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REACTION OF DIAZOMETHANE WITH 5-HYDROXY-4-PHENYLAZOBENZOFURAZAN AS A SYNTHETIC ROUTE TO DERIVATIVES OF A NEW HETEROCYCLE—PYRAZOLO [3,4-f]-1,2,3-BENZOTRIAZOLE

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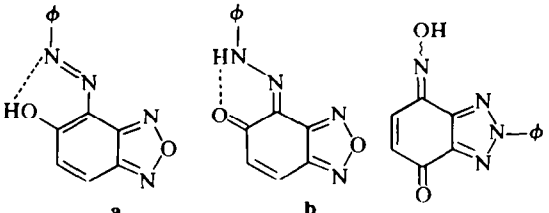
Abstract—Diazomethane adds to 5-hydroxy-4-phenylazobenzofurazan **1** giving a compound **3** which rearranges in alkaline solution to the 8-monoxime of 2-phenyl-5(6)*H*-pyrazolo [3,4-f]-1,2,3-benzotriazole-4,8-dione **4**, the structure of which has been demonstrated by chemical and spectroscopic methods. The probable structure of adduct **3** is discussed on the basis of the chemical reactivity of the compound. The orientation of the cycloaddition and the dipolarophilic behaviour of the 6,7 double bond of the benzofurazan are interpreted on the basis of the quinone hydrazone structure of **1**.

It has been reported in preceding papers that 7-hydroxy-4-phenylazobenzofurazan reacts with diazomethane to give, as the main product, the corresponding methoxy derivative,[1] while the isomer 5-hydroxy-4-phenylazobenzofurazan **1** (**a** and **b** represent the two tautomeric possibilities of the compound) gives, under the same experimental conditions, a product different from the expected O- or N-methyl derivative.[2] In the present work we re-examined the reaction of **1** with diazomethane. The results obtained are reported below.



a **b** **1**

2

RESULTS AND DISCUSSION

The reaction between **1** and diazomethane, in benzene, gives a red product $C_{16}H_{13}N_6O_2$, **3**, (70% yield), the NMR spectrum of which in TFA† does not give clear indications of its structure (multiplet at 2.2–2.8 τ (5H), broad singlet at 4.42 τ (2H) and benzene singlet, confirmed by enrichment, suggests the contribution of benzene of crystallisation to the molecular formula of the compound). Like compound **1**, **3** is soluble in aqueous alkaline solution, a medium which brings about the rearrangement **1** → **2**.[2] Acidification of the alkaline solution of **3** does not give the starting material, but a colourless product, **4**, indicating that **3** undergoes a rearrangement similar to that of **1**. With bromine, the adduct **3** yields a product, **5**, the NMR spectrum of which shows, besides the aromatic multiplet in the 2.1–2.8 τ region (5H), a singlet (1H) (1.35 τ (DMSO); 1.26 τ (TFA)); in aqueous alkaline solution compound **5** gives a product identical to **4**. The NMR spectrum of **4** both in DMSO and in TFA shows the multiplets of the aromatic protons and two singlets (1.71 and 1.36 τ (DMSO); 1.54 and 1.39 τ (TFA)) in DMSO a singlet (−3.22 τ) also appears, which readily exchanges with D_2O. Integration of the signals shows the ratio of the sum of the two singlets to the multiplet of the aromatic protons and the deuterable singlet to be 1 : 5 : 1 (Table 1).

The experimental results reported above can be explained by the addition of diazomethane to the 6,7 double bond of **1**, to give a pyrazoline derivative **3**‡ which can easily aromatized into the pyrazole derivative **5**. The ease of oxidation of **3** can explain the formation of an identical rearrangement product **4**, from **3** or **5**. Consequently, **4** should be attributed the structure of a derivative of pyrazolo[3,4-f]-1,2,3-benzotriazole.

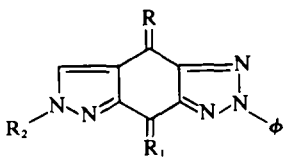
Concerning the direction of attack of diazomethane on the 6,7 double bond of **1**, the presence in **4** of two singlets for the methine proton can be interpreted on the basis of the co-existence of the *syn* and *anti* isomers of a monoxime form, in which the oxime group is located in peri-position with respect to the pyrazole methine proton (compound **2** in DMSO exists predominantly in the oxime form (Table 1)). Scheme 1 shows formulae consistent with the hypothesis formulated, described in one of the numerous tautomeric form.

In order to prove the structure of compound **4**, we have synthesized the quinone **6** and its mono- and di-oximation products (Scheme 2). The synthesis of **6** was performed by the reaction of diazomethane with 2-phenylbenzotriazole-4,7-dione[3] in dioxan, the pyrazole derivative being obtained directly, as in the analogous reaction of 1,4-naphthoquinone.[4] The treatment of **6** with one equivalent of hydroxylamine led to a mixture of two products. The NMR spectrum of this mixture showed, in addition to the signals of the aromatic protons, three singlets corresponding to methine protons, two of which resonate at field values identical with those of **4**, while the third corresponds to that of the 4-monoxime **7**, isolated in the pure state from the reaction mixture (see Experimental). In addition, by subsequent treatment with hydroxylamine, **4** and **7** gave the dioxime **8**, identical with that

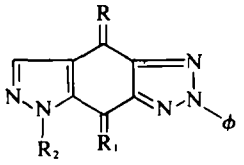
†Attempts to record the NMR spectrum of **3** in various solvents proved to be unsuccessful because of its low solubility or because of the ease with which it underwent rearrangement (see below).

‡Analytical results are in fair agreement with the figures required for the pyrazolinobenzofurazan structur with half a molecule of benzene.

Table 1. NMR data (at 60 MHz in ppm (τ)) of 2-phenyl-5(6)*H*-pyrazole[3,4-f]-1,2,3-benzotriazole-4,8-dione and derivatives



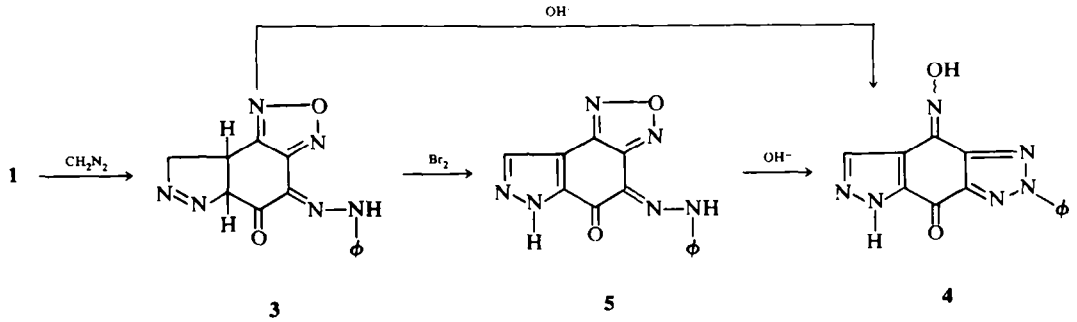
a



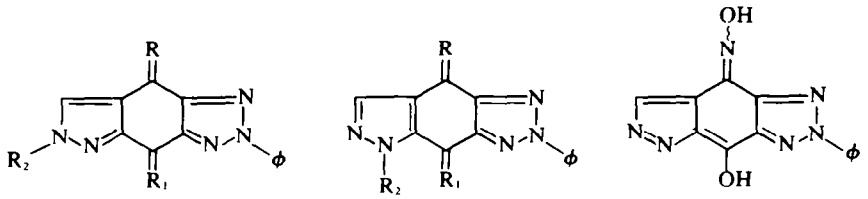
b

Compound[a]	R	R_1	R_2	Solv.[b]	CH	NR_2[f]	R/R_1[f]
2(*anti*)[c]	NOH	O	—	DMSO	3.34[d]	2.41[e]	v.b.[g]
2(*syn*)[c]	NOH	O	—	DMSO	3.35[d]	2.05[e]	v.b.[g]
4a,b(*anti*)[h]	NOH	O	H	DMSO	1.71	v.b.	−3.22
				TFA	1.54	—	—
4a,b(*syn*)[h]	NOH	O	H	DMSO	1.36	v.b.	v.b.
				TFA	1.39	—	—
6a,b	O	O	H	DMSO	1.34	v.b.	—
				TFA	1.36	—	—
7a,b	O	NOH	H	DMSO	1.56	v.b.	−3.70
				TFA[i]	—	—	—
8a,b(*anti*)[l]	NOH	NOH	H	DMSO	1.84	v.b.	−2.40; −2.72
				TFA[i]	—	—	—
8a,b(*syn*)[l]	NOH	NOH	H	DMSO	1.40	v.b.	−2.47; −3.16
				TFA[i]	—	—	—
9a(*anti*)[h]	NOAc	O	Ac	DMSO	1.11	7.21	7.59
				TFA[m]	0.88	6.97	7.37
9a(*syn*)[h]	NOAc	O	Ac	DMSO	0.97	7.21	7.54
				TFA[m]	0.67	7.01	7.36
10a	O	NOAc	Ac	DMSO	0.92	7.24	7.62
				DMSO-TFA	0.83	7.19	7.57
				TFA[n]	0.78	7.02	7.32
11a	O	O	Ac	DMSO	0.76	7.19	—
				DMSO-TFA	0.77	7.18	—
				TFA[o]	0.84	7.02	
12a,b(*anti*)[h]	NOAc	O	H	DMSO	1.40	v.b.	7.59
				TFA	1.39	—	7.37
12a,b(*syn*)[h]	NOAc	O	H	DMSO	1.35	v.b.	7.59
				TFA	1.15	—	7.37
13a,b	O	NOAc	H	DMSO[i]	—	—	—
				DMSO-TFA	1.22	—	7.57
				TFA	1.05	—	7.25

[a] Phenyl protons resonate at 1.7–2.1(2H) and 2.2–2.5 (3H). [b] DMSO, dimethyl sulphoxide-d_6; TFA, trifluoracetic acid; DMSO-TFA, dimethylsulphoxide-d_6/trifluoroacetic acid (about 98/2). [c] 2-Phenylbenzotriazole-4,7-dione-7-monoxime: *anti*, *syn* with respect to H-5, H-6. [d] H-5. [e] H-6. [f] v.b., very broad. [g] $J_{5,6}$: *anti* = 10.4; *syn* = 10.6. [h] *Anti*, *syn*, with respect to the pyrazole ring. [i] Insoluble. [l] *Anti*, *syn* refer to the oxime group R; geometrical configuration of the other oxime group R_1 is not detectable. [m] Partial deacetylation to **12** (isolated product) occurs. [n] Partial deacetylation to **13** (no isolated product) occurs. [o] Deacetylation to **6** occurs.



Scheme 1.

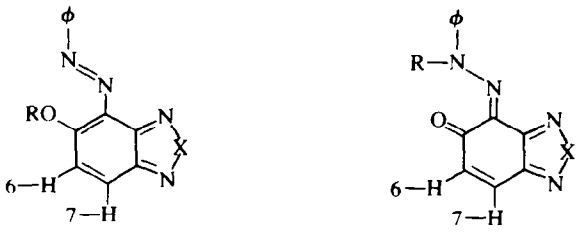


a **b** **4c**

4: R = NOH; R_1 = O; R_2 = H
6: R,R_1 = O; R_2 = H
7: R = O; R_1 = NOH; R_2 = H
8: R,R_1 = NOH; R_2 = H
9: R = NOAc; R_1 = O; R_2 = Ac
10: R = O; R_1 = NOAc; R_2 = Ac
11: R,R_1 = O; R_2 = Ac
12: R = NOAc; R_1 = O; R_2 = H
13: R = O; R_1 = NOAc; R_2 = H

Scheme 2.

Table 2. NMR data (at 60 MHz in ppm (τ)) of 5 - hydroxy - 4 - phenylazobenzothia(oxa)-diazole and derivatives



a **b**

Compd.[a]	R	X	Solvent[b]	H-6	H-7	NH/OCH_3	$J_{6,7}$
1b	H	O	DMSO-TFA[c]	3.07	2.04	—	10.1
			TFA	2.80	1.98	—	10.2
14b	H	S	DMSO	2.97	2.01	−6.00	10.3
15a	CH_3	S	DMSO	2.07	1.78	5.82	9.8

[a] Phenyl protons resonate at 2.0–2.7 τ. [b] See footnote to Table 1. [c] In DMSO **1** rearranges quickly to the oxime **2** (see Table 1), whereas in DMSO/TFA (about 98/2) the rearrangement slows down.

obtained from the quinone **6** (Scheme 2). In the NMR spectrum of **4**, therefore, the methine signal at higher field can be attributed to the *anti*† form and that at lower field to the *syn*† form,[5] while in the spectrum of **7** the methine proton resonates as a singlet since the reciprocal position of the NOH and the pyrazole CH groups makes magnetic anisotropy effects due to the oxime group unlikely.

The synthesis performed confirms the attack of the diazomethane carbon on C-7 of **1**, **4** is therefore the 8-monoxime derivative of 2 - phenyl - 5(6)*H* - pyrazolo[3,4-f] - 1,2,3 - benzotriazole - 4,8 - dione **6**. The predominant structure of **4** can be indicated by **a**, **b** (Scheme 2); the tautomeric structure **4c** may be regarded as unlikely, both on the basis of the IR spectrum (strong carbonyl band appears at 1685 cm^{-1}, in agreement with that present in the quinone **6**) and by comparison of the chemical shift of the pyrazole CH in the monoxime **4** and in the dioxime **8** (Table 1). The attack of diazomethane on C-7 of **1** agrees with that usually observed in α,β-unsaturated carbonyl compounds,[6] with which **1** may be compared on the basis of its NMR spectrum.

Comparison of the spectral data of **1** with those of the analogous sulphur- containing 5-hydroxy-4-phenylazobenzothiadiazole **14** and 5-methoxy-4-phenylazobenzothiadiazole **15** (Table 2), clearly shows that in the azo form **15a** the H-6 proton is strongly deshielded compared with that of **14**, this indicates that structure **14b** is the predominant one in solution. The close analogy between the spectral parameters of **14** and those of **1** (substitution of endocyclic sulphur by oxygen causes no significant changes[7]) leads to the conclusion that in solution **1** is also present predominantly in the quinone hydrazone form **1b**.

The fact that with excess diazomethane‡ the 5-hydroxybenzofurazan[8] gives the methylation product alone, provides indirect confirmation of the existence of **1** in the form **1b**, in which the 6,7 double bond may assume a dipolarophilic nature. The failure to isolate methylation products can be explained by the possibility of the existence in **1** of an intramolecular hydrogen bond which, as is well known, may inhibit the methylation.[9]

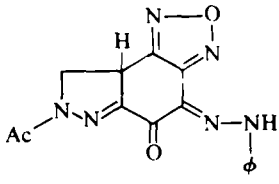
†*Syn* and *anti* with respect to the pyrazole ring.

‡At least 3 moles of diazomethane per mole of hydroxy derivative, under the same reaction condition used for **1**.

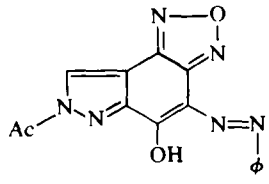
Treatment of **4**, **7** and **6** with acetic anhydride gives the corresponding diacetyl derivatives **9** and **10** and the monoacetyl derivative **11** (Scheme 2). X-Ray analysis of **9** indicates that the structure of the compound is that of the 8-acetoxime of 6 - acetyl - 2 - phenylpyrazolo[3,4-f] - 1,2,3 - benzotriazole - 4,8, - dione **9a**.†

In the NMR spectrum of **9**, both in DMSO and in TFA, it may be noted that in the *anti* isomer the methine proton is deshielded by about 0.6 ppm with respect to the same proton in the non-acetylated compound **4**, and that in the *syn* isomer this deshielding amounts to 0.72 ppm in TFA and 0.39 ppm in DMSO‡ (Table 1). In the spectra of the acetyl derivatives **10** and **11** (Table 1) the magnitude of the deshielding of the methine proton is of the same order as that observed in **9**, and therefore for these compounds as well a structure of type **a** (Scheme 2) is highly probable. In TFA the monoacetyl derivative **11** is rapidly deacetylated to **6** and, similarly, the diacetyl derivatives **9** and **10** are transformed into the monoacetyl derivatives **12** and **13** (Scheme 2). Comparison of the chemical shifts in compounds **6** and **11** and in compounds **4**, **9**, **12** and **7**, **10**, **13** seems to show that deacetylation of **9** and **10** affects the 6-acetylpyrazole group (Scheme 2, Table 1).

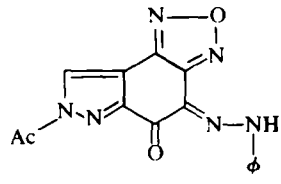
The interpretative uncertainty of the spectrum of **3**, prompted us to find other evidence for the structure of this compound. For this purpose, we subjected **3** and its reaction product with bromine, **5**, to acetylation. Compound **3** gave a mixture of two acetyl derivatives, **16** and **17**, while **5** gave a single acetyl derivative, identical to **17**. The NMR spectrum of **16** in TFA showed an aromatic multiplet in the 2.2–2.8 region (5H), an ill-resolved multiplet at 4.5–6.0 τ (3H), and a singlet at 7.49 τ (3H), the spectrum of **17** cannot be recorded in TFA because of the rapid deacetylation to the starting material, **5**, while in DMSO/TFA the deacetylation slows down and it is possible to observe the presence of a singlet at 0.73 τ (1H), an aromatic multiplet (5H) and a singlet at 7.17 τ (3H). From a qualitative point of view, the spectrum of **16**, may be compatible with the structure of an acetylation product of a pyrazolinobenzofurazan, which confirms the hypothesis put forward previously regarding the constitution of **3**§ on the basis of analytical results and chemical reactivity. The numerous tautomeric forms possible for **16** and **3** do not, however, permit the predominant structure of these compounds to be established on the evidence available. Similarly, it is not possible to indicate the predominant structure of the pyrazolobenzofurazan **5**, but the ready deacetylation of the corresponding acetyl derivative **17** in TFA, similar to that observed in the acetyl derivatives of the pyrazolebenzotriazoles **9**, **10** and **11**, combined with the magnitude of the deshielding effect observed for the methine proton with respect to that of **5** (about 0.6 ppm), indicates that the structures **17a,b** may be considered the most likely.



16



a



b

17

EXPERIMENTAL

M.p. (Buchi-Tottoli apparatus) are uncorrected. NMR spectra were recorded in internal lock mode on a Jeol C-60HL spectrometer. The chemical shifts are in ppm (τ) (±0.01) from internal TMS. Coupling constants (J) are in Hz (±0.10).

Preparation of **14** was performed according to Efros.[13]

Adduct from diazomethane addition to 5-hydroxy-4-phenylazobenzofurazan **3**. To a benzene soln of **1** (7.2 g in 600 ml), cooled to 12°C, was added, whilst stirring, a 0.53 M ethereal soln of diazomethane (60 ml). After stirring for 4 hr at 10–15°, the resulting ppt was filtered and stirred for 5 min with 170 ml of boiling benzene. Filtration of the hot slurry gave 6.5 g (67.5%) of **3**, m.p. 138–9° (dec). Concentration of the mother liquor *in vacuo* at 25–30° gave an additional 0.5 g of crude **3** m.p. 130–1°. **3** could be crystallised cautiously from benzene (m.p. 140–1° (dec)), but the compound melting at 138–9° was used without further purification. Analytical figures for **3** ($C_{16}H_{11}N_6O_2$) agree with the molecular formula $C_{13}H_{10}N_6O_2 \cdot 1/2\ C_6H_6$. Benzene was also retained after drying of **3** *in vacuo* at room temp for 2 weeks, at higher temperatures decomposition of **3** occurs. (Found: C, 59.90; H, 3.96; N, 26.26; $C_{13}H_{10}N_6O_2 \cdot 1/2\ C_6H_6$ requires: C, 59.50; H, 4.08; N, 26.16%).

Acetyl derivative of **3** (**16**). Compound **3** (3.2 g) was treated under reflux for 6 hr in anhyd benzene (950 ml) containing Ac_2O (9.5 ml). The resulting soln was cooled to room temp and a yellow ppt of **16** separated out, which was filtered: 1 g, m.p. 177–8° (dec); ν ($COCH_3$): 1670 cm^{-1} (Nujol mull). The crystallisation of **16** was hampered by its instability (when heated in soln, **16** rapidly underwent oxidation to the dehydro acetyl derivative **17**) (Found: C, 55.71; H, 3.73; N, 25.67. $C_{15}H_{12}N_6O_3$ requires: C, 55.55; H, 3.73; N, 25.92%). The benzene filtrate, gradually concentrated, gave a series of mixtures containing **16** and **17**, progressively rich in **17**.

Dehydro derivative of **3**(**5**). To a finely divided suspension of **3** (3.2 g) in $CHCl_3$ (40 ml) was added dropwise, whilst stirring at room temp., a $Br_2/CHCl_3$ soln (1.6 g in 30 ml). After 48 hr the mixture was filtered and the solid collected was suspended in H_2O (250 ml) and stirred for 5 h, to give crude **5**¶ (2.3 g), which crystallised from $CHCl_3$ ($CHCl_3$ of crystallisation could be removed from **5** by drying *in vacuo* at 55–60°). The m.p. of **5** was not characteristic of the compound.‖ (Found: C, 55.52; H, 2.75; N, 30.10; $C_{13}H_8N_6O_2$ requires: C, 55.71; H, 2.88; N, 29.99%).

Acetyl derivative of **5** (**17**), was obtained by heating **5** (2.8 g) at 70–5°, for 6 h in dioxan (300 ml) containing Ac_2O (9.5 ml). Reduction of the volume *in vacuo* to about 30 ml gave crude **17** (2 g) which was crystallised from Ac_2O. The m.p. of **17** was not characteristic of the compound:‖ ν ($COCH_3$): 1770 cm^{-1} (Nujol

†We are indebted to Prof. A. Tiripicchio *et al.* (Institute of General Chemistry of the University, Via M. D'Azeglio, 85, Parma) for the performance of the X-ray analysis, which will be published elsewhere.

‡In the 1- and 2-acetyl derivatives of 5-nitroindazole the deshielding observed for the methine protons are respectively 0.22 and 0.91 ppm in acetone.[10]

§The presence of the broad singlet at 4.42 τ in the NMR spectrum of **3** in TFA is difficult to interpret on the basis of a single pyrazoline structure. The possibility of protonation of the pyrazoline nitrogens in TFA and the rapid exchange between various protonated forms may lead to the presumption that the above-mentioned signal represents the averaged signal of the methylene of several forms in rapid equilibrium.

¶Similar experiments reacted for shorter times failed to furnish the bromine derivative of **3**.

‖On heating, the coloured solid turned into a colourless compound; this indicates a thermal rearrangement to the corresponding pyrazolobenzotriazole derivative.

mull). (Found: C, 56.03; H, 3.06; N, 26.21; $C_{15}H_{10}N_6O_3$ requires: C, 55.90; H, 3.13; N, 26.08%).

2 - *Phenyl* - 5(6)*H* - *pyrazolo*[3,4 - f]1,2,3 - *benzotriazole* - 4,8 - *dione* - 8 - *monoxime* **4**. A suspension of adduct **3** (3.2 g) in aqueous 0.1 N NaOH (150 ml) was stirred for 1.5 h at room temp. To the resulting solution was added boiling H_2O (150 ml) and a black ppt obtained, filtered off (unidentified material, 0.15 g). Acidification of the alkaline filtrate with dil HCl gave **4** (2 g, 71%, m.p. 325–30°) which was crystallised from isopropanol (m.p. 336–7°). ν (C=O): 1685 cm^{-1} (KBr). The same product was obtained using **5**, as the starting compound. (Found: C, 55.88; H, 3.08; N, 29.81. $C_{13}H_8N_6O_2$ requires: C, 55.71; H, 2.88; N, 29.99%).

2 - *Phenyl* - 5(6)*H* - *pyrazolo*[3,4 - f]1,2,3 - *benzotriazole* - 4,8 - *dione* **6**. To a dioxan soln of 2-phenylbenzotriazole-4,7-dione[3] (6.8 g in 600 ml) cooled to 15°, was added, whilst stirring, a 0.58 M ethereal soln of diazomethane (56 ml). After 48 h the soln was concentrated *in vacuo* and the residue (~30 ml) was precipitated with Et_2O (80 ml). The collected ppt was suspended in boiling MeOH (100 ml) and added to 4% KOH/MeOH (50 ml). The suspension was boiled for 5 min and the resulting K salt of **6** was filtered. Acidification of the aqueous soln of the salt with dil HCl gave **6** (4.3 g, 54.5%, m.p. 304–6°). Crystallised from AcOH, m.p. 307–8°; γ (C=O): 1687 cm^{-1} (KBr). (Found: C, 58.91; H, 2.59; N, 26.36. $C_{13}H_7N_5O_2$ requires: C, 58.87; H, 2.66; N, 26.41%).

2 - *Phenyl* - 5(6)*H* - *pyrazolo*[3,4 - f]1,2,3 - *benzotriazole* - 4,8 - *dione* - 4 - *monoxime* **7**. A suspension of **6** (2.65 g) in EtOH (700 ml) was added to a ethanolic soln of hydroxylamine hydrochloride (0.72 g in 100 ml), and the mixture boiled under reflux for 7 h. Reduction of the volume to about 350 ml, gave crude **7** (1.1 g), m.p. 288–9°, which was purified by crystallisation from EtOH (0.4 g, m.p. 299–300°). Further concentration of the mother liquor to a volume of about 100 ml, gave another fraction containing **7** and the isomer 8-monoxime **4** (by NMR analysis). (Found: C, 55.61; H, 2.93; N, 30.04. $C_{13}H_8N_6O_2$ requires: C, 55.71; H, 2.88; N, 29.99%).

2 - *Phenyl* - 5(6)*H* - *pyrazolo*[3,4 - f]1,2,3 - *benzotriazole* - 4,8 - *dione* - *dioxime* **8**, was obtained by heating **6** (2.65 g) under reflux for 16 h in EtOH (700 ml) containing 1.6 g of hydroxylamine hydrochloride. Removal of solvent and addition of H_2O (200 ml) to the residue, gave crude **8**, (2.8 g, m.p. 280–5°). Crystallisation from EtOH/H_2O 1:1 gave pure **8**, m.p. 296–8°. The same product was obtained by using the monoxime **4** or **7**, as the starting compound. (Found: C, 52.85; H, 3.12; N, 33.05. $C_{13}H_9N_7O_2$ requires: C, 52.89; H, 3.07; N, 33.21%).

Acetylation of 2 - *phenyl* - 5(6)*H* - *pyrazolo*[3,4 - f]1,2,3 - *benzotriazole* - 4,8 - *dioxime and its* 4- *and* 8-*monoximes* was performed by heating the compound (10 mmoles) at 100° for 4 h in Ac_2O (40 ml). Filtration of the resulting mixture and crystallisation of the collected ppt from Ac_2O gave pure acetyl derivatives. 2 - Phenyl - 6 - acetylpyrazolo[3,4 - f]1,2,3 - benzotriazole - 4,8 - dione 8 - acetoxime **9**, m.p. 238–9° (dec). (Found: C, 56.06; H, 3.47; N, 23.04. $C_{17}H_{12}N_6O_4$ requires: C, 56.04; H, 3.32; N, 23.07%). Compound **9** (1 g) was dissolved by stirring in TFA (10 ml) at room temp. After 2 h the resulting ppt. filtered and washed with H_2O, gave 2 - phenyl - 5(6)H - pyrazolo[3,4 - f]1,2,3 - benzotriazole - 4,8 - dione - 8 - acetoxime, **12**, m.p. 255–6° (from EtOH). (Found: C, 56.02; H, 3.09; N, 25.97. $C_{15}H_{10}N_6O_3$ requires: C, 55.90; H, 3.13; N, 26.08%). 2 - Phenyl - 6 - acetylpyrazolo[3,4 - f]1,2,3 - benzotriazole - 4,8 - dione **11**, m.p. 249–51°. (Found: C, 58.58; H, 2.89; N, 22.74; $C_{15}H_9N_5O_3$ requires: C, 58.63; H, 2.95; N, 22.79%). In TFA **11** underwent deacetylation to the starting compound **6**. 2 - Phenyl - 6 - acetylpyrazolo[3,4 - f]1,2,3 - benzotriazole - 4,8 - dione - 4 - acetoxime **10**, m.p. 245–6°. (Found: C, 55.92; H, 3.27; N, 22.97. $C_{17}H_{12}N_6O_4$ requires: C, 56.04; H, 3.32; N, 23.07%). In TFA deacetylation of **10** was slow and the monoacetyl derivative **13** (see text) (identified by NMR spectrum of **10**) was not isolated.

5 - *Methoxy* - 4 - *phenylazo* - 2,1,3 - *benzothiadiazole* **15**. Aqueous $AgNO_3$ (2.2 g in 15 ml) was added to the K salt of 5-hydroxy-4-phenylazobenzothiadiazole[13] (2.56 g in 100 ml of 0.1 N KOH). The dried Ag salt (3.45 g) was boiled, whilst stirring with MeI (35 ml) for 12 h. The mixture was filtered and the solid washed with Et_2O. The combined Et_2O and MeI filtrate was evaporated and the residue crystallised from *n*-heptane to give pure **15**, m.p. 93–4°. (Found: C, 57.65; H, 3.81; N, 20.68. $C_{13}H_{10}N_4OS$ requires: C, 57.77; H, 3.73; N, 20.73%).

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REFERENCES

[1]D. Dal Monte and E. Sandri, *Boll. Sci. Fac. Chim. Ind. Bologna* **26**, 127 (1968).
[2]D. Dal Monte, E. Sandri and S. Pollicino, *Ibid.* **26**, 153 (1968).
[3]A. S. Angeloni, V. Cerè, D. Dal Monte, E. Sandri and G. Scapini, *Tetrahedron* **28**, 303 (1972).
[4]H. Brockmann, K. Van Der Merwe and A. Zeeck, *Ber. Dtsch. Chem. Ges.* **97**, 2555 (1964).
[5]L. M. Jackman and S. Sternhell, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, 2nd Edn, p. 226. Pergamon Press, London (1969).
[6]R. Huisgen, R. Grashey and J. Sauer, *The Chemistry of Alkenes* (Edited by S. Patai), p. 829. Interscience, New York (1964).
[7]A. J. Boulton, P. J. Halls and A. R. Katritzky, *Org. Magn. Resonance* **1**, 311 (1969).
[8]D. Dal Monte and E. Sandri, *Ann. Chim. Ital.* **54**, 486 (1964).
[9]V. C. Farmer, N. F. Hayes and R. H. Thomson, *J. Chem. Soc.* 3600 (1956).
[10]J. Elguero, A. Fruchier and R. Jacquier, *Bull. Soc. Chim. Fr.* 2075 (1966).
[11]P. Bouchet, J. Elguero and R. Jacquier, *Tetrahedron Lett.* **52**, 6409 (1966).
[12]J. L. Aubagnac, J. Elguero and R. Jacquier, *Bull. Soc. Chim. Fr.* 3316 (1969).
[13]L. S. Efros, R. P. Polyakova and M. G. Argitti, *Zh. Obshch. Khim.* **32**, 516 (1962).