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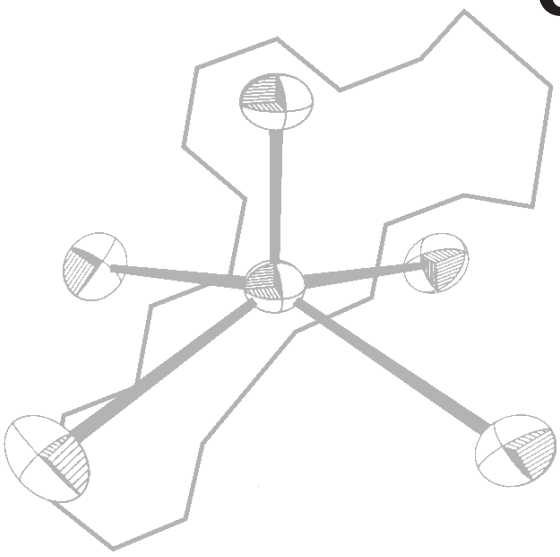

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Dihydro-1,2,4-triazin-6(1*H*)-ones. III* Oxidation Products of 1-Methyl-3-phenyl-4,5-dihydro-1,2,4-triazin-6(1*H*)-one

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1-Methyl-3-phenyl-4,5-dihydro-1,2,4-triazin-6(1*H*)-one (1) undergoes aerial oxidation to give a mixture of 1-methyl-3-phenyl-1,2,4-triazin-6(1*H*)-one (2) and 1-methyl-3-phenyl-1,4-dihydro-1,2,4-triazine-5,6-dione (3). The dehydro derivative (2) was cleanly prepared by the oxidation of (1) with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (ddq). The dehydro derivative (2) underwent a surprising rearrangement to the triazole (12) upon oxidation with Oxone[R]. Several attempts at unambiguous synthesis of the α-dicarbonyl derivative (3) were unsuccessful; it was obtained, together with the 1,4-dimethyl derivative (13) by methylation of 3-phenyl-1,4-dihydro-1,2,4-triazine-5,6-dione (4) with sodium hydride and methyl iodide.

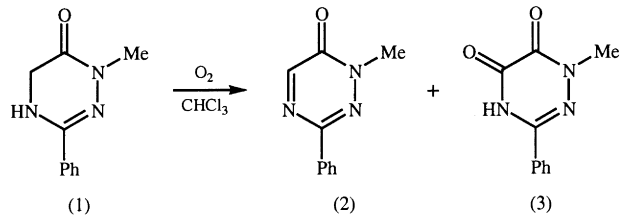
Introduction

During exploration of novel heterocycles[1] for use as potential crop protection agents, we became aware that the 4,5-dihydro-1,2,4-triazin-6(1*H*)-one ring system is readily susceptible to aerial oxidation. In this paper we report that aerial oxidation of 1-methyl-3-phenyl-4,5-dihydro-1,2,4-triazin-6(1*H*)-one (1) gives a dehydro derivative and a dicarbonyl derivative, and independent syntheses of them is described. Since these oxidative transformation products exhibited different levels and types of biological activity when they were separately tested as crop protection chemicals it became desirable to establish convenient and general synthetic routes to these materials for further biological studies.

Results and Discussion

Aerial Oxidation of the 1-Methylated Dihydrotriazinone (1)

When air was bubbled through a chloroform solution of 1-methyl-3-phenyl-4,5-dihydro-1,2,4-triazin-6(1*H*)-one[1] (1) it was readily oxidized to a mixture of the new dehydro analogue (2)† (56%) and the new dicarbonyl compound (3) (44%) (Scheme 1). The dehydro derivative (2) was identified by its methine resonances at δ 8.41 and 157.5 in the ^{1}H and ^{13}C n.m.r. spectra, respectively. The dicarbonyl derivative (3) was identified by the lack of a methylene resonance in its ^{1}H n.m.r. spectrum, and two carbonyl carbon resonances at δ 154.0 and 155.1 in the ^{13}C n.m.r. spectrum. Elemental analyses and accurate mass measurements were consistent with the structures (2) and (3). Aerial oxidation of crystalline (1) to the dehydro derivative (2) also occurred partially during radial chromatography. Aerial oxidation of the solid material is probably due to a photochemical process in which a trace of the u.v. indicator eluted from the silica gel during radial chromatography has acted as a photosensitizer. When compound (1) was purified by flash column chromatography over pure silica gel without the u.v. indicator, or simply by recrystallization, it was stable to aerial oxidation in the solid state.



(1) (2) (3)

Scheme 1

We next investigated the stability of (2) to aerial oxidation. Compound (2) was subjected to the original oxidation conditions ($CHCl_3$, air). No additional products were formed and compound (2) was recovered unchanged. Hence, the dehydro derivative (2) and the dicarbonyl compound (3) appear to be formed by independent routes, perhaps via a common intermediate, during aerial oxidation of 1-methyl-3-phenyl-4,5-dihydro-1,2,4-triazin-6(1*H*)-one (1).

* Part II, *Aust. J. Chem.,* 1999, **52**, 379.

† The dehydro compound (2) has the systematic name 1-methyl-3-phenyl-1,2,4-triazin-6(1*H*)-one, but use of the term 'dehydro' is appropriate in the present context.

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Not surprisingly, the pure compounds (1), (2) and (3) possessed different biological activities when tested as potential crop protection agents.* It is plausible that other 4,5-dihydro-1,2,4-triazin-6(1*H*)-ones may be at least partly oxidized to the corresponding 5,6-dicarbonyl compound and/or dehydro derivative(s) while undergoing biological testing, and the net biological activity observed may not be that of the original compound. It was therefore desirable to explore other synthetic routes to the dicarbonyl compound (3) and the dehydro compound (2) which may be applicable to the efficient generation of a range of analogues for measurement of their intrinsic biological activities.

Oxidation of the 1-Methylated Dihydrotriazinone (1) with 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone

There are several reports of 4,5-dihydro-1,2,4-triazin-6(1*H*)-ones being oxidized to the corresponding dehydro, aromatic derivatives;[2] these reactions were generally low-yielding and often entailed difficult workup procedures. To the best of our knowledge, no one has described the successful oxidation of a 4,5-dihydro-1,2,4-triazin-6(1*H*)-one to the corresponding dehydro 1,2,4-triazin-6(1*H*)-one using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (ddq) as the oxidant. Despite a claim by Taylor and Macor[3] that ddq failed to oxidize some dihydrotriazinones to their corresponding dehydro derivatives, we found that ddq can be used to effect this transformation cleanly. Treatment of 1-methyl-3-phenyl-4,5-dihydro-1,2,4-triazin-6(1*H*)-one (1) with ddq in dry dichloromethane afforded 94% of 1-methyl-3-phenyl-1,2,4-triazin-6(1*H*)-one (2) which was identical with the material prepared by aerial oxidation of (1).

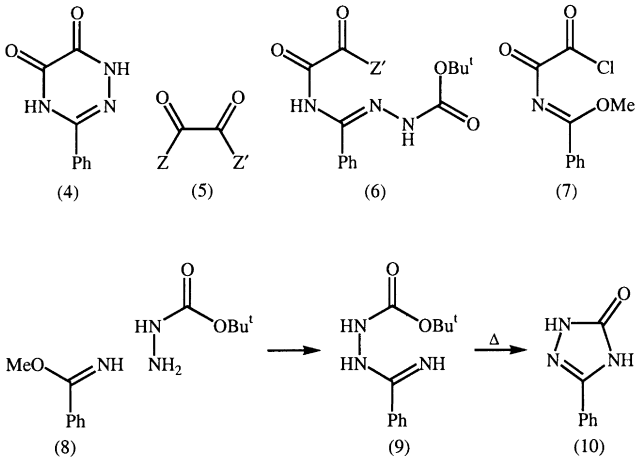
Attempted Synthesis of the 1-Methylated Dihydrotriazinedione (3)

Synthesis of 3-phenyl-1,4-dihydro-1,2,4-triazine-5,6-dione (4) and its 1-methyl analogue (3) proved to be a much more difficult problem. Indeed, relatively few syntheses of 1,2,4-triazine-5,6-diones have been reported in the literature.[4–7] Two general approaches have been used: (i) cycloaddition of an oxalate derivative with an amidrazone derivative; and (ii) oxidation of the preformed ring system to the 5,6-dione system.

Cyclization Reactions

Several 1,2,4-triazine-5,6-diones have been prepared by cyclization of amidrazone derivatives with diethyl oxalate (or other oxalic acid derivatives).[5,6] However, reaction of benzamidrazone[8] with either dimethyl oxalate or oxalyl chloride failed to afford any of the desired product (4).

To avoid problems associated with benzamidrazone, including its tendency towards self-condensation reactions,[9] the masked amidrazone derivative (9) was prepared. It was expected that compound (9) could react with an oxalate derivative (5) to give compounds of the type (6), which upon deprotection should cyclize to give the triazine-5,6-dione (4). Also, the use of *N*-methyl carbazates[1] in such reactions should regiospecifically provide the 1- or 2-methyl derivatives of (4).



Scheme 2

Methyl benzimidate[10] (8) was treated with t-butyl carbazate to give the new amidrazone derivative (9)† in 82% yield. The ^{1}H n.m.r. spectrum of (9) showed a resonance for the t-butyl group at δ 0.99, and signals for the amino protons at δ 5.42 (2H) and 8.38. The ^{13}C n.m.r. spectrum of (9) showed imine and carbonyl carbon resonances at δ 146.6 and 153.7, respectively. Upon being heated, (9) cyclized to give 5-phenyl-2,4-dihydro-3*H*-1,2,4-triazol-3-one (10) which was identified by comparison of its spectra with the reported data[11] (Scheme 2). Not surprisingly, the mass spectrum of (9) did not show the parent molecular ion, but gave the molecular ion of the triazolone (10); however, elemental analysis of (9) was consistent with the molecular formula $C_{12}H_{17}N_3O_2$.

Treatment of the protected amidrazone (9) with dimethyl oxalate or ethyl oxalyl chloride failed to yield any of the desired products (6) or (4). Interestingly, when the amidrazone (9) was treated with dimethyl oxalate at 200°C in a microwave reactor[12] for 5 min, the triazolone (10) was obtained in quantitative yield. This constitutes an efficient microwave conversion of the amidrazone derivative (9) into the triazolone (10).

The attempted cyclocondensation[13,14] of oxamic hydrazide (5; Z = NH_2, Z = $NHNH_2$) with trimethyl orthobenzoate failed to yield the desired 5,6-dione compound (4). Reaction of hydrazine with the oxalyl chloride derivative (7) was also considered. However, the oxalyl chloride derivative (7) was unable to be isolated from the reaction of methyl benzimidate hydrochloride[15] with oxalyl chloride.[16]

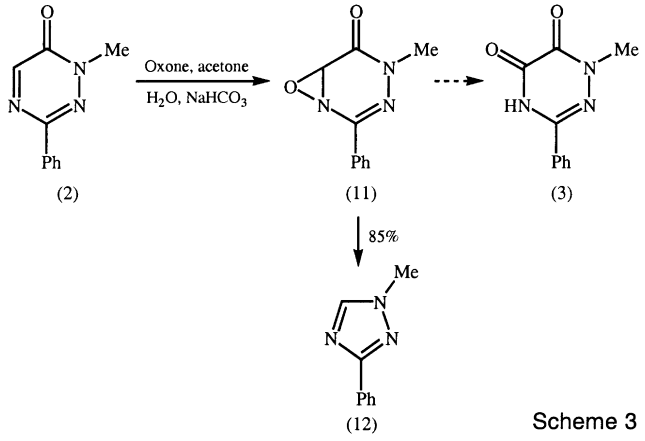
Oxidation Reactions

Attempted oxidations of the preformed triazinone system using bromine water, selenium dioxide or selenium dioxide/

* The results of biological testing of the compounds reported in this work will be published elsewhere.
† The compounds (9) and (10) may exist in different tautomers to the ones illustrated.

90% t-butyl hydroperoxide or Oxone[17]* failed to generate the desired 5,6-dione ring system.

However, we wish to report here an oxidative rearrangement of the 1-methyl dehydro triazinone (2) observed when Oxone^R was used as the oxidizing agent.

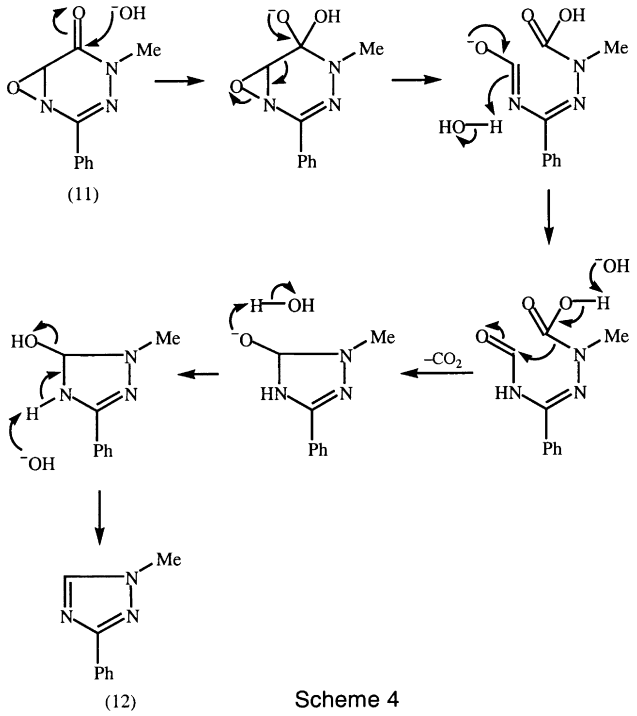


Scheme 3

Hajipour and Pyne[18] have described a general method of synthesizing oxaziridines from the corresponding imine with Oxone^R. It was expected that the oxaziridine (11), potentially available from the corresponding triazinone (2), could be rearranged into the desired 1-methyl-3-phenyl-1,4-dihydro-1,2,4-triazine-5,6-dione (3). However, attempts to generate the oxaziridine (11) by reaction of Oxone^R (cf. Corey and Ward[19]) with the dehydro 1,2,4-triazin-6(1*H*)-one (2) and sodium hydrogen carbonate in aqueous acetone gave 1-methyl-3-phenyl-1*H*-1,2,4-triazole (12) in 85% yield (Scheme 3). The melting point and the ^{1}H n.m.r. spectrum of (12) were consistent with the data reported.[20] The triazole (12) could result from a base-catalysed transformation of the oxaziridine (11); a possible rationalization of this is shown in Scheme 4. The dehydro triazinone (2) was stable under similar basic conditions, therefore ruling out an alternative base-catalysed mechanism for the rearrangement of (2) to (12).

Reaction of the 1-methyl-1,2,4-triazin-6(1*H*)-one (2) with hydrogen peroxide and sodium hydroxide under the conditions described by Felix *et al.*[21] gave a mixture of 12% of the methyl triazole (12) and 74% of starting material. However, oxidation of (2) with 3-chloroperbenzoic acid in dichloromethane (i.e. under non-aqueous and non-basic conditions) gave a mixture containing 40% of the methyl triazole (12), the remainder being some starting material and several other minor unidentified products.

Although the transformation of the 1-methyl triazinone (2) into the 1-methyl triazole (12) was unexpected, 1,2,4-triazines are known to undergo ring contractions to give 1,2,4-triazoles, 1,2,3-triazoles and imidazoles.[22–25] For example, Lee and Paudler[22] reported the ring contraction of some 1-methyl-1,2,4-triazinium iodides to the corresponding 1,2,4-triazoles upon attempted base-catalysed hydrolysis.



Scheme 4

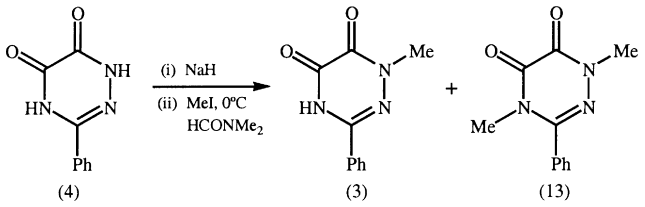
Methylation of the Dihydrotriazinedione (4)

Since attempts to prepare 1-methyl-3-phenyl-1,4-dihydro-1,2,4-triazine-5,6-dione (3) by cyclocondensation or oxidation procedures had failed, methylation of the dicarbonyl compound (4) was attempted. Treatment of 3-phenyl-1,4-dihydro-1,2,4-triazine-5,6-dione (4), which has two acidic (amidic) NH groups, with sodium hydride and methyl iodide gave a mixture of the 1-monomethylated derivative (3) (68%), and the 1,4-dimethylated compound (13) (32%) (Scheme 5). The monomethylated product was identified by comparison of its resonances in the ^{1}H and ^{13}C n.m.r. spectra of the mixture with those of an authentic sample of (3) prepared by aerial oxidation of 1-methyl-3-phenyl-4,5-dihydro-1,2,4-triazin-6(1*H*)-one (1). The mass spectrum of the mixture showed parent molecular ions of both products and an accurate mass measurement confirmed the presence of the dimethylated compound (13). The ^{1}H n.m.r. spectrum of the mixture showed resonances at δ 3.08 and 3.52 consistent with the *N*-methyl groups of the dialkylated product (13), and the ^{13}C n.m.r. spectrum showed two carbonyl resonances for (13) at δ 153.0 and 157.2. Compound (3), in the form of its enolate, could be readily separated from the mixture by base extraction.

The failure of several possible cyclocondensation and oxidative procedures to give the 5,6-triazinedione (4) may be due to electronic and/or steric effects. While the dione (3) was readily obtainable (together with (2)) by aerial oxidation of (1), the failure of the latter to undergo oxidation to (3) with bromine water, or selenium dioxide/t-butylhydroperoxide is surprising. From the point of view of developing potential

* Oxone is a registered trademark of E. I. Du Pont de Nemours & Co. Potassium peroxymonosulfate can be prepared by the method in ref. 17.

crop protection agents, the facile aerial oxidation of compounds of the type (1) may be blocked by appropriate disubstitution at C 5.



Scheme 5

Experimental

General experimental details were as previously described.[1]

*1-Methyl-3-phenyl-1,2,4-triazin-6(1*H*)-one (2)*

(i) *By oxidation of 1-methyl-3-phenyl-4,5-dihydro-1,2,4-triazin-6(1*H*)-one (1) with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.* 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (923 mg, 4.06 mmol) was added to a solution of 1-methyl-3-phenyl-4,5-dihydro-1,2,4-triazin-6(1*H*)-one[1] (1) (769 mg, 4.06 mmol) in dry dichloromethane (50 ml) under an argon atmosphere. The mixture was stirred overnight at room temperature, and then poured onto a short column of silica gel and eluted with dichloromethane. Recrystallization of the eluate from ethyl acetate/light petroleum afforded *1-methyl-3-phenyl-1,2,4-triazin-6(1*H*)-one* (2) (713 mg, 93%) as a white solid, m.p. 145–145.5°C. G.l.c. R_t 13.48 min, 100% (Found: C, 64.2; H, 5.1; N, 22.4%; $[M+1]^{+\bullet}$, 188.083. $C_{10}H_9N_3O$ requires C, 64.2; H, 4.9; N, 22.5%; $[M+1]^{+\bullet}$, 188.082). ν_{max} (KBr) 1669s, 1585m, 1566m, 1446m, 1271w, 745m, 693m, 608m cm^{-1}. ^1H n.m.r. δ 3.77, s, CH_3; 7.37–7.53, m, 3H, Ar; 8.05–8.18, m, 2H, Ar; 8.41, s, CH=N. ^{13}C n.m.r. δ 39.6, CH_3; 126.5, C 2′, C 6′ or C 3′, C 5′; 128.6, C 2′, C 6′ or C 3′, C 5′; 130.2, C 4′; 133.3, C 1′; 148.1, C 3; 153.6, C=O; 157.5, C 5. Mass spectrum: *m/z* (c.i.) 188 ($[M+1]^{+\bullet}$, 100%), 144 (8), 116 (9).

(ii) *By aerial oxidation of 1-methyl-3-phenyl-4,5-dihydro-1,2,4-triazin-6(1*H*)-one (1).* Air was vigorously bubbled through a solution of 1-methyl-3-phenyl-4,5-dihydro-1,2,4-triazin-6(1*H*)-one (1) (553 mg, 2.91 mmol) in chloroform (20 ml) overnight. The solvent was evaporated and the residue was triturated with dichloromethane. Recrystallization of the residue from methanol gave *1-methyl-3-phenyl-1,4-dihydro-1,2,4-triazine-5,6-dione* (3) (259 mg, 44%) as a white solid, m.p. 240–242°C (Found: $[M+1]^{+\bullet}$, 204.076. $C_{10}H_9N_3O_3$ requires $[M+1]^{+\bullet}$, 204.077). ν_{max} (KBr) 3576m, 3338m, 3120m, 1710s, 1613m, 1386m, 923m, 776m cm^{-1}. ^1H n.m.r. δ ($(CD_3)_2SO$) 3.40, s, CH_3; 7.12–7.34, m, 4H, Ar, NH; 7.54–7.75, m, 2H, Ar. ^{13}C n.m.r. δ ($(CD_3)_2SO$) 38.1, CH_3; 126.3, C 2′, C 6′ or C 3′, C 5′; 128.2, C 2′, C 6′ or C 3′, C 5′; 129.7, C 1′; 130.3, C 4′; 140.2, C 3; 154.0, C 5 or C 6; 155.1, C 5 or C 6. Mass spectrum: *m/z* (c.i.) 204 ($[M+1]^{+\bullet}$, 100%), 188 (93). The filtrate was evaporated to dryness at reduced pressure and the residue was recrystallized from ethyl acetate/light petroleum to afford 1-methyl-3-phenyl-1,2,4-triazin-6(1*H*)-one (2) (306 mg, 56%), as a white solid, m.p. 145–145.5°C, which was identical with the material obtained by method (i).

t-Butyl N′*-(Imino(phenyl)methyl)hydrazinecarboxylate (9)*

A solution of t-butyl carbazate (978 mg, 7.4 mmol) and methyl benzimidate[10] (8) (1.00 g, 7.4 mmol) in anhydrous ethanol (20 ml) was stirred overnight at room temperature under an argon atmosphere. The mixture was then evaporated to dryness under reduced pressure and the residue was recrystallized from ethyl acetate/light petroleum to afford the *amidrazone derivative* (9)* (1.34 g, 77%), m.p. >300°C† (Found: C, 61.5; H, 7.5; N, 17.9. $C_{12}H_{17}N_3O_2$ requires C, 61.3; H, 7.3; N, 17.9%). ν_{max} (KBr) 3484m, 3344m, 1704s, 1633s, 1520m, 1255m, 778m, 710m cm^{-1}. G.c.m.s. R_t 21.76 min, 100%. Mass spectrum: *m/z* (e.i.) 161 (95%), 118 (100), 130 (27), 91 (100), 77 (73), 51 (50). ^1H n.m.r. δ ($CDCl_3$/$(CD_3)_2SO$) 0.99, s, CH_3; 5.42, br s, NH_2; 6.72–6.88, m, 3H, Ar; 7.18–7.30, m, 2H, Ar; 8.38, br s, NH. ^{13}C n.m.r. δ ($CDCl_3$/$(CD_3)_2SO$) 28.2, C(**C**$H_3)_3$; 78.8, **C**$(CH_3)_3$; 125.9, C 2′, C 6′ or C 3′, C 5′; 127.6, C 2′, C 6′ or C 3′, C 5′; 128.7, C 4′; 134.6, C 1′; 146.6, C=O or C=N; 153.7, C=O or C=N. The mass spectrum was identical to that of 5-phenyl-2,4-dihydro-3*H*-1,2,4-triazol-3-one (10)

Attempted Synthesis of 3-Phenyl-1,4-dihydro-1,2,4-triazine-5,6-dione (4)

(i) *Reaction of benzamidrazone with oxalate derivatives.* A mixture of benzamidrazone[8] and 1 mole equiv. of dimethyl oxalate in dichloromethane was stirred at room temperature overnight, and the mixture was then evaporated to dryness at reduced pressure. ^1H and ^{13}C n.m.r. and mass spectroscopy of the residue showed, by comparison with data for an authentic sample of (4), that no 3-phenyl-1,4-dihydro-1,2,4-triazine-5,6-dione (4) had been formed. Similarly, 1 mole equiv. of either ethyl oxalyl chloride or oxalyl chloride was added to a solution of benzamidrazone and 1 mole equiv. of triethylamine (for the acid chloride reactions) in dichloromethane at –20°C and the mixture was allowed to warm to room temperature, and stirred overnight. ^1H and ^{13}C n.m.r. and mass spectroscopic examination of the residue showed that none of the desired 3-phenyl-1,4-dihydro-1,2,4-triazine-5,6-dione (4) had been formed.

(ii) *Reaction of t-butyl* N′*-[imino(phenyl)methyl]hydrazinecarboxylate (9) with oxalyl derivatives.* When a solution of the amidrazone derivative (9) (563 mg, 2.39 mmol) and dimethyl oxalate (282 mg, 2.39 mmol) in dichloromethane (or methanol) (20 ml) was allowed to stand at room temperature, or heated under reflux, n.m.r., mass spectroscopic, and t.l.c. analysis showed only starting materials. Heating the mixture to 200°C for 5 min in a microwave reactor gave triazol-3-one (10) in quantitative yield. Reaction of the amidrazone derivative (9) (500 mg, 2.13 mmol), ethyl oxalyl chloride (240 μl, 2.55 mmol) and anhydrous triethylamine (300 μl, 2.55 mmol) in anhydrous dichloromethane at –78°C gave a complex mixture but n.m.r. and mass spectroscopic analysis indicated that none of the desired product (4), or its possible cyclization products were present.

*1-Methyl-3-phenyl-1*H*-1,2,4-triazole (12)*

According to a modified version of the procedure described by Corey,[19] a solution of Oxone^R ($2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$; 2.82 g, 4.59 mmol) in water (15 ml) was added dropwise to a solution of sodium hydrogen carbonate (0.9 g, 10.38 mmol) and 1-methyl-3-phenyl-1,2,4-triazin-6(1*H*)-one (2) (452 mg, 2.42 mmol) in water (2.5 ml) and acetone (5 ml). The mixture was stirred at room temperature for 42 h, and then extracted with ethyl acetate (3×30 ml). The combined extract was washed with an equal volume of saturated sodium chloride solution, dried over anhydrous sodium sulfate, and concentrated to afford an oil. Distillation of this under reduced pressure gave 1-methyl-3-phenyl-1*H*-1,2,4-triazole (12) (325 mg, 84%), b.p. 70°C/0.05 mmHg (lit.[26] 94°C/0.5 mmHg), which slowly crystallized, m.p. 22°C (lit.[20] 23°C). G.l.c. R_t 11.88 min, 98%. ν_{max} (film) 3066w, 1676m, 1577w, 1522w, 1502m, 1440m, 728s, 696m cm^{-1}. ^1H n.m.r. δ 3.96, s, CH_3; 7.31–7.50, m, 3H, Ar; 7.97–8.18, m, 3H, Ar and H 5. ^{13}C n.m.r. δ 36.2, CH_3; 126.2, C 2′, C 6′ or C 3′, C 5′; 128.6, C 2′, C 6′ or C 3′, C 5′; 129.2, C 4′; 130.8, C 1′; 144.3, C 3; 162.5, C 5. Mass spectrum: *m/z* (c.i.) 160 ($[M+1]^{+\bullet}$, 100%); (e.i.) 159 ($M^{+\bullet}$, 100%), 131 (38), 104 (30), 89 (5), 77 (10), 63 (5).

1-Methyl-3-phenyl-1,4-dihydro-1,2,4-triazine-5,6-dione (3): Methylation of 3-Phenyl-1,4-dihydro-1,2,4-triazine-5,6-dione (4)

A solution of 3-phenyl-1,4-dihydro-1,2,4-triazine-5,6-dione[27] (4) (535 mg, 2.8 mmol) in anhydrous dimethylformamide (10 ml) was

* Compound (9) may exist in different tautomeric forms to the one shown.

† The compound (9) cyclizes to compound (10) with loss of t-butyl alcohol when heated (see also *m/z* 161 in mass spectrum).

added dropwise with stirring to an ice-cold suspension of sodium hydride (171 mg, 6.0 mmol, 80%) in anhydrous dimethylformamide (2 ml) under an argon atmosphere. The cooling bath was then removed and the mixture was stirred for 1 h, then recooled to 0°C and a solution of freshly distilled methyl iodide (176 μl, 2.8 mmol) in anhydrous dimethylformamide (5 ml) was added dropwise. The mixture was stirred for 2 h at 0°C, and then evaporated to dryness (eventually 25°C/0.05 mmHg). ^{1}H and ^{13}C n.m.r. spectroscopy and t.l.c. analysis indicated that the crude product was a mixture of 1-methyl-3-phenyl-1,4-dihydro-1,2,4-triazine-5,6-dione (3) (68%) and *1,4-dimethyl-3-phenyl-1,4-dihydro-1,2,4-triazine-5,6-dione* (13) (32%). No starting material, and no other methylation products were observed. The spectroscopic data for (13) are as follows (Found: $[M+1]^{+\bullet}$, 218.094. $C_{10}H_9N_3O_3$ requires $[M+1]^{+\bullet}$, 218.093). ^{1}H n.m.r. δ ($(CD_3)_2SO$) 3.08, s, 1-CH_3 or 4-CH_3; 3.52, s, 1-CH_3 or 4-CH_3; 7.56, s, Ar. ^{13}C n.m.r. δ ($(CD_3)_2SO$) 33.6, 1-CH_3 or 4-CH_3; 38.5, 1-CH_3 or 4-CH_3; 126.6, C 2′, C 6′ or C 3′, C 5′; 128.2, C 2′, C 6′ or C 3′, C 5′; 128.9, C 4′; 131.5, C 1′; 136.7, C 3; 153.0, C 5; 157.2, C 6. Mass spectrum: *m/z* (c.i.) 218 ($[M+1]^{+\bullet}$, 100%).

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