1,2,3-Benzotriazinone 1-Oxides

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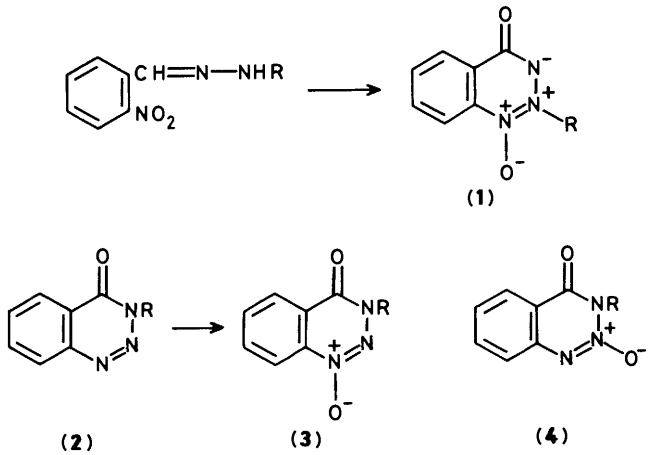
3-Substituted 1,2,3-benzotriazin-4(3*H*)-one 1-oxides are formed on peracid oxidation of 3-alkyl- and 3-methoxy-1,2,3-benzotriazin-4(3*H*)-ones. The 3-(α-alkoxyalkyl) 1-oxide derivatives could be dealkylated to the tautomeric 3-unsubstituted compound. The acidities of the isomeric *N*-oxides of the 1,2,3-benzotriazinone system are compared. Phenyl iodosodiacetate converts *o*-nitrobenzaldehyde benzyl- and phenyl-hydrazones into the 2-substituted 4-oxido-1,2,3-benzotriazine 1-oxide betaines (**1**).

In an earlier paper[1] the literature on the *N*-oxides of the 1,2,3-benzotriazine series was summarized, and the preparation and properties of 1,2,3-benzotriazin-4-one 2-oxide were described. We now report on efforts to obtain the corresponding 1-oxide, which were finally successful using a simple approach, involving attachment and removal of a suitable protective group at N(3).

The only 1,2,3-benzotriazine 1-oxides reported to date are the mesomeric betaines (**1**), which were first isolated by Chattaway *et al.*[2] Their structures were in doubt for some years, but were finally settled by Kerber[3] and McKillop and Kobylecki.[4] Our first attempts to isolate the tautomeric structure (**3a**) were *via* derivatives of (**1**), and we also tried to cyclise *o*-nitrobenzoylhydrazine. The results from these approaches, which were all fruitless, are described at the end of the next section of this paper.



(**1**) (**2**) (**3**) (**4**)

a; R = H
b; R = Me
c; R = CH_2Ph
d; R = CH_2OMe
e; R = CH(Me)OEt
f; R = tetrahydropyran-2-yl
g; R = Ph

Results and Discussion

The usual site of *N*-oxidation of a 1,2,3-benzotriazine in which all three nitrogen atoms are two-co-ordinate is at N(2).[1] Exceptions are few, and are found mainly in the monocyclic (unfused) series. The situation can be expected to be different when one of the nitrogens is three-co-ordinate, and indeed we find that oxidation of 3-substituted 1,2,3-benzotriazin-4(3*H*)-ones (**2**) takes place at N(1), rather than N(2). We were unsuccessful in isolating any product from the unalkylated compound (**2a**) itself, but the 3-methyl derivative (**2b**), slowly, formed an oxide with *m*-chloroperoxybenzoic acid (MCPBA). The m.p. of this compound was 180 °C, and, being different from the 2-oxide (**4b**) (m.p. 145—146 °C), its identity was established as the 1-oxide (**3b**). Oxidation at N-3 is highly improbable, and is ruled out by the fact that compounds (**3d, e**), when hydrolysed, do not form (**2**; R = OH). The 3-benzyl derivative (**3c**) was prepared similarly. For oxidation of the 3-phenyl derivative (**2g**), it was necessary to use peroxytrifluoroacetic acid.

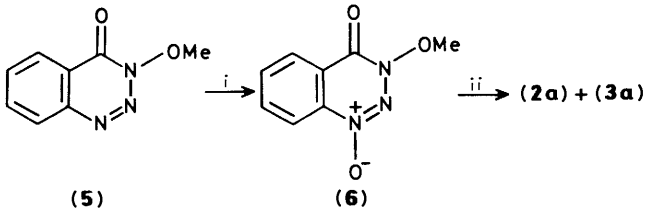
In order to obtain the tautomeric derivative (**3a**), an *N*(3)-protected derivative of (**2a**) was prepared and oxidised. The methoxymethyl compound (**2d**) was the first to be tried, but we found that this was less convenient to prepare than the ethoxyethyl compound (**2e**) or the tetrahydropyranyl derivative (**2f**), and the derivative (**2e**) also had the advantage of greater solubility in organic solvents than the methoxymethyl compound. Both of the α-alkoxyalkyl derivatives (**2d, e**) could be oxidised by MCPBA in refluxing chloroform, and from the oxides the same 1,2,3-benzotriazin-4(3*H*)-one 1-oxide (**3a**) was prepared by hydrolysis.

This last compound (**3a**) was found to be considerably weaker as an acid (pK_a 5.3) than its isomer (**4a**) (pK_a 1.64), although somewhat stronger than the unoxidised 1,2,3-benzotriazin-4(3*H*)-one (**2a**; pK_a 8.23).[1] Determination of the acidity of (**3a**) was made difficult by its slow decomposition in alkaline solution, but by rapid work the required measurements could be made.

The comparison of acidities of (**3a**) and (**4a**) illustrates the contrast in electronic effects of the two different ends of the azoxy chain. Quantitative figures (*e.g.* the various σ constants) for substituents which allow a similar comparison from other reactions are not easy to discover. Happer and Vaughan[5] reviewed the area, and suggested, with reservations, values of +0.38, +0.43, and +0.75 for σ° of the PhN=N, PhN(O)=N, and PhN=N(O) groups, respectively. These figures are at least in the right order, with respect to the acidities of (**2a**), (**3a**), and (**4a**). In their study of the methoxazonyl group, MeON=N(O), Woodward and Wintner[6] suggested that its electron-withdrawing effects were principally inductive in character; the isomeric system MeON(O)=N (*O*-methyl isonitramide) is less stable, and has not been investigated in such detail.

The action of diazomethane on the 1-oxide (**3a**) yielded only the *N*-methyl derivative (**3b**); no methoxy compound was found. The same product was obtained on methylation of the anion with methyl iodide.

3-Methoxy-1,2,3-benzotriazin-4(3*H*)-one (**5**) was also oxidised, again with difficulty, by H_2O_2/TFA. To identify the site of oxidation, the product was hydrogenolysed ($Pd/C/H_2$). Uptake of hydrogen was rapid, and although the reaction was stopped as soon as 1 equiv. of hydrogen had been absorbed, the major product isolated was the deoxygenated and demethoxylated compound (**2a**). However, some of the 1-oxide (**3a**) was identified in the solution, by t.l.c.; this was clearly differentiated from the considerably more polar 2-oxide (**4a**). The oxidation



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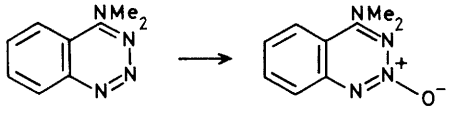
Scheme 1. *Reagents:* i, TFA/H_2O_2; ii, $H_2/Pd/C$

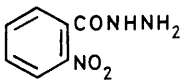


(7) (8)

product of the *N*-methoxy compound (**5**) was therefore 3-methoxy-1,2,3-benzotriazin-4(3*H*)-one 1-oxide (**6**).

We were also interested to test the generality of the statement, above, that the usual site of *N*-oxidation of 1,2,3-benzotriazines is N-2, provided that no nitrogen atom carries a substituent (*i.e.*, is three-co-ordinate). We had detected some of the 3-oxide, on oxidation of the 4-methyl compound.[1] The 4-amino compound gave no oxidation product (its 3-oxide is a known compound),[7] but the 4-dimethylamino derivative (**7**) gave a single product, which proved to be identical with the 2-oxide (**8**) we had prepared earlier.[1] It therefore seems that not even a dimethylamino group can divert oxidation from N-2 as the favoured site. Since it is well-established that 4-amino-1,2,3-benzotriazines are alkylated preferentially at N-2,[8] this result is really not surprising.

Before the successful isolation of the 1-oxide (**3a**) as described above, several fruitless approaches were tried: (1) base-catalysed cyclisation of *o*-nitrobenzoylhydrazide (**9**); (2) thermal cyclisation of (**9**); (3) hydrogenolysis of the 2-benzyl betaine (**1c**); (4) acidolysis (HBr in HOAc) of (**1c**); and (5) dealkylation of the 2-methyl and 2-benzyl betaines (**1b**, **c**). None of these reactions provided the hoped-for product. Reaction (1) gave no identified material, besides starting compound. Reaction (2) gave a small yield of a high-melting, sublimable compound, the mass spectrum of which was consistent with the bis(*o*-nitrobenzoyl)-hydrazine structure (**10**). Reactions (3) and (4) furnished white crystalline materials; these were identified as anthranilamide (**11**) from reaction (3), and 5-bromoanthranilic acid (**12**) from reaction (4). The betaines (**1**) were consumed in reaction (5) (using NaOAc in AcOH, and NaOMe), but we were not successful in isolating any well-defined product.



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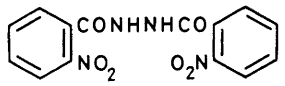

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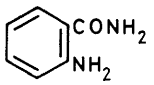

(11)

(12)

Chattaway's original preparation of the betaines (**1**; R = aryl) involved bromination of an *o*-nitrobenzaldehyde arylhydrazone, and treatment of the α-bromohydrazone with base.[2] Norman and co-workers[9] later found that the products (**1**) could be obtained in one step from the hydrazone using lead tetra-acetate. This avoided bromination of the arylhydrazine residue, which usually occurred in the Chattaway procedure. We have found that in most cases there is some advantage in convenience, and no detriment in yield, by use of phenyliodine(III) diacetate or bis(trifluoroacetate) for the oxidation, rather than the lead(IV) compound. The methylhydrazone produced only small amounts of the methyl derivative (**1**; R = Me), when the I^{III} reagents were used; in this case the Pb^{IV} reagent was satisfactory, as McKillop and Kobylecki have also found.[4]

Experimental

Spectral instrumentation and sample handling was as earlier described.[10] I.r. spectra are of samples in bromoform mull. N.m.r. coupling constants were within the expected ranges, and are not listed here. Nitrogen chemical shifts are quoted relative to [$^2H_3$]nitromethane ($\delta = 0$). Mass spectral peaks are listed when of intensity >40% of the base peak and $m/z > 70$, weaker or lighter peaks only when of significance to the structure.

The pK_a determinations were made by the spectrophotometric method in the usual way,[11] using M/100 buffer solution in water containing 5% ethanol.

All descriptions of dissymmetric compounds refer to racemic materials. Light petroleum refers to the fraction b.p. 60—80 °C. The following compounds were prepared by the published procedures indicated: the 2-methyl betaine (**1b**);[4] 1,2,3-benzotriazin-4(3*H*)-one (**2a**)[12] and its 3-methyl (**2b**),[13] 3-benzyl (**2c**)[14] and 3-phenyl (**2g**)[15] derivatives; 1,2,3-benzotriazine-4(3*H*)-thione;[16,17] 4-amino-1,2,3-benzotriazine;[18] iodosobenzene diacetate[19] and bis(trifluoroacetate).[20] 3-Hydroxy-1,2,3-benzotriazin-4(3*H*)-one (Fluka) and *m*-chloroperoxybenzoic acid (MCPBA) (Aldrich) were commercial products.

3-*Methoxymethyl*-1,2,3-*benzotriazin*-4(3H)-*one* (**2d**).—1,2,3-Benzotriazinone (**2a**) (6.0 g) was suspended in dimethoxymethane (200 ml), and hydrogen chloride was slowly passed in, with stirring and cooling to 10 °C. The solid dissolved, and the solution was allowed to stand for 36 h. Excess of dimethoxymethane was removed by distillation, and ice and saturated aqueous $NaHCO_3$ (50 ml) were added. The pH was adjusted to 10 with 1M NaOH and the solution was extracted with dichloromethane (3 × 50 ml). The combined extracts were dried ($MgSO_4$) and evaporated to dryness. The residue was recrystallised from light petroleum–ethyl acetate, giving the *methoxymethyl product* (4.9 g, 63%), m.p. 96—97.5 °C (Found: C, 56.5; H, 4.6; N, 22.0. $C_9H_9N_3O_2$ requires C, 56.5; H, 4.7; N, 22.0%).

3-(1-*Ethoxyethyl*)-1,2,3-*benzotriazin*-4(3H)-*one* (**2e**).—Benzotriazinone (**2a**) (4.05 g) was suspended in dry toluene (80 ml) containing ethyl vinyl ether (5 ml) and toluene-*p*-sulphonic acid (30 mg), and the mixture was stirred for 3 h at 20 °C. (With too much acid, extended reaction times, or heating, or even simply on three-fold scaling-up of quantities, the reaction mixture became brown, and yields were reduced. Completion of the reaction was indicated by dissolution of the starting material, and work-up should follow shortly thereafter.) The clear solution was washed with 0.5M aqueous NaOH (10 ml) and water and then dried (Na_2SO_4). The solvent and excess of ether were evaporated under reduced pressure and the residue was recrystallised from CCl_4–light petroleum to give needles (5.02 g, 85%) of the *ethoxyethyl derivative*, m.p. 68—69 °C; $\nu_{max.}$ 1 680 cm^{-1}; δ_H 1.21 (3 H, t) and 3.42—3.74 (2 H, m) (ABX_3 of OEt), 1.83 (3 H, d) and 6.57 (1 H, q) (CH_3CH), and 7.81 (dt), 7.98 (dt), 8.20 (dd), 8.37 (dd) (4 ArH); δ_N 26.6 (N-2), −14.3, (N-1), and −140.6 p.p.m. (N-3). The signal at 26.6 p.p.m. was

intensified in the spectrum of a sample prepared from benzotriazinone ^{15}N-enriched at N-2.[10] (Found: C, 60.3; H, 5.65; N, 19.1. $C_{11}H_{13}N_3O_2$ requires C, 60.3; H, 6.0; N, 19.2%).

3-*Tetrahydropyran*-2-*yl*-1,2,3-*benzotriazin*-4(3H)-*one* (**2f**).—Benzotriazinone (**2a**) (1.0 g) was dissolved in the minimum quantity of dichloromethane at 20 °C, and 3,4-dihydro-2*H*-pyran (1.8 ml) and toluene-*p*-sulphonic acid (20 mg) were added. The solution was stirred at 20 °C for 4 h and then washed with 0.5M aqueous NaOH (15 ml) and water and dried (Na_2SO_4). Removal of solvent under reduced pressure left a residue which was cooled and triturated with light petroleum, giving the *tetrahydropyran* (**2e**), which crystallised from light petroleum as plates, m.p. 112—114 °C; $\nu_{max.}$(C=O) 1 690 cm^{-1} (Found: C, 62.1; H, 5.7; N, 18.1. $C_{12}H_{13}N_3O_2$ requires C, 62.3; H, 5.7; N, 18.2%).

Oxidation with MCPBA: formation of 1-*Oxides* (**3b—f**).—The 3-substituted benzotriazinones (**2b—g**) (10—20 mmol) were refluxed with a 5—6-fold excess of MCPBA in dry chloroform for 24 h, or in dry dichloromethane for 3 days. After cooling, *m*-chlorobenzoic acid was filtered off and washed with chloroform. The combined organic solvents were washed with dilute (*ca.* 0.1M) aqueous NaOH and then dried ($MgSO_4$). After solvent removal under reduced pressure and recrystallisation of the residue the product was normally obtained without the need for chromatography. If t.l.c. indicated appreciable contamination with starting material or other impurity [di-*m*-chlorobenzoyl peroxide was isolated on one occasion; $\nu_{max.}$(C=O) 1 790m and 1 765s cm^{-1}], separation was effected on a silica-gel column, eluting with CH_2Cl_2, then with CH_2Cl_2–acetone (10:1). The following 1-oxides were obtained.

3-*Methyl* (**3b**): needles (EtOAc), 62%, m.p. 181—182 °C; $\nu_{max.}$(C=O) 1 725w and 1 680 cm^{-1}; $\lambda_{max.}$(EtOH) 328 (log ε 3.64), 265 (3.63), and 220 (4.31); *m/z* 177 (30, M^+), 134 (70), and 104 (100) (Found: C, 54.1; H, 3.7; N, 23.4. $C_8H_7N_3O_2$ requires C, 54.2; H, 3.5; N, 23.7%).

3-*Benzyl* (**3c**): prisms (EtOAc), 64%, m.p. 143—144.5 °C; ν(C=O) 1 680 cm^{-1}; $\lambda_{max.}$(EtOH) 332 (log ε 3.87), 265 (3.94), 260sh, and 224 (4.37); *m/z* 253 (20, M^+), 209 (40), 180 (20), 134 (30), 109 (60), and 91 (100%) (Found: C, 66.5; H, 4.4; N, 16.7. $C_{14}H_{11}N_3O_2$ requires C, 66.4; H, 4.4; N, 16.6%).

3-*Methoxymethyl* (**3d**): needles (EtOAc), 52%, m.p. 121—123 °C; $\nu_{max.}$(C=O) 1 690 cm^{-1}; *m/z* 207 (M^+, 1%) (Found: C, 52.1; H, 4.3; N, 20.15. $C_9H_9N_3O_3$ requires C, 52.2; H, 4.4; N, 20.3%). An attempt to prepare this compound (**3d**) using H_2O_2/trifluoroacetic acid gave instead the deprotected material (**2a**).

3-(1-*Ethoxy*)*ethyl* (**3e**): needles (CCl_4–light petroleum), m.p. 142—144 °C; δ 1.21 (3 H, t) and 3.59 (2 H, br d q) ($AA'X_3$ of OEt), 1.70 (3 H, d) and 6.39 (1 H, q) (CH_3CH), and 7.86—8.12 (2 H, m) and 8.35—8.86 (2 H, m) (4 ArH) (Found: C, 56.0; H, 5.3; N, 17.7. $C_{11}H_{13}N_3O_3$ requires C, 56.2; H, 5.3; N, 17.7%).

3-*Phenyl* (**3g**). MCPBA proved ineffective for oxidation of (**2g**). Trifluoroacetic acid (10 ml) was added with stirring and cooling to aqueous hydrogen peroxide (60% w/v; 3.3 ml). The 3-phenyl compound (**2g**) (0.5 g) was added, with stirring, and the solution was allowed to stand at 20 °C for 2 days. Addition of 4% aqueous Na_2CO_3 to neutralise the acid produced a yellowish precipitate, which was extracted with CH_2Cl_2 (2 × 25 ml). The combined extracts were washed with water, dried, and evaporated under reduced pressure, and the residue was crystallised from ethanol to give needles (0.32 g, 60%), m.p. 213—214 °C; $\nu_{max.}$(C=O) 1 690 cm^{-1}; *m/z* 239 (M^+, 12%), 223 (3), 195 (12), 167 (20), 134 (40), 104 (60), 77 (100), and 76 (45) (Found: C, 65.1; H, 3.8; N, 17.6. $C_{13}H_9N_3O_2$ requires C, 65.3; H, 3.8; N, 17.6%).

3-*Methoxy*-1,2,3-*benzotriazin*-4(3H)-*one* 1-*Oxide* (**6**).—3-Methoxy-1,2,3-benzotriazin-4(3*H*)-one (**5**), m.p. 149—150 °C (lit.,[21] m.p. 134—135 °C), was prepared by methylation (CH_2N_2) of the 3-hydroxy compound, in Et_2O (87% yield). It was identical (i.r., m.p.) with a sample prepared according to Ahern *et al.*,[21] despite the discrepancy in m.p. with the published value. No other methylated derivative was detected (n.m.r.) in the product; $\nu_{max.}$(C=O) 1 700 cm^{-1}; *m/z* 177 (M^+, 10%), 149 (1), 134 (25), 118 (25), 106 (30), 104 (50), 91 (80), 90 (75), and 78 (100%); δ_H 4.22 (3 H, s, OMe) and 7.965 (t), 8.13 (t), 8.24 (d), and 8.28 (d) (each 1 H) (Found: C, 54.5; H, 3.9; N, 23.6. Calc. for $C_8H_7N_3O_2$: C, 54.2; H, 4.0; N, 23.7%).

Trifluoroacetic acid (22 ml) was added with stirring and cooling to aqueous hydrogen peroxide (60% w/v; 6.3 ml). The methoxybenzotriazinone (**5**) (1.6 g) was added, and the mixture was allowed to stand at 20 °C for 18 h, after which time it was heated to 60 °C for 4 h. (After this time, although starting-material was still present, work-up began, since the product appeared to decompose to some extent.) Ice (100 g) and water (100 ml) were added, and the mixture was neutralised to pH 8 with aqueous Na_2CO_3 and then extracted with CH_2Cl_2 (4 × 25 ml). The combined extracts were dried and evaporated and the residue was crystallised from ethanol, giving the 3-*methoxy* 1-*oxide* (**6**) as needles, m.p. 186—187.5 °C (1.1 g, 62%); $\nu_{max.}$(C=O) 1 705 cm^{-1}; $\lambda_{max.}$(EtOH) 325 ($\log_{10}$ ε 3.47), 264 (3.57), 258sh, and 220 (4.0); δ_H 4.10 (3 H, s, OMe) and 8.06 (t), 8.14 (t), 8.305 (d), and 8.335 (d) (each 1 H) (Found: C, 49.75; H, 3.45; N, 21.8. $C_8H_7N_3O_3$ requires C, 49.75; H, 3.65; N, 21.75%).

The methoxy oxide (**6**) (0.050 g, 0.26 mmol) in ethanol (10 ml) was shaken with Pd/C (5%, 50 mg) under H_2 in a gas burette at 1 atm. Absorption of gas was rapid; shaking was stopped after 24 ml (1 mmol) had been taken up (*ca.* 1 min), and the hydrogen was removed. The catalyst was filtered off, and the solvent was evaporated, leaving a solid residue which contained two major fractions (t.l.c. silica gel, eluant CH_2Cl_2–acetone, 7:1). The major component, R_F 0.4, was isolated, and found to be identical with the benzotriazinone (**2a**); the minor, R_F 0.2, ran alongside a sample of the 1-oxide (**3a**), and was clearly different from the 2-oxide (**4a**)[1] (R_F *ca.* 0.05).

1,2,3-*Benzotriazin*-4(3H)-*one* 1-*Oxide* (**3a**).—(*a*) The 3-methoxymethyl derivative (**3d**) (2.5 g) was dissolved in methanol (200 ml) and water (15 ml) and hydrogen chloride was passed into the solution until it was saturated. The mixture was then left for 30 h at 20 °C, after which the methanol was removed at the same temperature, leaving an aqueous suspension of the product. This was filtered off and recrystallised from ethanol to give micro-plates or -prisms of the N-*oxide* (1.30 g, 66%), m.p. 153—155 °C (decomp.).

(*b*) The ethoxyethyl derivative (**3e**) (0.5 g) was allowed to stand for 2 days in methanol (50 ml) containing conc. aqueous HCl (2 ml). The solvents were evaporated to leave a residue of the product (**3a**) (0.30 g, 85%), identical with that obtained above. $\nu_{max.}$ 3 300—2 600vb (NH) and 1 690 (C=O) cm^{-1}; $\lambda_{max.}$(EtOH + 1 drop H_2SO_4) 320 (log ε 3.49), 262 (3.54), and 220 (4.3); $\lambda_{max.}$(aqueous phosphate buffer, pH 8.5) 350 (3.63), 270 (3.50), and 220 (4.0); pK_a 5.3; *m/z* 163 (M^+, 23%), 134 (70), and 104 (100) (Found: C, 51.3; H, 3.0; N, 25.4. $C_7H_5N_3O_2$ requires C, 51.5; H, 3.1; N, 25.7%).

When treated at 0 °C with ethereal diazomethane, the oxide (**3a**) gave the 3-methyl derivative (**3b**) (74% yield), as the only product isolated.

N-*Oxidation of* 4-*Dimethylamino*-1,2,3-*benzotriazine* (**7**).—1,2,3-Benzotriazine-4(3*H*)-thione[17] was converted into the 4-methylthio compound in good yield by alkylation (MeI), as described by earlier workers,[16,22] with the precaution that excess of methoxide, and consequent formation of the 4-

methoxy compound,[10] was avoided. 4-Methylthio-1,2,3-benzotriazine (1.6 g) in methanol (20 ml) was kept for 5 days with dimethylamine (40% in H_2O; 2.5 ml). Evaporation of volatile materials left the *dimethylamino derivative* (**7**) which was recrystallised from CH_2Cl_2–light petroleum as plates (0.8 g, 50%), m.p. 113—114 °C; δ_H 3.46 (6 H, s) and 7.6—8.3 (4 H, m) (Found: C, 62.1; H, 6.0; N, 32.4. $C_9H_{10}N_4$ requires C, 62.1; H, 5.7; N, 32.2%).

The dimethylaminobenzotriazine (0.2 g) was heated to reflux in dry chloroform (15 ml) with MCPBA (0.6 g) for 6 h and then left for 3 days. Acid residues were removed from the mixture which was then dried and evaporated to leave a yellowish residue which was recrystallised from CH_2Cl_2–toluene. The product (0.18 g, 80%), m.p. 186—188 °C, was identical (i.r., m.s.) with the 4-dimethylamino 2-oxide (**8**) reported earlier.[1] *m/z* 190 (M^+, 100%) and 160 ($M - 30$, 12); $M - 28 < 1\%$. Loss of NO is characteristic of benzotriazine 2-oxides; the 3-oxides lose N_2.[1]

An attempt to oxidise 4-amino-1,2,3-benzotriazine under similar conditions led only to tarry material; no crystalline product, other than starting material, was isolated.

Attempted Cyclisation of 2-Nitrobenzohydrazide (**9**).—2-Nitrobenzohydrazide[23] (1.0 g) was heated 2.5 h to reflux in *o*-dichlorobenzene (20 ml). On cooling of the mixture, a small amount of solid crystallised out, and more could be obtained, along with unchanged starting-material, by evaporation of the solvent under reduced pressure. Recrystallisation of the residue from ethanol gave very pale yellow crystals, m.p. 300 °C, which were tentatively identified as the diacylhydrazine (**10**) (lit.,[24] m.p. 298 °C) (Found: N, 16.7. Calc. for $C_{14}H_{10}N_4O_6$: N, 17.0%).

Preparation of the Benzotriazinium Betaines (**1c**) *and* (**1g**).—*o*-Nitrobenzaldehyde benzylhydrazone (0.8 g) stirred for 4 h in dry CH_2Cl_2 (30 ml) with iodosobenzene diacetate (1.0 g). The solution was washed with water, aqueous $NaHCO_3$, and again water, and then dried ($MgSO_4$). Removal of solvent under reduced pressure left a yellow-green residue of the *betaine* (**1c**), which was recrystallised from benzene–light petroleum to give needles (0.62 g, 82%), m.p. 161—163 °C (softening, with some decomposition, *ca.* 155 °C); $\nu_{max.}$(C=O) 1 635 cm^{-1}; δ_H 5.85 (2 H, s) and 7.2—8.5 (9 H, m); *m/z* 253 (M^+, 3%), 134 (45), 104 (60), 91 (100), and 76 (45) (Found: C, 66.7; H, 4.4; N, 16.7. $C_{14}H_{11}N_3O_2$ requires C, 66.4; H, 4.35; N, 16.6%)

Use of iodosobenzene bis(trifluoroacetate) (1.34 g) in place of the diacetate gave the same product (0.48 g, 60%).

o-Nitrobenzaldehyde phenylhydrazone (5.6 g) suspended in dry CH_2Cl_2 (100 ml) was oxidised with iodosobenzene diacetate (7.5 g), as above, yielding the phenyl betaine (**1g**) (4.25 g, 75%), m.p. 147—149 °C (lit.,[4] m.p. 147—149 °C). The betaine (0.7 g, 35%) was also obtained, in rather poorer yield, from the phenylhydrazone (2.0 g) using the bistrifluoroacetate (3.6 g) for oxidation.

o-Nitrobenzaldehyde methylhydrazone was not oxidised satisfactorily with either reagent, under the above conditions. In this case lead tetra-acetate was effective.[4]

Attempted Debenzylation of 2-Benzyl-4-oxo-1,2,3-benzotriazin-2-ium-1-olate (**1c**).—(a) The betaine (**1c**) (1 g) was shaken in ethanol with Pd/C (5%; 0.2 g) under hydrogen. The yellow colour was rapidly discharged. The catalyst was filtered off and the filtrate evaporated to leave a residue which proved to be anthranilamide (**11**), by comparison with an authentic sample.

(b) The betaine (**1c**) (1 g) was dissolved in acetic acid containing HBr (25%). The yellow colour faded, and on addition of water a white solid, m.p. 216—218 °C, separated, which according to the mass spectrum contained one atom of bromine. Comparison (i.r., m.p.) with an authentic sample, prepared by bromination of anthranilic acid, proved its identity with 5-bromoanthranilic acid (**12**).

Attempts to dealkylate the betaine (**1c**) with sodium hydroxide in methanol, and with sodium acetate in acetic acid, and the betaine (**1b**) similarly, were also unsuccessful in providing (**3a**), but the products were not identified, in any case.

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