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5-OXIMINOBENZO-2,1,3-OXADIAZOLE-4-ONE DERIVATIVES

REARRANGEMENT AND GEOMETRIC ISOMERISM*

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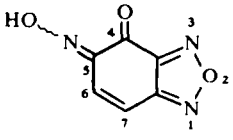
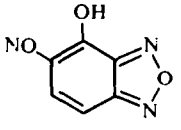
Abstract—The preparation of some derivatives of 5-oximinobenzo-2,1,3-oxadiazole-4-one is reported and their rearrangement to 4,7-dioximino derivatives of benzo-2,1,3-oxadiazole, 2-phenylbenzotriazole and benzotriazole described. Geometric isomerism related to oximino group was investigated. NMR spectra of 4,7-dioximes show the existence in solution of three geometrical isomers, whose configuration was assigned. The derivatives of 5-oximinobenzo-2,1,3-oxadiazole-4-one here investigated appear to exist only in one form.

IN A previous paper,[1] it was reported that I [the tautomeric possibilities of this compound are shown in Ia (5-oximinobenzo-2,1,3-oxadiazole-4-one) and Ib (4-hydroxy-5-nitrosobenzo-2,1,3-oxadiazole†)], reacts with hydroxylamine yielding the 4,7-dioxime (III) rather than the expected 4,5-isomer (II).



Ia



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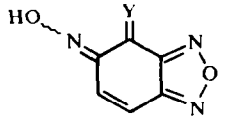
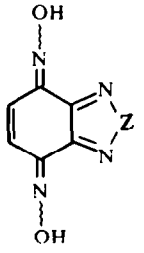


II : Y = NOH
IV : Y = N—NH—C_6H_5
V : Y = N—NH—$CONH_2$



III : Z = O
VI : Z = N—C_6H_5
VII : Z = NH

* This investigation was made by financial support of C.N.R. (Roma, Italy).

† For convenience we shall hereafter refer to benzo-2,1,3-oxadiazole by the alternative name of benzofurazan.

We interpreted these results by supposing that II is formed first, and then rearranges quickly to III (a similar rearrangement was reported for benzofuroxan derivatives[2]).

For the purpose of obtaining evidence for this supposition and in order to investigate whether the rearrangement occurs also for other derivatives of I, we prepared the 4,5-dioxime (II), the 4-phenyl-hydrazone-5-oxime (IV) and the 4-semicarbazone-5-oxime (V) of benzofurazan-4,5-dione, and studied their chemical behaviour.

It was found that II, IV and V, when heated in alkaline solutions or in polar aprotic solvents, rearrange to 4,7-dioximino derivatives of benzofurazan (III) 2-phenyl benzotriazole (VI) and benzotriazole (VII).

Since these compounds are likely to give geometrical isomers, we investigated I-VII by NMR spectroscopy, which had been used as a reliable technique for assigning configuration to oximes.[3]

RESULTS AND DISCUSSION

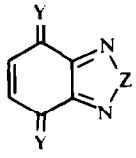
Compounds II, IV and V were prepared from I by standard methods, precautions being taken to avoid rearrangement. The structure of II, less stable than both IV and V, was proved by reduction to the known 4,5-diamino-benzofurazan.[4]

Compound III was obtained quantitatively by heating an alkaline solution (1% NaOH) of II; the structure of III was proved by the independent synthesis of dioxime from benzofurazan-4,7-dione (VIII).

Compound IV has a similar chemical behaviour to II, yielding VI, identified by comparison with the dioxime obtained from 2-phenylbenzotriazole-4,7-dione (IX). Derivative V in alkaline solution yields mainly VII (~90%) presumably by rearrangement followed by hydrolysis and decarboxylation of 2-carbamylbenzotriazole-4,7-dione dioxime (XV).

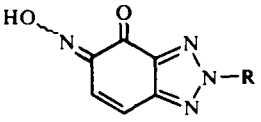
This mechanism agrees with the well known low stability of derivatives of 1-carbamyl- and 1-benzenesulphonylbenzo (or naphtho) triazole.[5,6]

The structure of VII was confirmed by comparing the reduction product with 4,7-diaminobenzotriazole obtained from the known 4-amino-7-phenylazobenzotriazole.[7]

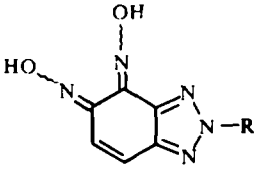


VIII: Y = O ; Z = O
IX : Y = O ; Z = N—C_6H_5
X : Y = O ; Z = S
XI : Y = NOH; Z = S
XII : Y = $NOCH_3$; Z = S
XIII: Y = $NOCH_3$; Z = O
XIV: Y = $NOCH_3$; Z = N—C_6H_5
XV : Y = NOH ; Z = N—$CONH_2$

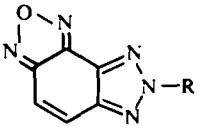
Compound V in DMSO solution at 110° yields an approximately equimolecular mixture of VII and [1.2.3]triazole[4.5-e]benzofurazan XVIII, the latter being identified by the independent synthesis from benzotriazole-4,5-dione dioxime (XVII) obtained via intermediate XVI.



XVI: R = H
XIX: R = C_6H_5



XVII: R = H
XX : R = C_6H_5



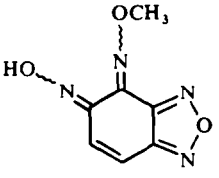
XVIII: R = H
XXI : R = C_6H_5

Small amounts of XVIII were obtained also when V rearranged in alkaline solution, as shown by NMR spectra.

The formation of both XVIII and VII from V, shows that interaction of the 4-substituent can occur either with the furazan ring (like in rearrangement of II and IV), either with the 5-oximino group, yielding, in this case, cyclization to the triazole.

By comparing NMR spectra of IV, heated in alkaline or DMSO solution, and of the model compound XXI, we concluded that derivative IV does not undergo the cyclization observed for V.

The NMR investigation was extended to include the following compounds: 4-O-methyloximino-5-oximinobenzofurazan XXII; benzo-2,1,3-thiadiazole-4,7-dione X and their dioxime XI and dioxime O-methyl ether XII; benzofurazan-4,7-dione VIII, 2-phenylbenzotriazole-4,7-dione IX and their dioximes O-methyl ethers XIII and XIV respectively.



XXII

The main results obtained from the NMR spectra of oximes and related compounds, can be summarized as follows:

(i) There is no general agreement on the geometry of the magnetic anisotropy of the oximino group. A large amount of experimental evidence indicated that protons *syn*-coplanar to the oximino group or the O-methyloximino group resonate at lower magnetic field than those in *anti*[3,8] position.

(ii) The magnetic anistropy of C=N—$O^{(-)}$ has been less extensively investigated: recent NMR studies indicate that the relationship reported in (i) appears reversed in oxime anions.[9]

(iii) When the solvent is changed from aliphatic to aromatic (benzene, pyridine), the latter increases the difference in chemical shifts between *syn* and *anti* protons;[10,11] the increase being larger for oximes than for the corresponding O-alkyl ethers.[8,11] The magnitude of the aromatic-induced changes in chemical shifts, were taken as an indication of configuration or conformation.[10,12]

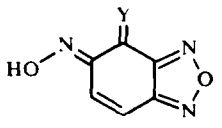
Since the compounds investigated have a planar and rigid structure, the above criteria were confidently applied for assignments of chemical shifts of protons (numbering as shown in Ia) (H-6)-6, H-7 and H-5, H-6 in derivatives of 4,5-diones and 4,7-diones respectively.

Owing to sparing solubility, the derivatives of benzofurazan-4,5-dione and 4,7-dioximes III, VI, VII and XI cannot be examined in CCl_4 or $CDCl_3$*, therefore DMSO-d_6 was used as "aliphatic solvent" (see Table 1 and 2). This does not appear to invalidate the applicability of solvent effect, as shown by the comparison of spectra of compounds II (Table 1) and III (Table 2) in DMSO-d_6 and THF solutions.

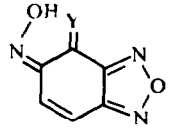
The solvent effect was measured in pyridine-d_5, owing to the sparing solubility of all compounds in benzene.

In derivatives of benzofurazan-4,5-dione, NMR spectra show that the 4,5-dioxime, the 4-phenylydrazone-5-oxime, the 4-semicarbazone-5-oxime are in forms II, IV and V respectively. No forms corresponding to other tautomeric possibilities were detected under the present experimental conditions.

The oximino group in the above compound can be *syn* (**A**) or *anti* (**B**) to H-6.



A



B

The NMR spectra indicate the presence of only one isomer; signals of H-6 and H-7 fall in the range 2–3 τ (Table 1), and were assigned from the solvent effect.

The deshielding effect of pyridine on H-6 ($\Delta\nu \sim -11$ to -19 c/s)† similar to that observed for *syn*-protons in 4,7-dioximes (see below), indicate configuration **A**.

In I, $J_{6,7}$ (> 10 c/s) is higher than J_{ortho} in benzofurazan,[13] while the spectral pattern is similar to that of II, IV and V; furthermore by comparing the chemical shifts of H-6 and H-7 and $J_{6,7}$ in compounds I and XXII, one can conclude that, under present experimental conditions, form Ia prevails.‡

The 4,7-derivatives such as 4,7-dioximes (III, VI, VII, XI), the O-methyl ethers (XIII, XIV, XII) and 4,7-diones (VIII, IX, X) show the signals of H-5, H-6 in the range 2·0–3·5 τ (Table 2); the chemical shifts differences of these protons in 4,7-diones and 4,7-dioximes or their O-methyl ethers can be ascribed to electronic and anisotropic effects of the oximino group.[3]

The spectra of 4,7-dioximes and their O-methyl ethers show two A_2 singlets, assigned to isomers *anti-anti* **C** and *syn-syn* **E**, and an AB pattern, assigned to isomer *syn-anti* **D**.§

The chemical shifts of H-5, H-6 in isomer **C**, **D** and **E** were assigned by considering the deshielding effect of the oximino group on *syn* coplanar protons (see i).

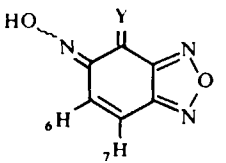
* The spectra of the other derivatives were recorded in $CDCl_3$.

† For the meaning of $\Delta\upsilon$ see footnote (c) to Table 1.

‡ Tautomerism Ia ⇌ Ib is being investigated.

§ For derivatives XI and XII the isomer anti-anti is not detectable.

TABLE 1. DATA OF NMR SPECTRA AT 60 MHz IN PPM (τ)[a]



Compounds								
n°	Y =	solv.[b]	H-6	H-7	$\Delta\nu$[c]	$J_{6,7}$ c/s	N-OH	Other signals
I	O	DMSO-d_6	2·43 d	2·66 d	—	10·4	v.b.	
		Py-d_5	2·12 d	2·75 d	−18·6	10·5	−2·12 s (w ≃ 1·5	
XXII	N-OCH_3	DMSO-d_6	2·43 d	2·73 d	—	10·4	−2·97 s (w ≃ 5)	N-OCH_3: 5·75 s
		Py-d_5	2·11 d	2·87 d	−19·2	10·5	v.b.	N-OCH_3: 5·78 s
II	N-OH	DMSO-d_6	2·39 d	2·72 d	—	10·5	v.b.	
		THF	2·37 d	2·87 d	-	10·4	v.b.	
		Py-d_5[d]	—	—	—	—		
IV	N-NH-C_6H_5	DMSO-d_6	2·30 d	2·55 d	—	10·0	−3·42 s (w≃3)	N-NH: v.b; H-arom.: 2·3–3·0 m (5H)
		Py-d_5	2·09 d	2·71 d	−12·6	10·0	−3·58 s (w≃5)	N-NH: v.b.; H-arom.: 2·5–3·1 m (5H)
V	N-NH-$CONH_2$	DMSO-d_6	2·34 d	2·54 d		10·4	−3·33 s (w≃9)	N-NH: −2·28 s (w≃3); $CONH_2$: 2·98 s (w ≃ 5)
		Py-d_5	2·15 d	2·72 d	−11·4	10·4	−2·92 s (w≃6)	N-NH: v.b. ; $CONH_2$: 2·13 s (w ≃10)

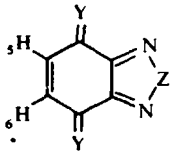
[a] s, singlet; d, doublet; m, multiplet; w, width at half-height in c/s; v.b., very broad signal.

[b] DMSO-d_6, dimethyl sulfoxide-d_6; Py-d_5, pyridine-d_5; THF, tetrahydrofuran; NaOD, NaOD 2 N in D_2O; $CDCl_3$, chloroform-d

[c] $\Delta\nu = (\nu_{DMSO\text{-}d_6} - \nu_{Py\text{-}d_5})$ for H_6; negative values mean that resonance in DMSO-d_6 is at higher field; for convenience the differences are expressed in c/s.

[d] The spectrum cannot be recorded because II rearranges quickly to III.

TABLE 2. DATA OF NMR SPECTRA AT 60 MHz IN PPM (τ)[a]



compounds				H-5, H-6[b]					N-OH[c] or N-OCH$_3$			
n°	Z =	Y =	Solv.[a]	aa	sa		ss	$J_{5,6}$ (c/s)	aa	sa		ss
					a	s				a	s	
III	O	N-OH	DMSO-d_6	3·07s	2·99d	2·66d	2·58s	10·5	−3·48	−3·70	−3·08	−3·30
			THF	3·17s	3·11d	2·63d	2·56s	10·8	−2·45	−2·60	−2·10	−2·27
			Py-d_5	2·93s	2·88d	2·32d	2·27s	10·7	v.b.	v.b.	v.b.	v.b.
			NaOD	3·17s	3·04d	2·95d	2·86s	10·8	—	—	—	—
VI[d]	N-C_6H_5	N-OH	DMSO-d_6	3·14s	3·04d	2·62d	2·52s	10·6	v.b.	v.b.	v.b.	v.b.
			Py-d_5	2·86s	2·79d	2·16d	2·07s	10·8	v.b.	v.b.	v.b.	v.b.
			NaOD	3·17s	3·08d	2·88d	2·80s	10·7	—	—	—	—
VII[b]	N-H	N-OH	DMSO-d_6	3·19s	3·12d	2·65d	2·60s	10·0	−3·05	−2·70	−2·28	−2·50
			Py-d_5	2·92s	2·89d	2·12d	2·11s	10·2	v.b.	v.b.	v.b.	v.b.
			NaOD	2·78s	2·89d	3·19d	3·31s	10·2	—	—	—	—
XI	S	N-OH	DMSO-d_6	—	3·02d	2·61d	2·48s	10·4	—	−3·12	−2·70	−2·93
			Py-d_5	—	2·82d	2·18d	2·09s	10·6	—	v.b.	v.b.	v.b.
			NaOD	—	3·06d	2·88d	2·77s	10·8	—	—	—	—

XIII	O	N–OCH_3	$CDCl_3$	3·15s	3·13d	2·70d	2·66s	10·6	5·67s	5·69s	5·77s	5·76s
			Py-d_5	3·12s	3·09d	2·75d	2·71s	10·4	5·77s	5·80s	5·91s	5·89s
XIV[a, f]	N–C_6H_5	N–OCH_3	$CDCl_3$	3·25s	3·22d	2·73d	2·67s	10·5	5·74s	5·73s	5·82s	5·81s
			Py-d_5	3·11s	3·07d	2·65d	2·65s	10·5	5·76s	5·75s	(5·88)	(5·88s)
XII[f]	S	N–OCH_3	$CDCl_3$	—	3·12d	2·64d	2·58s	10·7	—	5·70s	(5·75)	(5·75s)
			Py-d_5	—	3·04d	2·63d	2·58s	10·5	—	5·78s	(5·85)	(5·85s)
VIII	O	O	$CDCl_3$		2·78s							
			DMSO-d_6		2·73s							
IX[d]	N–C_6H_5	O	$CDCl_3$		3·02s							
			DMSO-d_6		2·92s							
X	S	O	$CDCl_3$		2·82s							
			DMSO-d_6		2·78s							

[a] See footnotes *a*, *b* to Table 1.

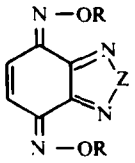
[b] aa, sa, ss, anti–anti, sin–anti, sin–sin configuration with respect to H–5, H–6.

[c] The width at half-height (w) is 2–10 c/s.

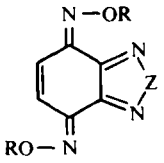
[d] H-arom.: VI in DMSO-d_6: 1·6–2·0m (2H), 2·1–2·6m (3H); in Py-d_5: 1·4–1·9m (2H), 2·2–3·0m (3H)
in NaOD: 1·8–2·3m (2H), 2·4–2·8m (3H).
XIV in DMSO-d_6: 1·5–1·9m (2H), 2·3–2·8m (3H); in Py-d_5: 1·6–1·9m (2H), 2·3–2·7m (3H)
IX in DMSO-d_6: 1·6–1·9m (2H), 2·1–2·5m (3H); in $CDCl_3$: 1·5–1·8m (2H), 2·2–2·5m (3H)

[e] The signal of NH group was not observed.

[f] The chemical shifts in parenthesis indicate overlapping of signals.



C



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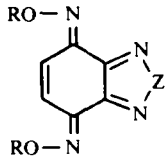

E

R = H or CH_3; Z as in VII–XIV

The chemical shifts of the OH protons of dioximes often cannot be detected because of associative or rapid exchange phenomena involving the water contained in the solvent. When H-bonding between the oximino group and the solvent is strong enough (as in DMSO-d_6), the chemical shifts can be detected and OH protons resonate at lower magnetic field when *anti* to H-5, H-6 than when *syn* ($\Delta\nu \sim 10$–40 c/s; the assignment was confirmed by integration ratio of the isomers present in solution). This behaviour is in agreement with results of Kleinspehn[14] for some aldoximes and ketoximes.

The deshielding effect on the OH proton near to the heterocyclic ring has been observed also on OMe groups in the corresponding 4,7-dioximes O-methyl ethers [$\Delta\nu \sim 3$–7 c/s]. In these derivatives the assignments for H-5, H-6 and the OMe group are in agreement with the integration ratios.

The above results confirm the assignments made and show that the resonance of the OMe group can give independent information on isomers of the type investigated.

With regard to solvent effect in 4,7-dioximes, pyridine produces deshielding of H-5, H-6, larger for *syn* protons ($\Delta\nu \sim -13$ to -30 c/s); the shift is lower in the corresponding O-methyl ethers* (see iii and Table 2).

This behaviour is in agreement with that observed by Carraro and Cavalli[11] for aliphatic oximes.

In anions of 4,7-dioximes (Table 2), the chemical shifts of H-5 and H-6 (assignments confirmed by comparing isomers ratio with that of dioximes) show that in derivatives III, VI and XI, the C=N—$O^{(-)}$ group has a shielding effect, larger for *syn* protons ($\Delta\nu \sim 15$–17 c/s) than for *anti* ($\Delta\nu \sim 2$–6 c/s).†

The anomalous behaviour of VII can be explained in terms of salification of the triazole ring.

The coupling constants $J_{5,6}$ or $J_{6,7}$ in derivatives of 4,7- and 4,5-diones are similar to the *cis* coupling constants of the ethylene-type,[15] showing high π electrons localization and, thus, the quinoid character of the compounds investigated.

The rearrangement of benzofurazan II, IV and V to the corresponding 4,7-dioximes has been followed also by NMR spectroscopy.

At room temperature, II, dissolved in 2N NaOD or in pyridine-d_5, rearranges quickly to the *syn-anti* isomer of III, while in DMSO-d_6 at 40°, the same transformation takes about 2 hr and in THF it is much slower (see manuscript).

* For dioximes O-methyl ethers $\Delta\upsilon$ is the difference in $CDCl_3$ and Py-d_5.

† $\Delta\nu = (\nu_{\text{DMSO-}d_6} - \nu_{\text{NaOD}})$; positive values mean that resonance in DMSO-d_6 is at lower field, negative, reverse.

By heating II at higher temperatures, a mixture of isomers *syn-syn*, *syn-anti* and *anti-anti* of III is obtained, whose composition appears to depend on the temperature and not on the solvent.

The same composition is obtained, under similar experimental conditions, by heating the mixture of geometrical isomers isolated from rearrangement of II or from the reaction between benzofurazan-4,7-dione and hydroxylamine.

Compounds V and VI rearrange slowly in comparison to II: here too the ratio of the isomers appears to be affected by temperature.

We are presently investigating further the influence of some factors on rearrangement and equilibration of isomers of 4,7-dioximes.

EXPERIMENTAL

M.ps are uncorrected. NMR spectra were measured with either a Varian A-60 or Jeol C-60 HL spectrometer.

As internal references, TMPS was used for 2N NaOD solns in D_2O and TMS for all other solns ($CDCl_3$, DMSO-d_6, Py-d_5, THF). The chemical shifts are in ppm (τ) ($\pm$0·02) and coupling constants (J) in c/s ($\pm$0·2). Sample concentrations were 4–10% w/v.

*Preparations of 5-oximinobenzofurazan-4-one derivatives**

Benzofurazan-4,5-dione dioxime (II). Dry EtOH solns of I (1·65 g in 30 ml) and hydroxylamine hydrochloride (1·40 g in 60 ml) were mixed and allowed to stand at 20–25° for 30 hr. Reduction of the volume of the solvent to about 15 ml (25°/10 mm) and addition of water (80 ml) gave a white ppt which was dried *in vacuo* over P_2O_5 at room temp. (Found: C, 39·90; H, 2·18; N, 31·12. $C_6H_4N_4O_3$ requires: C, 40·01; H, 2·24; N, 31·11%).

The compound II (1·8 g) in ether (300 ml) containing 10% Pd–C (0·2 g), hydrogenated at room temp and pressure, yielded a mixture of 4,5-diamino- (85–90%; m.p. 152°[4]) and 4,7-diaminobenzofurazan (15–10%, m.p. 192–3°[4]), which was separated by chromatography on silica-gel, eluent C_6H_6: EtOH (20:1).

The 4,7-diaminobenzofurazan obtained by reduction of the 4,7-dioximinobenzofurazan probably produced by partial rearrangement, under these conditions, of II; NMR spectra of II before and after solution in ether, proved this supposition.

Benzofurazan-4,5-dione-4-phenylhydrazone-5-oxime (IV). I (1·65 g) in MeOH (30 ml) was treated with phenylhydrazine (1·1 g) in 13% AcOH (18 ml), and the mixture stirred for 10 min at room temp. The ppt, was washed with ether and crystallized cautiously from dioxan. (Found: C, 56·50; H, 3·71; N, 27·33. $C_{12}H_9N_5O_2$ requires: C, 56·47; H, 3·55; N, 27·44%).

Benzofurazan-4,5-dione-4-semicarbazone-5-oxime (V). I (1·65 g) in boiling EtOH (20 ml) was treated with semicarbazide hydrochloride (1·12 g) and KOAc (1·0 g) in water (10 ml), and the soln refluxed on a steam-bath until formation of a white solid. The cooled mixture was filtered and the solid crystallized cautiously from water and dried *in vacuo* on P_2O_5 at room temp. (Found: C, 37·65; H, 2·81; N, 37·76. $C_7H_6N_6O_3$ requires: C, 37·84; H, 2·72; N, 37·83%).

Preparations of 4,7-diones. The preparation of benzofurazan-4,7-dione is described in Ref 16.

2-Phenylbenzotriazole-4,7-dione (IX). The 4-hydroxy-7-amino-2-phenylbenzotriazole hydrochloride[17] (2·65 g) was added to a stirred mixture of 30% HNO_3 (100 ml) and chloroform (200 ml) cooled in water, at such a rate that the temp did not exceed 20°. When addition was complete (about 20 min) the dilute HNO_3, after separation of solvent, was further extracted with chloroform. The extracts were washed with 5% $NaHCO_3$ and water and dried. After removal of solvent, the residue was crystallized (3 times) from AcOH: m.p. 224–5° (dec). (Found: C, 63·56; H, 3·28; N, 18·53. $C_{12}H_7N_3O_2$ requires: C, 64·00; H, 3·13; N, 18·66%).

Benzo-2,1,3-thiadiazole-4,7-dione (X). A soln of 4,7-dihydroxybenzo-2,1,3-thiadiazole (1·7 g) in acetone (25 ml) was rapidly added with shaking to a mixture of KH_2PO_4 (3·8g), Fremy's salt[18] (8·0 g), water (300 ml) and chloroform (150 ml), at room temp. The chloroform was separated, washed, dried and removed by distillation at reduced pressure. The residue was crystallized from CCl_4-$CHCl_3$ (9:1), m.p. 156–7°. (Found: C, 43·44; H, 1·15; N, 16·63. $C_6H_2N_2O_2S$ requires: C, 43·37; H, 1·21; N, 16·86%).

* Melting points are not reported, because these derivatives, by heating, probably, rearrange to 4,7-dioximino compounds.

4,7-Dihydroxybenzo-2,1,3-thiadiazole. A mixture of 4,7-dimethoxybenzo-2,1,3-thiadiazole[19] (2·0 g), dry $AlCl_3$ (6·0 g) and dry toluene (60 ml) was refluxed for 40 min, then poured into dil HCl cooled in ice. After separation of toluene, the dil HCl soln was extracted with ether. The residue obtained after removal of both solvents, was crystallized from toluene, m.p. 195–6°. (Found: C, 43·00; H, 2·52; N, 16·53. $C_6H_4N_2O_2S$ requires: C, 42·85; H, 2·40; N, 16·66%).

Rearrangement of 5-oximinobenzofurazan-4-one derivatives

4,7-Dioximinobenzofurazan (III). A soln of II (1·8 g) in 1% NaOH (80 ml) was refluxed for 1 hr. The cooled soln was acidified with 2N HCl, the dioximinobenzofurazan was extracted in ether and the solvent, dried and removed by distillation. The residue, dried at 100°/5 mm, to give III: the m.p. (226°, dec) was not improved by crystallisation from water. (Found: C, 39·95; H, 2·30; N, 31·06. $C_6H_4N_4O_3$ requires: C, 40·01; H, 2·24; N, 31·11%). The above product obtained by rearrangement of II, was identical (IR, mixed m.p.) with the 4,7-dioximinobenzofurazan prepared from VIII and hydroxylamine hydrochloride in boiling MeOH, or by the method of Borsche and Weber[4] (using tetraoximinocycloexene and acetic anhydride). NMR spectra show that the product (anyhow obtained) is a mixture of geometrical isomers C, D and E in the ratio about 1:3:1.

4,7-Dioximino-2-phenylbenzotriazole (VI). A soln of IV (2·55 g) in 1% NaOH (100 ml) were treated as described for III. The m.p. (264–5°, dec) was not improved by crystallisation for aqueous EtOH (1:1). (Found: C, 56·31; H, 3·48; N, 27·36. $C_{12}H_9N_5O_2$ requires; C, 56·47; H, 3·55; N, 27·44%).

The above compound was identical (IR, mixed m.p.) with 4,7-dioximino compounds obtained from IX or 4-oximino-2-phenylbenzotriazole-7-one[17] and hydroxylamine hydrochloride. NMR spectra show that the product (anyhow obtained) is a mixture of geometrical isomers C, D and E in the ratio about 1:4:3.

4,7-Dioximinobenzo-2,1,3-thiadiazole (XI) was obtained from X by the standard method and crystallized from aqueous EtOH (15:10), m.p. 284° (dec). (Found: C, 36·65; H, 2·15; N, 28·45. $C_6H_4N_4O_2S$ requires: C, 36·73; H, 2·05; N, 28·56%). NMR spectra show that the product is a mixture of geometrical isomers D and E whose ratio is about 1:6.

4,7-Dioximinobenzotriazole (VII) (A). A soln of V (2·2 g) in 1% NaOH (150 ml) was treated as described for III. The crude product was crystallized from water and dried at 140°/5 mm, m.p. >300°. (Found: C, 40·15; H, 2·70; N, 39·15. $C_6H_5N_5O_2$ requires: C, 40·22; H, 2·81; N, 39·10%). NMR spectra show that the product is a mixture of geometrical isomers C, D and E in the ratio about 3:8:1.

(B) A soln of V (2·2 g) in DMSO (12 ml) was heated at 120° for 2 hr. Most of the solvent was then removed at 120°/3 mm. Addition of water gave a ppt, which collected and dried (1·8 g, m.p. 240–250° (dec), was dissolved in boiling abs EtOH (180 ml) and treated with 4% KOH–EtOH soln (27 ml). The mixture was cooled and a ppt of 4,7-dioximinobenzotriazole dipotassium salt was collected, washed with EtOH (40–50 ml) and dissolved in water: addition of 2N HCl gave a crude VII, identical with that obtained in (A).

After removal of the dipotassium salt of VII, the filtrate was evaporated: the residue, after soln in water and acidification with 2N HCl gave crude XVIII, which was identical with [1.2.3]triazole [4.5-e]benzofurazan below described.

4-Oximinobenzotriazole-5-one (XVI). A soln of 5-hydroxybenzotriazole[20] (1·35 g) in 1% NaOH (50 ml), was treated with 4% H_2SO_4 (50 ml) and cooled in ice at 5–8°. $NaNO_2$ (0·7 g) in water (15 ml) was added dropwise with stirring. When addition was complete the mixture was stirred for a further 3 hr. The yellow solid obtained by filtration, was crystallized cautiously from water, m.p. 290° (dec). (Found: C, 44·10; H, 2·70; N, 34·06. $C_6H_4N_4O_2$ requires: C, 43·91, H, 2·46; N, 34·14%).

4,5-Dioximinobenzotriazole (XVII). A soln of XVI (1·75 g) in MeOH (900 ml) was treated with hydroxylamine hydrochloride (1·4 g) in water (50 ml) and refluxed for 3 hr. Reduction of the volume to about 20 ml and filtration, gave a yellow solid, which was washed and crystallized from water, m.p. 233° (dec). (Found: C, 40·36; H, 3·00; N, 39·05. $C_6H_5N_5O_2$ requires: C, 40·22; H, 2·81; N, 39·10%).

[1,2,3]Triazole [4,5-e]benzofurazan (XVIII). A soln of XVII (1·8 g) in 6% NaOH (60 ml) was refluxed for 15 min, then cooled and acidified. The white solid separated was crystallized from water, m.p. 175–6°. (Found: C, 44·80; H, 2·00; N, 43·36. $C_6H_3N_5O$ requires: C, 44·72; H, 1·88; N, 43·47%). NMR in DMSO-d_6: H-vinylic τ 1·93d (1H) and τ 2·05d (1H), J = 10·0 c/s: in Py-d_5: H-vinylic τ 2·02d (1H) and τ 2·24d (1H), J = 10·0 c/s.

4,5-Dioximino-2-phenylbenzotriazole (XX), was obtained from 4-oximino-2-phenylbenzotriazole-5-one,[21] by a procedure as described for the analog XVII and crystallized from aqueous EtOH (1:1), m.p. 200–2°. (Found: C, 56·51; H, 3·46; N, 27·41. $C_{12}H_9N_5O_2$ requires: C, 56·47; H, 3·55; N, 27·44%).

7-Phenyl[1,2,3]triazole[4,5-e]benzofurazan (XXI) was obtained from XX by the procedure described

for the analog XVIII and crystallized from ligroin (b.p. 80–120°), m.p. 178–9°. (Found: C, 60·65; H, 3·00; N, 29·61. $C_{12}H_7N_5O$ requires: C, 60·75; H, 2·97; N, 29·53%). NMR in DMSO-d_6: H-vinylic τ 1·88d (1H) and τ 2·01d (1H), J = 10·1 c/s; H-arom τ 1·6–1·9 m (2H) and τ 2·1–2·5 m (3H). In Py-d_5: H-vinylic τ 2·12 d (1H) and τ 2·23 d (1H), J = 9·5 c/s; H-arom τ 1·5–1·8 m (2H) and τ 2·2–2·7 m (3H).

4,7-Diaminobenzotriazole. VII (1·8 g) in MeOH (300 ml) containing 10% Pd-C (0·6 g), hydrogenated at room temp and pressure, yielded 4,7-dimainobenzotriazole identical (IR, mixed m.p.) with the compound obtained from hydrogenation of 4-amino-7-phenylazobenzotriazole,[7] needles yellow-green, m.p. 212–3 from toluene-ethanol (9:1). (Found: C, 48·40; H, 4·65; N, 47·00. $C_6H_7N_5$ requires: C, 48·31; H, 4·73; N, 46·95%).

Preparation of oximes O-methyl ethers

4-O-Methyloximino-5-oximinobenzofurazan (XXII). A mixture of I (1·65 g), O-methylhydroxylamine hydrochloride (1·65 g) in 50% EtOH (60 ml) was refluxed for 2 hr. Reduction of the volume of solvent to about 15 ml, followed by the addition of water, gave a white solid which was crystallized from EtOH, m.p. 204–5°. (Found: C, 43·25; H, 3·21; N, 28·79. $C_7H_6N_4O_3$ requires: C, 43·30; H, 3·12; N, 28·86%).

4,7-O-Methyldioximinobenzo-2,1,3-thiadiazole (XII). A mixture of X (1·7 g), O-methylhydroxylamine hydrochloride (3·25 g) in EtOH (250 ml), was refluxed for 2 hr. Most of the solvent was then removed and the ppt was collected by filtration and washed with water. This product was air-dried and melted at 183-90°; NMR spectra show that this product was a mixture of geometrical isomers (as demonstrated also by the broad m.p. range) D and E, in the ratio about 1:3. (Found: C, 43·01; H, 3·55; N, 24·86. $C_8H_8N_4O_2S$ requires: C, 42·85; H, 3·60; N, 24·99%).

4,7-O-Methyldioximinobenzofurazan (XIII) was obtained from VIII by a procedure described for the analog XII and melted at 150–60°. NMR spectra show that this product was a mixture of geometrical isomers C, D and E in the ratio about 1·5:2·5:1. (Found: C, 46·03; H, 3·90; N, 26·87. $C_8H_8N_4O_3$ requires: C, 46·15; H, 3·87; N, 26·92%).

4,7-O-Methyldioximino-2-phenylbenzotriazole (XIV) was obtained from IX by the procedure described for the analog XII and melted at 153–60°. NMR spectra show that this product was a mixture of geometrical isomers C, D and E in the ratio about 4:4:1. (Found: C, 59·21; H, 4·71; N, 24·65. $C_{14}H_{13}N_5O_2$ requires: C, 59·35; H, 4·63; N, 24·72%).

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