml of dry dichloromethane was added in portions over 3-5 min 2.88 g (6.5 mmole) of lead tetraacetate. The mixture was stirred for 2 h, 2 ml of ethylene glycol added, and after a further 15 min, 100 ml of water. The mixture was then kept at 0-5°C for 1 h, and the colorless solid (1.5 g, lead salts) filtered off. The aqueous layer was separated and extracted with dichloromethane (150 ml). The organic solutions were combined, and dried over anhydrous sodium sulfate. The residue (0.47 g) after removal of the solvent was purified on a column of alumina (chloroform), the first fraction (R_f 0.55) being collected. Yield of (XV) 0.24 g (22%), pale green crystals, mp 192-194°C (from alcohol), with lachrymatory properties. IR spectrum (Vaseline grease): 1675, 1720 (C=O), 2155 (N=N), 2200, 2230 cm^{-1} (C≡N). Mass spectrum (40°C), m/z (%): 206 (99, M^+), 180 (14.4), 149 (12.4), 123 (5.9), 122 (5.7) 121 (63.1), 95 (22.4), 94 (50.5), 93 (100), 92 (15.6), 82 (14.9), 81 (65.8), 80 (33.1), 78 (25.7), 71 (8.4), 70 (5.5), 69 (63.3), 68 (18.1), 67 (90.6), 66 (37.7), 65 (6.1), 64 (14.4).

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