Condensed 1,2,4-Triazines: Synthesis of 5-Benzyl-5*H*-imidazo[4,5-*e*]-1,2,4-triazine 1-Oxides (9-Benzyl-6-azapurine 6-Oxides)

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A number of 5-benzyl-5*H*-imidazo[4,5-*e*]-1,2,4-triazine 1-oxides, bioisosteric isomers of antiviral 9-benzylpurines, have been prepared. Oxidation of 6-amino-5-benzylamino-3-methylsulfanyl-1,2,4-triazine **1** with excess of *m*-chloroperbenzoic acid afforded 6-amino-5-benzylamino-3-methylsulfonyl-1,2,4-triazine 1-oxide **2** in 75% yield. The 3-methylsulfonyl group, which is a good leaving group, has been replaced with various nucleophiles to give 3-amino **4**, 3-methoxy **5** and 3-hydrazino **8** derivatives. Oxidative dehydrazination of **8** with mercury(II) oxide (HgO) in ethanol gave 6-amino-5-benzylamino-1,2,4-triazine 1-oxide **9** in a moderate yield. The 1,2,4-triazine 1-oxides were then cyclized with triethyl orthoformate (TEOF) to afford the title compounds in 28–88% yields.

A number of 9-benzylpurines have been synthesized and tested for antirhinovirus activity.[1-3] One of the most active compounds against rhinovirus serotype 1B was 6-dimethylamino-2-trifluoromethyl-9-benzylpurine which had an IC_{50} value of 0.04 μmol dm^{-3}.[4] Structure–activity studies reveal that optimum activity against serotype 1B is associated with a lipophilic, electron-withdrawing group at the 2-position,[5] but none of these analogues has a uniform profile of potent antirhinovirus serotype activity. To study the effect of structural modification at the 6-position with respect to optimal antirhinovirus activity, a series of 6-substituted derivatives were prepared and evaluated for their potency. Among them, the 6-dimethylamino and 6-anilino derivatives proved to be two of the best.[6,7] To establish further the structure–activity relationship, we initiated the present research programme involving the synthesis of a novel series of 9-benzylpurine analogues with an *N*-oxide substituted at the 6-position. The bioisosteric replacement of an enolizable carbonyl or amino group with an *N*-oxide group leading to the discovery of potential therapeutical agents has been previously described.[8-11]

Results and Discussion

Oxidation of 6-amino-5-benzylamino-3-methylsulfanyl-1,2,4-triazine **1**[12] with 4.4 mol equiv. of *m*-chloroperbenzoic acid (MCPBA) gave the *N*-oxide product whose structure is tentatively assigned as 6-amino-5-benzylamino-3-methylsulfonyl-1,2,4-triazine 1-oxide **2** from the ^{13}C NMR spectra, elemental analyses, and mass spectrum (in addition to the molecular ion peak at *m*/*z* 295, a peak of M − 16 was also detected). Several papers[13-16] have dealt with the *N*-oxidation of 1,2,4-triazines with the conclusion that the oxidation of 3-amino and 3-substituted amino 1,2,4-triazines affords the 2-oxides as the major products while oxidation at N-1 occurs when C-3 is either unsubstituted or is substituted by a methoxy or phenoxy group. However, the reaction of **1** with MCPBA is more complicated, as it involves not only the *N*-oxidation but also an *in situ* *S*-oxidation. From the spectral data it appears that *N*-oxidation is likely to occur at N-1. However, we were reluctant to make this critical structural assignment founded only on this evidence and therefore we sought a more definitive answer; an X-ray crystallographic analysis of 5-benzyl-3-methylsulfonyl-5*H*-imidazo[4,5-*e*]-1,2,4-triazine 1-oxide **3** which was prepared by the ring closure of compound **2** with triethyl orthoformate (TEOF).[17-19] A view of a single molecule of **3** is given in Fig. 1. As can be seen from the figure, the oxidation occurs at N-1. Selected bond lengths and bond angles are presented in Tables 1 and 2, respectively. Treatment of compound **2** or **3** with liquid ammonia gave 3,6-diamino-5-benzylamino-1,2,4-triazine 1-oxide **4** in 80% yield. When the reaction was carried out under the same conditions except that methanolic ammonia (saturated at 5 °C) was used instead of liquid ammonia, the desired compound **4** was not obtained. The ^1H NMR spectrum of the sole product isolated showed a sharp singlet at δ 3.73, ascribable to 3-OMe, along with absorptions at δ 4.62, 6.15 and 8.14 corresponding to $ArCH_2$, 6-NH_2, and 5-NH, respectively. The ^{13}C NMR spectrum supported the ^1H NMR spectrum in confirming the presence of one methoxy carbon, resonance appeared at δ 54.43, and three heteroaromatic carbons, resonances at δ 127.50, 150.60 and 158.06, respectively. The elemental analysis was in accord with the molecular formula $C_{11}H_{13}N_5O_2$ which, taken together with spectral evidence, suggests a structure of 6-amino-5-benzylamino-3-methoxy-1,2,4-triazine 1-oxide **5**. Ring closure of

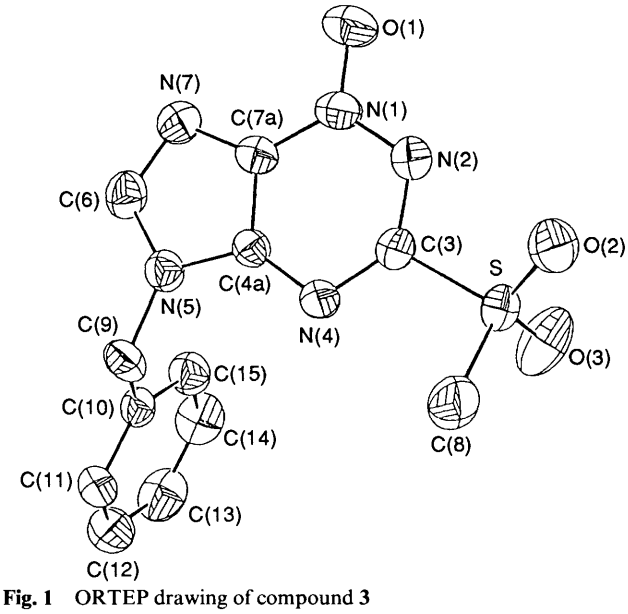


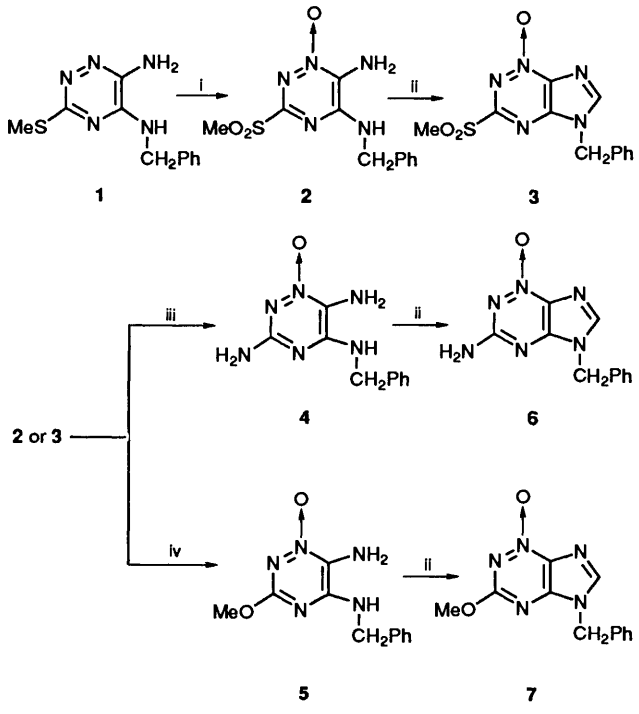
Fig. 1 ORTEP drawing of compound **3**

Table 1 Selected bond lengths (Å) of compound **3**

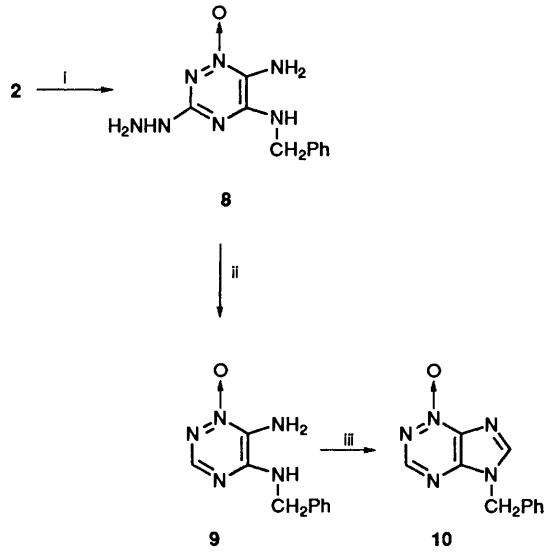
Atoms	Distance
O(1)–N(1)	1.247(3)
N(1)–N(2)	1.355(4)
N(1)–C(7a)	1.357(4)
N(2)–C(3)	1.334(4)
S–C(3)	1.802(3)
N(4)–C(3)	1.319(4)
N(4)–C(4a)	1.324(4)
N(5)–C(4a)	1.362(4)
N(5)–C(6)	1.377(4)
N(5)–C(9)	1.463(4)
N(7)–C(6)	1.316(4)
N(7)–C(7a)	1.359(4)
C(4a)–C(7a)	1.395(4)

Table 2 Selected bond angles (°) of compound **3**

O(1)–N(1)–N(2)	118.2(3)
O(1)–N(1)–C(7a)	122.7(3)
N(2)–N(1)–C(7a)	119.1(3)
N(1)–N(2)–C(3)	115.8(3)
C(3)–N(4)–C(4a)	109.4(3)
C(4a)–N(5)–C(6)	106.1(3)
C(4a)–N(5)–C(9)	125.4(3)
C(6)–N(5)–C(9)	128.4(3)
C(6)–N(7)–C(7a)	102.4(3)
S–C(3)–N(2)	112.24(23)
S–C(3)–N(4)	116.10(23)
N(2)–C(3)–N(4)	131.7(3)
N(4)–C(4a)–N(5)	129.3(3)
N(4)–C(4a)–C(7a)	126.6(3)
N(5)–C(4a)–C(7a)	104.1(3)
N(5)–C(6)–N(7)	114.3(3)
N(1)–C(7a)–N(7)	129.5(3)
N(1)–C(7a)–C(4a)	117.3(3)
N(7)–C(7a)–C(4a)	113.2(3)
N(5)–C(9)–C(10)	113.3(3)



Scheme 1 *Reagents:* i, MCPBA; ii, $CH(OEt)_3$; iii, NH_3; iv, NH_3–MeOH



Scheme 2 *Reagents:* i, NH_2NH_2; ii, HgO; iii, $CH(OEt)_3$

compound **5** with triethyl orthoformate (TEOF) under acidic conditions afforded 5-benzyl-3-methoxy-5*H*-imidazo[4,5-*e*]-1,2,4-triazine 1-oxide **7** in 88% yield. Ring closure of compound **4** with TEOF under acidic conditions was not successful due to the poor solubility of **4** in TEOF. To circumvent this situation, a mixed solvent of equal volumes of TEOF and dimethylformamide (DMF) was used instead of neat TEOF. The cyclization product thus obtained was a mixture of 3-amino-5-benzyl-5*H*-imidazo[4,5-*e*]-1,2,4-triazine 1-oxide **6** and its 3-formamido derivative which were very difficult to separate and purify. Therefore, the initial product was treated with methanolic ammonia to furnish pure compound **6** in 45% yield (Scheme 1).

According to Lee and Paudler,[20] a hydrazino group substituted on the C-3 of a 1,2,4-triazine can be eliminated by oxidation. A similar reaction of compound **2** with hydrazine in ethanol gave 6-amino-5-benzylamino-3-hydrazino-1,2,4-triazine 1-oxide **8** which was oxidized with mercury(II) oxide in ethanol to give 6-amino-5-benzylamino-1,2,4-triazine 1-oxide **9**. Ring closure of **9** with TEOF afforded 5-benzyl-5*H*-imidazo-[4,5-*e*]-1,2,4-triazine 1-oxide **10** in 65% yield (Scheme 2).

Experimental

M.p.s were determined with a Thomas-Hoover apparatus and are uncorrected. The UV spectra were determined in 0.1 mol dm^{-3} HCl (pH 1), methanol and 0.1 mol dm^{-3} NaOH (pH 13) with a Hitachi U-2000 spectrophotometer. NMR (^1H and ^{13}C) spectra were recorded on a Varian VSR-300S spectrometer. Samples were dissolved in [$^2H_6$]dimethyl sulfoxide, and the chemical shifts are expressed in ppm with respect to tetramethylsilane (TMS) as an internal standard. *J*-Values are given in Hz. The progress of the reactions was followed by thin-layer chromatography (TLC) on silica gel 60 F-254 plates purchased from E. Merck. Mass spectra were determined with a Quattro VG-5022 mass spectrometer in the electron-impact (EI) mode.

Crystal Data.—$C_{12}H_{11}N_5O_3S$, M = 305.25, monoclinic, a = 6.794(2), b = 14.834(2), c = 13.759(2) Å, β = 104.04(2)°, V = 1345.2(5) Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, λ = 0.710 69 Å), space group $P2_1/n$, Z = 4, D_c = 1.508 g cm^{-3}, crystal dimensions (distance to faces from centre) 0.20 × 0.25 × 0.35 mm, μ(Mo-Kα) = 2.3 cm^{-1}.

Data collection and processing. CAD4 diffractometer, ω–

2θ mode with 2θ scan width = 1.4 + 0.7 tan θ, 2θ scan speed 2.0–8.24 deg min^{-1}, graphite-monochromated Mo-Kα radiation; 2412 reflections measured ($1.5 \leqslant \theta \leqslant 25°$, $\pm h, k, l$), 2352 unique, giving 1524 with $I > 2\sigma(I)$.

Structure analysis and refinement. Direct methods were used followed by the full matrix least-squares refinements with all non-hydrogen atoms anisotropic and hydrogens in calculated positions. The weighting scheme $w = 1/\sigma^2(F_o)$ with $\sigma^2(F_o)$ from counting statistics gave satisfactory agreement analyses. Final R and R_w values are 0.041, 0.030. Programs used NRCVAX[21] on microvax computer.

Atomic coordinates bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.*

6-*Amino*-5-*benzylamino*-3-*methylsulfonyl*-1,2,4-*triazine* 1-*Oxide* **2**.—To a solution of *m*-chloroperbenzoic acid (900 mg, 4.4 mmol) dissolved in chloroform (20 cm^3) was added compound **1**[12] (247 mg, 1.0 mmol) in chloroform (20 cm^3). The reaction mixture was stirred at room temperature for 2 h during which time the solution turned red. The solid thus formed was collected and crystallized from ethanol to give the title compound **2** (225 mg, 75%), m.p. 211–213 °C; λ_{max}/nm (pH 1) 326 (ε/dm^3 mol^{-1} cm^{-1} 15 300) and 237 (19 700); (methanol) 326 (19 000) and 236 (23 000); (pH 13) 309 (12 000) and 236sh (18 000); δ_H[$(CD_3)_2SO$] 3.24 (s, 3 H, CH_3), 4.71 (d, 2 H, CH_2), 7.34–7.43 (m, 5 H, ArH), 7.24 (s 2 H, NH_2) and 8.48 (br t, 1 H, NH); δ_C[$(CD_3)_2SO$] 39.29 (SO_2CH_3), 44.93 (CH_2), 127.66, 128.21, 128.70, 137.63 (ArCs), 132.63 (C-6), 148.51 (C-5) and 153.83 (C-3); *m*/*z* 295 (M^+, 0.28%), 279 (5.0), 278 (5.3), 200 (2.5) and 91 (100) (Found: C, 44.55; H, 4.2; N, 23.8. $C_{11}H_{13}N_5O_3S$ requires C, 44.71; H, 4.44; N, 23.73%).

5-*Benzyl*-3-*methylsulfonyl*-5H-*imidazo*[4,5-e]-1,2,4-*triazine* 1-*Oxide* **3**.—To a well stirred suspension of compound **2** (295 mg, 1.0 mmol) in triethyl orthoformate (25 cm^3) was added concentrated hydrochloric acid (0.3 cm^3). The reaction mixture was then heated at reflux for 1 h. After this period, the solution was allowed to stand at room temperature for 16 h. The solid was removed by filtration and the filtrate was evaporated to 20 cm^3, allowed to cool and then kept at 4 °C for 16 h, the solid thus formed was collected and crystallized from chloroform to give the title compound **3** (86 mg, 28%) as needles, m.p. 216–218 °C; λ_{max}/nm (pH 1) 310 (ε/dm^3 mol^{-1} cm^{-1} 11 500) and 237 (15 800); (methanol) 310 (12 500) and 237 (19 600); (pH 13) 326 (10 900); δ_H[$(CD_3)_2SO$] 3.45 (s, 3 H, SO_2CH_3), 5.57 (s, 2 H, CH_2), 7.39–7.41 (m, 5 H, ArH) and 9.04 (s, 1 H, 6-H); δ_C[$(CD_3)_2SO$] 40.49 (SO_2CH_3), 47.87 (CH_2), 128.10, 128.48, 128.98, 135.15 (ArCs), 138.29 (C-7a), 148.73 (C-4a), 149.22 (C-6) and 159.75 (C-2); *m*/*z* 305 (M^+, 16%), 289 (5.6), 288 (4.3), 226 (6.6), 210 (15.6) and 91 (100) (Found: C, 47.1; H, 3.6; N, 22.85. $C_{12}H_{11}N_5O_3S$ requires C, 47.20; H, 3.63; N, 22.94%).

3,6-*Diamino*-5-*benzylamino*-1,2,4-*triazine* 1-*Oxide* **4**.—A mixture of compound **2** (2.95 g, 10 mmol) and liquid ammonia (25 cm^3) was heated in a stainless steel vessel at 80 °C for 2 days. The reaction mixture was allowed to cool to room temperature and then the excess ammonia was vented off, and the residual solid was suspended in water (2 × 10 cm^3). The green precipitate was collected and crystallized from ethanol to give the title compound **4** (1.85 g, 80%), m.p. 230–232 °C (decomp.); λ_{max}/nm (pH 1) 332 (ε/dm^3 mol^{-1} cm^{-1} 8300) and 236 (18 400); (methanol) 336 (8700) and 236 (21 000); (pH 13) 330 (9000) and 233 (20 300); δ_H[$(CD_3)_2SO$] 4.60 (s, 2 H, CH_2), 5.69 (s, 2 H, 3-NH_2), 5.85 (s, 2 H, 6-NH_2), 7.34 (s, 5 H, ArH) and 7.68 (br s, 1 H, NH); δ_C[$(CD_3)_2SO$] 43.99 (CH_2), 125.07 (C-6), 127.27, 127.78, 128.59, 138.78 (ArCs), 150.50 (C-5) and 156.44 (C-3); *m*/*z* 232 (M^+, 4.5%), 216 (10.8), 215 (25.3) and 91 (100) (Found: C, 51.4; H, 5.2; N, 36.1. $C_{10}H_{12}N_6O$ requires C, 51.71; H, 5.21; N, 36.19%).

6-*Amino*-5-*benzylamino*-3-*methoxy*-1,2,4-*triazine* 1-*Oxide* **5**.—A mixture of compound **2** (295 mg, 1.0 mmol) and methanolic ammonia (30 cm^3, previously saturated at 5 °C) was heated in a steel bomb at 80 °C for 24 h. The reaction mixture was concentrated to 10 cm^3, and the white precipitate was collected and crystallized from methanol to give the title compound **5** (155 mg, 63%), m.p. 208–210 °C; λ_{max}/nm (pH 1) 328 (ε/dm^3 mol^{-1} cm^{-1} 13 400) and 225 (21 000); (methanol) 327 (14 100) and 226 (23 600); (pH 13) 326 (9700); δ_H-[$(CD_3)_2SO$] 3.73 (s, 3 H, OCH_3), 4.62 (d, *J* 5, 2 H, CH_2), 6.15 (s, 2 H, NH_2), 7.28–7.35 (m, 5 H, ArH) and 8.14 (t, *J* 5, 1 H, NH); δ_C[$(CD_3)_2SO$] 44.38 (CH_2), 54.43 (OCH_3), 127.40, 127.81, 128.62, 138.25 (ArCs), 127.50 (C-6), 150.60 (C-5) and 158.06 (C-3); *m*/*z* 247 (M^+, 6.8%), 231 (5.1), 230 (33.6) and 91 (100) (Found: C. 53.4; H, 5.15; N, 28.5. $C_{11}H_{13}N_5O_2$ requires C, 53.43; H, 5.30; N, 28.33%).

3-*Amino*-5-*benzyl*-5H-*imidazo*[4,5-e]-1,2,4-*triazine* 1-*Oxide* **6**.—To a well stirred suspension of compound **4** (232 mg, 1.0 mmol) in triethyl orthoformate (15 cm^3) and dimethylformamide (3 cm^3) was added concentrated hydrochloric acid (0.3 cm^3). The mixture was then heated at reflux (oil bath) for 2 h. The hot filtrate was evaporated under reduced pressure to give a brown syrup to which was added methanolic ammonia (25 cm^3) and then the mixture was stirred at room temperature for 16 h. The excess solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel with chloroform–methanol (20:1) as eluent. The homogeneous fractions were pooled and evaporated. The residue was crystallized from ethanol to afford the title compound **6** (135 mg, 45%), m.p. 262–264 °C; λ_{max}/nm (pH 1) 362 (ε/dm^3 mol^{-1} cm^{-1} 7100), 258 (8900) and 233 (24 000); (methanol) 363 (7600), 258 (9600) and 234 (25 200); (pH 13) 347 (5400) and 233 (17 900); δ_H[$(CD_3)_2SO$] 5.30 (s, 2 H, CH_2), 7.11 (s, 2 H, 3-NH_2), 7.31–7.37 (m, 5 H, ArH) and 8.34 (s, 1 H, 6-H); δ_C[$(CD_3)_2SO$] 46.74 (CH_2), 127.43, 128.08, 128.94, 136.09 (ArCs), 131.40 (C-7a), 143.36 (C-6), 150.42 (C-4a) and 161.63 (C-2); *m*/*z* 242 (M^+, 26.8%), 225 (9.0) and 91 (100) (Found: C, 54.4; H, 4.2; N, 34.4. $C_{11}H_{10}N_6O$ requires C, 54.54; H, 4.16; N, 34.69%).

5-*Benzyl*-3-*methoxy*-5H-*imidazo*[4,5-e]-1,2,4-*triazine* 1-*Oxide* **7**.—Compound **7** was prepared from compund **5** in 88% yield by using a procedure similar to that which afforded compound **3**. An analytical sample was prepared by crystallization from methanol–chloroform (1:10), m.p. 198–200 °C; λ_{max}/nm (pH 1) 328 (ε/dm^3 mol^{-1} cm^{-1} 13 500) and 225 (21 000); (methanol) 327 (14 100) and 226 (23 600); (pH 13) 326 (9700); δ_H[$(CD_3)_2SO$] 3.97 (s, 3 H, OCH_3), 5.40 (s, 2 H, CH_2), 7.33–7.41 (m, 5 H, ArH) and 8.64 (s, 1 H, 6-H); δ_C[$(CD_3)_2SO$] 47.30 (CH_2), 56.04 (OCH_3), 128.03, 128.30, 128.94, 135.61 (ArCs), 134.0 (C-7a), 145.76 (C-6), 150.1 (C-4a) and 162.91 (C-3); *m*/*z* 257 (M^+, 7%), 241 (26), 240 (11) and 91 (100) (Found: C, 55.8; H, 4.4; N, 26.9. $C_{12}H_{11}N_5O_2$ requires C, 56.02; H, 4.31; N, 27.23%).

6-*Amino*-5-*benzylamino*-3-*hydrazino*-1,2,4-*triazine* 1-*Oxide* **8**.—Hydrazine (4 cm^3, 95% solution) was added to a solution of compound **2** (1.18 g, 4.0 mmol) in absolute ethanol (30 cm^3). The resulting solution was refluxed (oil bath) for 3 h. After this period, the clear solution was evaporated under reduced

* For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, 1994, Issue 1.

pressure to 15 cm^3 and was allowed to cool to room temperature. The precipitate was collected and crystallized from ethanol to give the title compound **8** (740 mg, 75%) as colourless needles, m.p. 218–220 °C; λ_{max}/nm (pH 1) 338 (ε/dm^3 mol^{-1} cm^{-1} 8500) and 240 (20 200); (methanol) 326 (9700) and 225 (17 200); (pH 13) 336 (7400) and 239 (16 800); δ_H[$(CD_3)_2SO$] 3.87 (br s, 2 H, hydrazino NH_2), 4.61 (d, 2 H, CH_2), 5.77 (s, 2 H, NH_2), 7.27–7.35 (m, 5 H, ArH) and 7.82 (t, 1 H, NH); δ_C[$(CD_3)_2SO$] 44.08 (CH_2), 127.32, 127.94, 128.58, 138.71 (ArCs), 125.45 (C-6), 150.12 (C-5) and 158.06 (C-3); *m*/*z* 247 (M^+, 7.4%), 231 (5.7), 230 (17) and 91 (100) (Found: C, 48.2; H, 5.4; N, 39.2. $C_{10}H_{13}N_7O$ requires C, 48.58; H, 5.30; N, 39.59%).

6-*Amino*-5-*benzylamino*-1,2,4-*triazine* 1-*Oxide* **9**.—To a suspension of compound **8** (741 mg, 3.0 mmol) in absolute ethanol (80 cm^3) was added yellow mercury(II) oxide (3 g). The resulting mixture was stirred and refluxed (oil bath) for 24 h. The hot filtrate was concentrated to 25 cm^3 and allowed to cool to 4 °C overnight. The yellow precipitate was collected and crystallized from ethanol to give the title compound **9** (358 mg, 55%), m.p. 263–266 °C; λ_{max}/nm (pH 1) 319 (ε/dm^3 mol^{-1} cm^{-1} 9400) and 222 (14 900); (methanol) 322 (10 500) and 223 (20 100); (pH 13) 317 (7700); δ_H[$(CD_3)_2SO$] 4.64 (d, *J* 5, 2 H, CH_2), 6.63 (s, 2 H, NH_2), 7.27–7.35 (m, 5 H, ArH), 7.90 (s, 1 H, 3-H) and 7.96 (t, *J* 5, 1 H, NH); δ_C[$(CD_3)_2SO$] 44.38 (CH_2), 127.40, 127.76, 128.67, 138.41 (ArCs), 131.81 (C-6), 146.55 (C-3) and 148.83 (C-5); *m*/*z* 217 (M^+, 4.5%), 201 (5.2), 200 (33) and 91 (100) (Found: C, 55.2; H, 4.8; N, 32.5. $C_{10}H_{11}N_5O$ requires C, 55.30; H, 5.07; N, 32.26%).

5-*Benzyl*-5H-*imidazo*[4,5-e]-1,2,4-*triazine* 1-*Oxide* **10**.—To a well stirred suspension of compound **9** (217 mg, 1.0 mmol) in triethyl orthoformate (25 cm^3) was added concentrated hydrochloric acid (0.3 cm^3). The mixture was heated at reflux (oil bath) for 2 h. After this period, the hot filtrate was evaporated under reduced pressure to give an orange syrup which was purified by column chromatography on silica gel with chloroform–methanol (30:1) as eluent. The homogeneous fractions were pooled and evaporated to obtain an oil which was cooled to 4 °C for 16 h to give the title compound **10** (148 mg, 65%), m.p. 110–112 °C; λ_{max}/nm (pH 1) 308 (ε/dm^3 mol^{-1} cm^{-1} 13 400) and 225 (16 700); (methanol) 308 (12 300) and 227 (15 000); (pH 13) 329 (8200) and 228sh (23 100); δ_H[$(CD_3)_2SO$] 5.48 (s, 2 H, CH_2), 7.38 (s, 5 H, ArH), 8.23 (s, 1 H, 3-H) and 8.74 (s, 1 H, 6-H); δ_C[$(CD_3)_2SO$] 48.51 (CH_2), 128.16, 129.08, 129.27, 133.57 (ArCs), 137.28 (C-7a), 144.69 (C-6), 148.43 (C-4a) and 152.76 (C-3); *m*/*z* 227 (M^+, 9.6%), 210 (2) and 91 (100) (Found: C, 57.9; H, 4.0; N, 30.6. $C_{11}H_9N_5O$ requires C, 58.15; H, 3.99; N, 30.82%).

Acknowledgements

We gratefully acknowledge the financial support from the National Science Council of the Republic of China (NSC 82-0208-M-037-013).

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Paper 4/01696C
Received 22*nd March* 1994
Accepted 10*th May* 1994