1,2,3-Benzotriazine 2-Oxides

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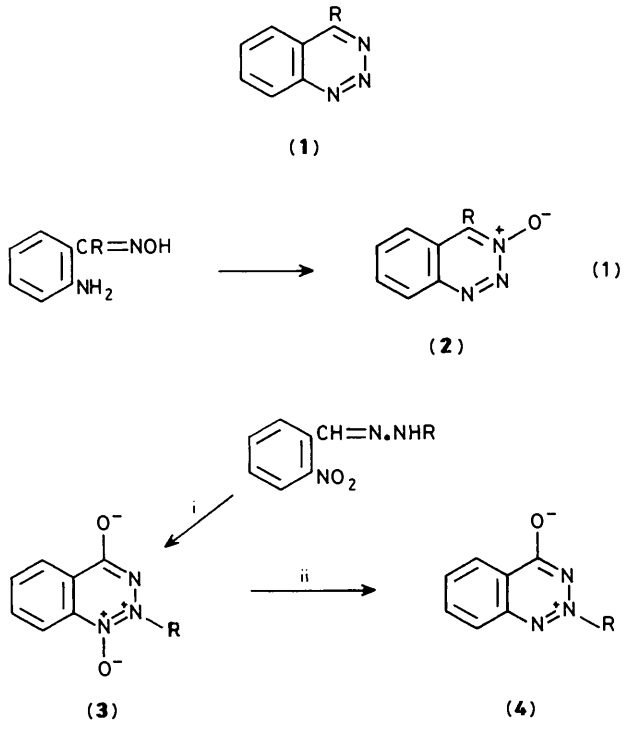
4-Methoxy-1,2,3-benzotriazine, like the 4-methyl and 4-phenyl compounds, forms the 2-oxide on N-oxidation; this is hydrolysed to the acidic 3,4-dihydro-4-oxo-1,2,3-benzotriazine 2-oxide, which is N-methylated by diazomethane at the 3-position. The 4-methoxy 2-oxide was converted into 4-amino- and 4-hydrazino-derivatives. 5-Amino-3-methylisoxazole-2-carbonitrile forms 3,4-dihydro-5-methyl-4-oxoisoxazolo[5,4-*d*]-1,2,3-triazine 2-oxide on reaction with nitric and sulphuric acids. The ^{15}N n.m.r. spectra of some 1,2,3-benzotriazines and their *N*-oxides are reported.

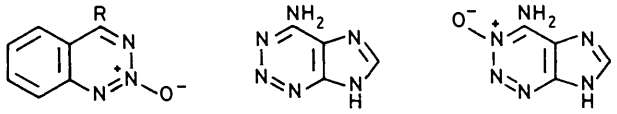
Of the three possible series of *N*-oxides of the 1,2,3-benzotriazines (**1**), the longest known are the 3-oxides (**2**), which are formed on diazotisation of 2-aminophenyl aldoximes or ketoximes (equation 1). This reaction was investigated by Bamberger,[1] but he misinterpreted the evidence, obtained from the aldoxime series, and it was Meisenheimer[2] who first identified the products as benzotriazine oxides. They are usually yellow in colour, and rather unstable.

The only 1,2,3-benzotriazine 1-oxides which are known to us are the mesomeric betaines (**3**), which were first prepared by Chattaway and co-workers[3] in the 1920s, and which presented a structural problem which was finally resolved only recently.[4] They are reactive materials, often explosive, and they are fairly readily reduced to the corresponding betaines (**4**), which are much more stable compounds. Their mode of formation is shown in Scheme 1.



Scheme 1. *Reagents:* i, Br_2/OH^- or $Pb(OAc)_4$; ii, $SnCl_2$

When we began our work, no 1,2,3-benzotriazine 2-oxides (**5**) had been reported, although some 1,2,3-triazine 2-oxides had been prepared by peroxy acid oxidation.[5] In the unfused series, the simpler alkyl 1,2,3-triazines appear to be oxidised preferentially at the 2-position, while aryl-substituted examples are reported to be more often oxidised solely or preferentially at the 1- or 3-positions. The imidazotriazine (**6**) (an aza-adenosine) was found by Brown and co-workers[6] to give two oxides on N-oxidation. The major product was unequivocally the 3-oxide (2-aza-adenosine 1-oxide) (**7**); the authors were uncertain of the structure of the other oxide.

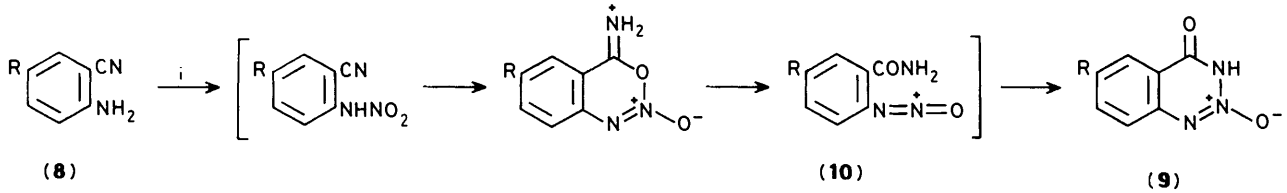


Attempts to N-oxidise 1,2,3-benzotriazines were reported by Stanovnik and Tisler,[7] but in only one case was a product isolated: the 4-arylthio derivative [**1**; R = 2,4,6-$C_6H_2(NO_2)_3S$] gave a mono-oxide which was tentatively assigned as a 3- or a 1-oxide, mainly on the basis of H.M.O. charge-density calculations[8] on the unsubstituted compound. As we shall show later, these calculations were misleading as a guide to the site of oxidation.

Shortly after we had begun this study, an extremely interesting patent[9] from the Baeyer Laboratories, Leverkusen, appeared in the Abstracts. In this work, an *o*-aminobenzonitrile (**8**) was treated with an acidic nitrating mixture (*e.g.*, H_2SO_4–HNO_3, or HF–HNO_3), to form the 2-oxide (**9**) of a 4*H*-1,2,3-benzotriazin-4-one. The synthesis was restricted to those aminonitriles which were not susceptible to nitration in the aromatic ring; the best yields were reported with 2-amino-5-nitrobenzonitrile (**8**: R = NO_2). A plausible reaction sequence, *via* a nitramine and the intermediate (**10**), which contains the unusual nitroso-nitrenium, or diazonio-oxide grouping, $(-N{=}N{=}O)^+$, is shown in Scheme 2.

Results and Discussion

We have investigated the site of N-oxidation of 1,2,3-benzotriazines, by use of ^{15}N n.m.r. It is known that when heterocycles contain two imine nitrogens which are adjacent, the signals from both are located at unusually low field (high frequency), compared with those from nitrogens which are separated by carbon atoms. The three adjacent nitrogens of a 1,2,3-benzotriazine show the absorption from the central nitrogen at still lower field (*ca.* δ = +40, downfield of $MeNO_2$, δ = 0), while the two which are also flanked by carbon absorb in the same general region as a pyridazine (1,2-diazine).[10,11] Removal of the lone pair of electrons from the central nitrogen, by quaternisation or N-oxidation, is expected to shift the signals of all the nitrogen atoms upfield, while oxidation of one of the flanking nitrogens leaves lone pairs adjacent on the other two,



Scheme 2. *Reagent:* i, HNO_3–H_2SO_4

which should remain absorbing in the low-field region. This is just what is observed in the spectrum of 4-methyl-1,2,3-benzotriazine-3-oxide (**2**; R = Me) which was prepared by standard methods. The chemical shifts are listed in the Table.

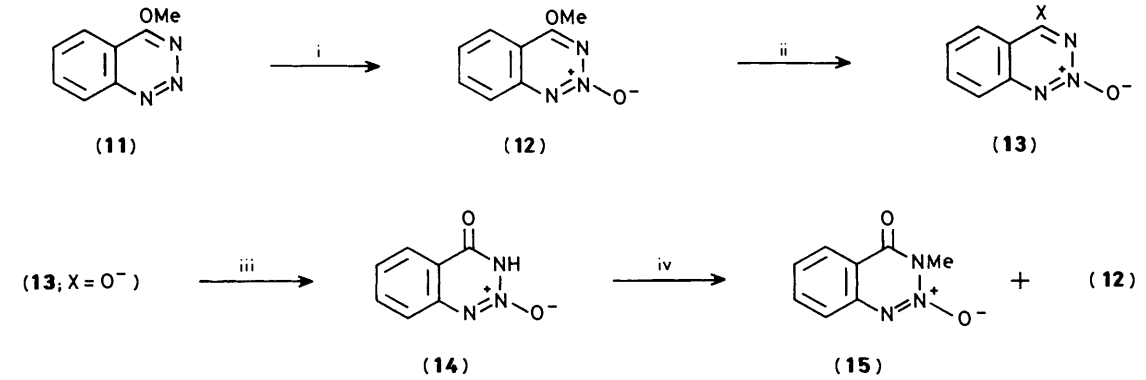
4-Methyl and 4-phenyl-1,2,3-benzotriazines (**1**; R = Me, Ph) and the 6-chloro-4-phenyl compound, were oxidised by *m*-chloroperbenzoic acid (MCPBA). The principal product obtained from each proved to be chemically different from, and much stabler than, the corresponding 3-oxide (**2**), although the melting-points, coincidentally, were almost identical. The ^{15}N n.m.r. spectrum of the products showed all the signals well to high field (low frequency) of nitromethane, and so did not contain two 'adjacent lone pairs'. The *N*-oxide group was therefore at the 2-position, in each case. A small amount of the 3-oxide was also isolated from the oxidation of the 4-methyl derivative. On oxidation of 4-methoxy-1,2,3-benzotriazine (**11**), the 2-oxide (**12**) was the only product found (Scheme 3). These 2-oxides proved to be remarkably resistant to deoxygenation by triethyl phosphite or phosphorus trichloride. The mass spectra of the 2-oxides contrasted with those of the isomeric 3-oxides in showing fragments corresponding to loss of 30 a.m.u. ($M^+ - NO$), instead of 28 ($M^+ - N_2$).

The methoxy group of 4-methoxy-1,2,3-benzotriazine 2-oxide (**12**) could be displaced by a variety of nitrogen nucleophiles (see Scheme 3). The hydrazino compound (**13**; X = $NHNH_2$) was stronger acids than the corresponding amides (*e.g.*, benzamide, pK_a *ca.* 14.5[14]). However, the strength of the acid (**14**) surprised us.

Compound (**14**) is the parent of the compounds (**9**) prepared by the Baeyer group,[9] described above; the synthesis by cyclisation of the *o*-aminonitriles is not applicable to the preparation of the unsubstituted compound (**14**), but comparison of the i.r. spectra of our material with that of the 6-nitro derivative, a sample of which was provided by Dr. Wedemeyer, showed that they were closely similar in essential details. As expected, the 6-nitro compound was still more acidic (pK_a 0.86) than (**14**).

Reaction of compound (**14**) with diazomethane gave the *N*-methyl derivative (**15**) (Scheme 3), m.p. 145—146 °C, with a u.v. spectrum closely similar to that of the tautomeric compound; this confirms the tautomeric structure of the acid (**14**). A minor product of the methylation was the methoxy compound (**12**).

Hydrogenolysis of the isoxazole ring of (**18**) might provide a monocyclic hydroxy triazinone *N*-oxide. With this in view, we treated 5-amino-4-cyano-3-methylisoxazole (**17**) with concentrated nitric and sulphuric acids, following the Baeyer method. The expected product (**18**) was formed, but the yield was poor, and it was found to be very difficult to isolate the highly polar and water-soluble material from the reaction mixture. This project was therefore not proceeded with further.



Scheme 3. *Reagents:* i, MCPBA; ii, ammonia, dimethylamine, hydrazine, or hydroxide; iii, H^+; iv, CH_2N_2

oxidised by manganese dioxide, in an attempt to obtain the 4-unsubstituted benzotriazine 2-oxide, but all that was isolated was a very small amount of an oil which was probably (according to i.r.) 2-azidobenzonitrile. Hydrazine oxidation has been reported before to be unsuccessful in producing a 4-unsubstituted 1,2,3-benzotriazine.[12]

After several unsuccessful attempts at demethylation, the methoxy compound (**12**) was hydrolysed to the tautomeric *N*-oxide (**14**), using potassium hydroxide in methanol. (Scheme 3) This product proved to be a remarkably strong acid, of pK_a 1.64. For comparison, the pK_a values of 1,2,3-benzotriazin-4(3*H*)-one (**16**); R = H) and the 3-hydroxy derivative (**16**; R = OH) were measured to be 8.23 and 4.23, respectively. That compound (**16**; R = OH) is a stronger acid than (**16**; R = H) is expected; hydroxamic acids (*e.g.*, benzohydroxamic acid, pK_a 8.81[13]) are

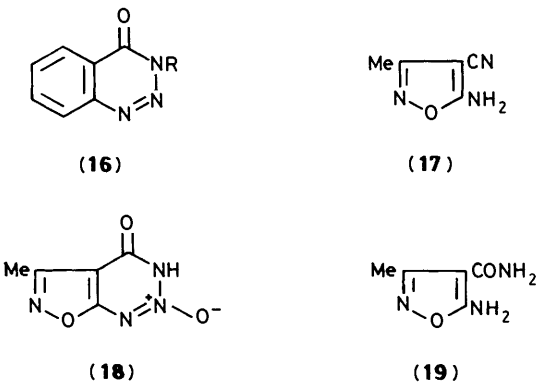


Table. ^{15}N Chemical shifts (δ) relative to external nitromethane (δ = 0) of some 1,2,3-benzotriazines and their *N*-oxides.

Compound	N-1	N-2	N-3
(**1**; R = Me)	+15.9	+66.6	−16.1
(**2**; R = Me)	+18.5	+39.1	−51.8
(**5**; R = Me)	−49.5	−48.1	−75.6
(**11**)	+5.1	+61.2	−66.3
(**12**)	−85.0	−54.4	−95.5

The major product of the fused triazinone oxide preparation was the amide (**19**), which we were unable to convert into the isoxazolotriazinone with nitrous acid.

Nitrogen N.M.R. Spectra.—The chemical shifts of some of the compounds prepared in this work are recorded in the Table.

The figures in the Table required little comment. A nitrogen atom carrying an electron 'lone pair', adjacent to another similar atom, experiences a down-field shift (to more positive δ values), which is particularly marked with N-2 of compound (**1**; R = Me). The 4-methoxy group in compounds (**11**) and (**12**) exerts a pronounced shielding effect on the N atoms in *ortho* and *para* positions.

Experimental

Spectroscopic instrumentation was as described previously.[11] All n.m.r. spectra were of samples in $CDCl_3$ solution. The pK_a determinations were made by the spectrophotometric method in the usual way,[15] using M/100 buffer solutions in water.

The following compounds were prepared by the literature methods cited: 4-methyl- (**2**; R = Me),[2] 4-phenyl- (**2**; R = Ph),[2] and 6-chloro-4-phenyl-1,2,3-benzotriazine 3-oxide;[16] 1,2,3-benzotriazin-4(3*H*)-one (**15**; R = H)[17]; and 5-amino-4-cyano-3-methylisoxazole (**17**).[18] 3-Hydroxy-1,2,3-benzotriazine-4(3*H*)-one (**15**; R = OH) was a commercial product (Fluka).

4-*Methyl*-1,2,3-*benzotriazine* (**1**; R = Me).—This was prepared from 2-nitrobenzoic acid, *via* 2-azidoacetophenone hydrazone, as described by Adger *et al.*,[12] with modification to the final stage, as follows: lead(IV) acetate (6.0 g, 13.5 mmol) was added to a rapidly stirred solution of 2-amino-3-methylindazole (1.8 g, 12.2 mmol) in dry dichloromethane (75 ml) containing calcium oxide (10 g), cooled by ice-salt to −8 °C. After being stirred for 3 h, the mixture was filtered, and the residue was washed with dichloromethane (100 ml). The filtrate and washings were combined, boiled briefly with charcoal, filtered, and evaporated to dryness. The residue was sublimed at 95—100 °C/0.15 mmHg, then crystallised from ethanol, giving 4-methyl-1,2,3-benzotriazine (1.0 g, 57%), m.p. 120—121.5 °C (lit.,[12] m.p. 120—121 °C).

4-Phenyl-1,2,3-benzotriazine (**1**; R = Ph), prepared from 1-amino-3-phenylindazole, as described by Adger *et al.*,[12] had m.p. 156 °C (lit.,[12] m.p. 156—157 °C). 6-Chloro-4-phenyl-1,2,3-benzotriazine, m.p. 140—141 °C (lit.,[12] m.p. 126—127 °C) was prepared by oxidation of 2-amino-5-chlorobenzophenone hydrazone[12] (Found: C, 64.5; H, 3.2; N, 17.4. Calc. for $C_{13}H_8ClN_3$: C, 64.6; H, 3.3; N, 17.4%).

4-*Methyl*-1,2,3-*benzotriazine* 2-*Oxide* (**5**; R = Me).—*m*-Chloroperbenzoic acid (MCPBA) (0.2 g) was added portionwise to a stirred solution of 4-methyl-1,2,3-benzotriazine (0.102 g, 0.7 mmol) in dichloromethane (15 ml) at 20 °C. The solution was stirred for a further 15 h, diluted with dichloromethane (10 ml), washed with aqueous Na_2CO_3 (10%; 3 × 25 ml) and water (2 × 25 ml), then dried ($MgSO_4$), and evaporated to dryness. The residue was passed through a short column of neutral alumina, eluting with diethyl ether–ethyl acetate (1:4). The 2-*oxide* (0.54 g, 48%) was crystallised from dichloromethane–light petroleum (1:1) and sublimed (147—155 °C/0.15 mmHg); m.p. 176—178 °C; $\lambda_{max.}$ 213 (log ε 4.3), 260 (4.4), 290 (3.9), and 350sh nm; δ 8.24—7.44 (4 H, m) and 2.86 (3 H, s); *m/z* 161 (M^+), 145, 131, 116, 103, 90, and 76 (Found: C, 60.0; H, 4.4; N, 25.9. $C_8H_7N_3O$ requires C, 59.6; H, 4.4; N, 26.1%).

Further elution gave 4-methyl-1,2,3-benzotriazine 3-oxide (**2**; R = Me (0.11 g, 10%), m.p. 175—177 °C, identical with an authentic sample.

4-*Phenyl*-1,2,3-*benzotriazine* 2-*Oxide* (**5**; R = Ph).—MCPBA (1.1 g, 6.4 mmol) was added portionwise to 4-phenyl-1,2,3-benzotriazine (0.53 g, 2.6 mmol) in dichloromethane (50 ml), and the mixture stirred at room temperature for 8 h. After being washed with aqueous Na_2CO_3 and dried, the residue was crystallised from methanol to give yellow needles of the 2-*oxide* (0.35 g, 61%), m.p. 156.5—157.5 °C; $\lambda_{max.}$ 211 (log ε 4.1), 267 (4.3), and 366 nm (3.3); *m/z* 223 (M^+), 207, 193, 179, 165, 152, 139, 126, 119, 103, 90, and 77 (Found: C, 69.5; H, 4.0; N, 18.4. $C_{13}H_9N_3O$ requires C, 69.9; H, 4.1; N, 18.8%).

Similarly, 6-*chloro*-4-*phenyl*-1,2,3-*benzotriazine* 2-*oxide*, yellowish laths from methanol, m.p. 190—194 °C (decrepitation, and slight browning, > 150 °C), was prepared by oxidation of 6-chloro-4-phenyl-1,2,3-benzotriazine, $\lambda_{max.}$ 213 (log ε 4.5), 268 (4.6), and 375 nm (3.8) (Found: C, 60.9; H, 3.1; N, 16.3. $C_{13}H_3ClN_3O$ requires C, 60.6; H, 3.1; N, 16.3%).

4-Phenyl-1,2,3-benzotriazine 2-oxide was recovered (90%) after 6 h reflux in triethyl phosphite, and (> 95%) after 8 h reflux with PCl_3 in CH_2Cl_2.

4-Methoxy-1,2,3-benzotriazine (**11**) was prepared *via* the 4-methylthio compound as described in ref. 11.

4-*Methoxy*-1,2,3-*benzotriazine* 2-*Oxide* (**12**) *and its Reactions with Nucleophiles.*—MCPBA (4.95 g, 28 mmol) was stirred for 7 h at 20 °C with 4-methoxy-1,2,3-benzotriazine (2.95 g, 18 mmol) in dichloromethane (75 ml), after which time t.l.c. showed that the reaction was complete. Precipitated *m*-chlorobenzoic acid was filtered off and washed with dichloromethane. The filtrate and washings were combined, shaken with aqueous Na_2CO_3, dried ($MgSO_4$), and evaporated to dryness. The residue was crystallised from methanol to give the 4-*methoxy* 2-*oxide* (**12**) as needles (2.5 g, 77%), m.p. 180—182 °C; $\lambda_{max.}$ 220 (log ε 4.4), 246 (4.3), and 294 nm (4.0); δ 8.20—7.48 (m, 4 H) and 4.28 (s, 3 H); *m/z* 177 (M^+), 161, 147, 132, 119, 104, 90, 76, and 63 (Found: C, 54.2; H, 3.7; N, 23.6. $C_8H_7N_3O_2$ requires C, 54.2; H, 4.0; N, 23.7%).

The methoxy oxide (**12**) was recovered (80%) after 8 h reflux with PCl_3 in dichloromethane.

The 4-methoxy 2-oxide (**12**) (0.5 g) in methanol (100 ml) was cooled to 0 °C and a stream of anhydrous ammonia was passed through for 2 h. After being stirred for a further 2.5 h at 20 °C the solution was again cooled, to −8 °C, and 4-*amino*-1,2,3-*benzotriazine* 2-*oxide* (**13**; X = NH_2) was filtered off. The mother-liquor was concentrated and cooled again to provide further product. Recrystallisation from methanol gave needles (0.25 g, 54%), m.p. 314—319 °C (decomp.); $\lambda_{max.}$ 204 (log ε 4.1), 254 (4.4), and 312 nm (3.9); *m/z* 162 (M^+), 146, 132, 118, 104, 91, 77, and 64 (Found: C, 51.7; H, 3.6; N, 34.4. $C_7H_6H_4O$ requires C, 51.9; H, 3.7; N, 34.5%).

Dimethylamine (26% w/w in methanol) (15 ml) was added to a suspension of the 4-methoxy 2-oxide (0.43 g) in methanol (15 ml), and the mixture was stirred at 20 °C for 2 h. The solution was diluted with water (100 ml) and extracted with dichloromethane (3 × 50 ml). The combined organic extracts were treated with charcoal, dried ($MgSO_4$), filtered, and evaporated to dryness. The residue was crystallised from

toluene to give fine needles of 4-*dimethylamino*-1,2,3-*benzotriazine* 2-*oxide* (**13**; X = NMe_2) (0.27 g, 59%), m.p. 182.5—184 °C; $\lambda_{max.}$ 206 (log ε 4.3), 253 (4.5), and 326 nm (4.1); δ 8.12—7.24 (m, 4 H), 3.40 (s, 6 H, separating into two 3 H singlets at low temperature); *m/z* 190 (M^+), 178, 174, 160, 145, 131, 118, 102, 91, 76, and 63 (Found: C, 56.9; H, 5.3; N, 29.1. $C_9H_{10}N_4O$ requires C, 56.8; H, 5.3; N, 29.4%).

Hydrazine hydrate (1 ml) was added to a stirred suspension of the 4-methoxy 2-oxide (0.35 g) in methanol (5 ml). After 30 min the precipitated solid was filtered off, washed with ethanol, and recrystallised from methanol, giving brownish leaflets of 4-*hydrazino*-1,2,3-*benzotriazine* 2-*oxide* (**13**; X = $NHNH_2$) (0.24 g, 69%), m.p. 254—257 °C; $\lambda_{max.}$ 204 (log ε 4.2), 250 (4.4), and 326 nm (4.0); *m/z* 177 (M^+, weak), 159, 147, 133, 118, 103, 91, and 76 (Found: C, 47.3; H, 3.8; N, 39.1. $C_7H_7N_5O$ requires C, 47.5; H, 4.0; N, 39.5%).

An attempt to oxidise (MnO_2–CH_2Cl_2) the hydrazine (0.2 g) to the 4-unsubstituted 2-oxide gave an oil (4 mg) which was not identified; $\nu_{max.}$ 2 230, 2 145, and 2 115 cm^{-1}.

3,4-*Dihydro*-4-*oxo*-1,2,3-*benzotriazine* 2-*oxide* (**14**).—4-Methoxy-1,2,3-benzotriazine 2-oxide (0.5 g, 2.8 mmol) was added to potassium hydroxide (0.3 g, 5 mmol) in methanol–water (1:1, 25 ml) and the mixture was stirred for 17 h at 20 °C. The solution was acidified carefully to pH 3 and extracted with dichloromethane to remove impurities. Addition of further hydrochloric acid to the aqueous solution precipitated the 4-*oxo* 2-*oxide* (**14**) which was recrystallised from methanol as white leaflets (0.27 g, 60%), m.p. 270—276 °C (decomp.); $\nu_{max.}$ 1 675 cm^{-1} (C=O); $\lambda_{max.}$ (1M H_2SO_4) 220 (log ε 4.4), 245 (4.3), and 300 nm (4.1); $\lambda_{max.}$ (pH 7) 224 (log ε 4.2), 252 (4.4), and 310 nm (4.1); pK_a 1.64; *m/z* 163 (M^+), 147, 135, 119, 104, 92, and 76. (Found: C, 51.5; H, 3.0; N, 25.9. $C_7H_5N_3O_2$ requires C, 51.5; H, 3.1; N, 25.8%).

3,4-*Dihydro*-3-*methyl*-4-*oxo*-1,2,3-*benzotriazine* 2-*Oxide* (**15**).—The *N*-oxide (**14**) (97 mg) was suspended in cold ether–methanol (1:1) and treated at 0 °C with an excess of ethereal diazomethane. After being stirred for 1 h, the solution was evaporated to dryness and the residue was chromatographed on silica gel, eluting with ethyl acetate–light petroleum (3:5). The first compound to be eluted was the N-*methyl derivative* (**15**; R = Me) (52 mg, 50%), which formed needles from cyclohexane, m.p. 145—146 °C; $\nu_{max.}$ 1 700 cm^{-1} (C=O); $\lambda_{max.}$ 225 (log ε 4.17), 297 (3.72), 308 (3.70), and 320sh nm; *m/z* 177 (M^+), 161, 147, 132, 117, 104, 90, and 77 (Found: C, 53.9; H, 3.8; N, 23.3. $C_8H_7N_3O_2$ requires C, 54.2; H, 4.0; N, 23.7%).

Further elution gave the methoxy compound (**12**) (11 mg, 11%).

3,4-*Dihydro*-5-*methyl*-4-*oxoisoxazolo*[5,4-d]-1,2,3-*triazine* 2-*Oxide* (**18**).—The aminoisoxazole carbonitrile (**17**)[18] (2.46 g) was added at 0 °C to a mixture of sulphuric acid (98%, 13 ml) and fuming nitric acid (95%; 1.36 g). The mixture was kept in a refrigerator at 9 °C for two days, then poured onto ice, and the pH adjusted to *ca.* 10 with 10% NaOH. The solution was continuously extracted with ethyl acetate for 8 h. The extract was dried and the solvent was evaporated. The residue (1.7 g, 60%) proved to be the substantially pure amino-amide (**19**), m.p. 190 °C (lit.,[18] m.p. 190—193 °C, decomp.). The pH of the aqueous fraction was then reduced again to 0 with sulphuric acid, and ethyl acetate extraction was continued. After 24 h the extract was dried, filtered, and evaporated. The residue was crystallised from light petroleum—ethyl acetate, to give the *isoxazolotriazinone oxide* (**18**) (0.6 g, 18%), m.p. 186.5—188.5 °C (decomp.) (Found: C, 35.9; H, 2.1; N, 33.4. $C_5H_4N_4O_3$ requires C, 35.7; H, 2.4; N, 33.3%).

Acknowledgements

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