Extended Tandem Reactions of 2*H*-1,2,3-Triazole *N*-Oxides with Dialkyl Acetylenedicarboxylates and *N*-Phenylmaleimide: Substituted Monocyclic 2,5-Dihydro-1,2,3-triazines and New Tetrahydrofuro[2,3-*d*]-1,2,3-triazoles. Azolium 1,3-Dipoles Part 5.†

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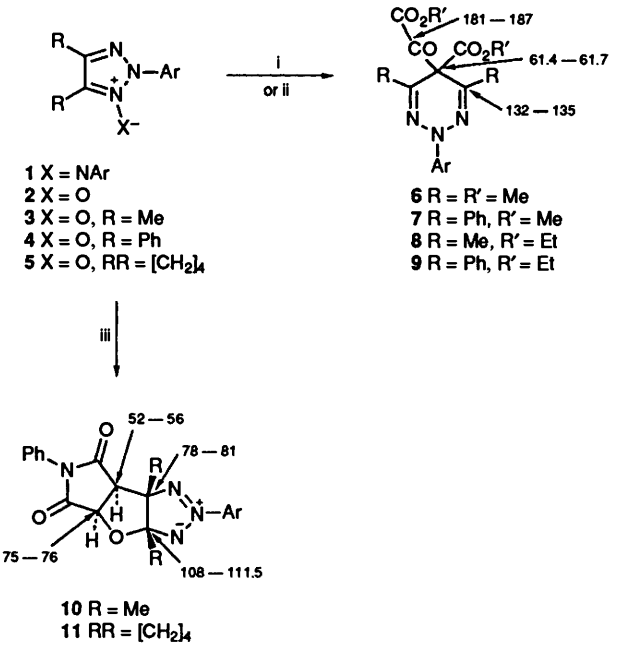
The reaction of substituted 1,2,3-triazole 1-oxides with dialkyl acetylenedicarboxylate dipolarophiles gave a new route to monocyclic 1,2,3-triazine derivatives *via* a multi-step sequence of cycloaddition, sigmatropic rearrangements, and ring expansion. With *N*-phenylmaleimide as dipolarophile, derivatives of a new tetrahydrofuro[2,3-*d*]-1,2,3-triazole system were formed. Mechanisms are discussed. An X-ray crystal structure of 2-(*p*-bromophenyl)-5-methoxalyl-5-methoxycarbonyl-4,6-dimethyl-2,5-dihydro-1,2,3-triazine is reported.

Recently we have described[1–3] the wide synthetic scope for 1,2,3-triazolium imides **1** as 1,3-dipoles in reactions with 2π-systems. Although two of the four π-electrons of the 1,3-dipole system form part of the aromatic triazole ring, rapid rearrangements after the initial cycloaddition result in the retention of the 1,2,3-triazole moiety so that the N–N–N chain can be carried intact through a range of steps, thus adding an important synthetic dimension which provides routes to monocyclic hetero-1,2,3-triazines,[1–3] such as oxatriazines, thiatriazines and tetrazines. The related oxygen analogues, the 1,2,3-triazolium 1-oxides **2** have not yet been explored as 1,3-dipoles for synthesis. Herein,[4] we examine these to allow a comparison with the imides already reported.[1–3] The oxides **2** were less versatile and only exhibited cycloadditions with strongly π-deficient dipolarophiles containing two carbonyl groups conjugated to the 2π-system. Thus, under normal conditions in toluene as solvent, no reactions were observed between the *N*-oxides **2** and dipolarophiles such as acrylonitrile, ethyl acrylate, methyl methacrylate, fumaronitrile and others. Interesting new reactions[4] were observed with dimethyl acetylenedicarboxylate (DMAD), diethyl acetylenedicarboxylate (DEAD) and *N*-phenylmaleimide (PMA) all of which contain comparable low lying LUMOs.[5] These reactions gave a new[4] effective route to high yields of derivatives of the monocyclic 1,2,3-triazine system, the rarest[6] of the triazine class. Most of the known 1,2,3-triazine compounds are fused benzo-derivatives, and reactions which give monocyclic 1,2,3-triazines are of particular interest.[6–10] Derivatives of the new furo[2,3-*d*]-1,2,3-triazole ring system were formed from the reactions with PMA. Both reactions were related and followed an extended tandem sequence similar to that observed[1–3] for 1,2,3-triazolium-1-imide, 1,3-dipoles; namely, a cycloaddition, a number of sigmatropic rearrangements and finally a ring expansion. The generality of this new tandem reaction is now expanded to include 1,2,3-triazolium oxide 1,3-dipoles also.



1 X = NAr
2 X = O
3 X = O, R = Me
4 X = O, R = Ph
5 X = O, RR = $[CH_2]_4$
6 R = R' = Me
7 R = Ph, R' = Me
8 R = Me, R' = Et
9 R = Ph, R' = Et
10 R = Me
11 RR = $[CH_2]_4$

Scheme 1 *Reagents:* i, DMAD; ii, DEAD; iii, PMA. Ar = **a**, Ph; **b**, C_6H_4Br-*p*; **c**, $C_6H_4NO_2$-*p*. (Some ^{13}C NMR shift ranges are shown).

Results and Discussion

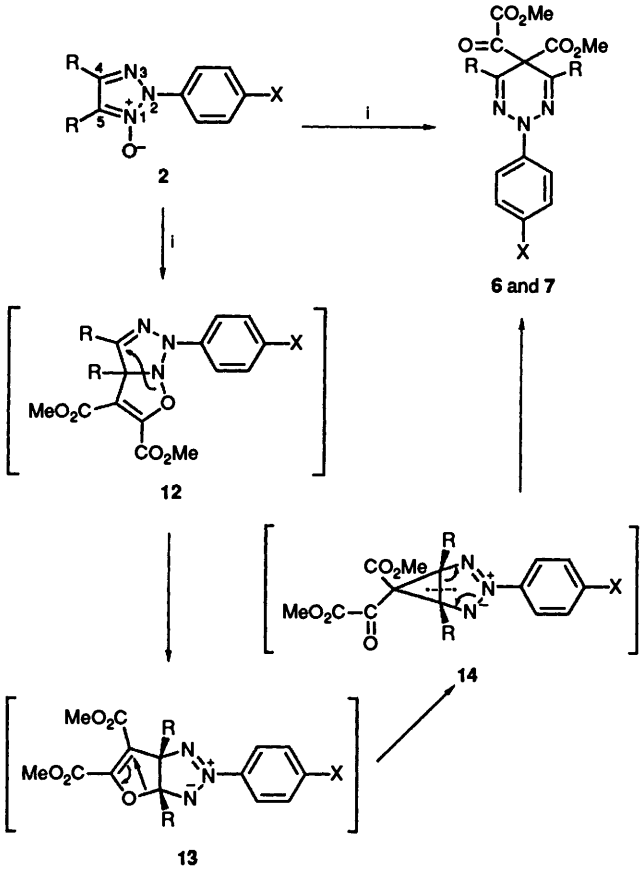
When a range of triazolium oxide compounds **2** were heated under reflux in toluene with DMAD as dipolarophile, high yields of the substituted 1,2,3-triazines **6** were obtained (Scheme 1) (Table 1). The reactions also occurred in *p*-xylene and benzene as solvent but the yields were lower due to decomposition (Table 1, Nos. 2, 3, 4). Polar solvents inhibited the process and no reaction was observed in solvents such as acetone and ethyl methyl ketone. The reactions also occurred readily with DEAD as dipolarophile and gave the compounds **8** and **9** (Table 1). By analogy with reactions which gave rise to 1,2,3-triazine systems similar to **6** but containing O, N and S atoms in place of the sp^3 carbon[1–3] we suggest that the reaction occurs through the sequence shown in Scheme 2. This involves an initial 1,3-dipolar cycloaddition and sigmatropic rearrangement to give the fused furano-(1,2,3)-triazole system **13** *via* **12** (Scheme 2). The driving force for the rearrangement is the replacement of the weak N–O bond by the stronger C–O bond in the fused furan ring and the conversion of substituents from *endo*- to *exo*- orientations. A key feature of structure **13** is the π-bond at the 2,3-site of the furan moiety. This allows for a further

† Part 4 is ref. 2.

Table 1. Substrates and products

No.	Substrate Cpd	R	M.p. (°C)	Dipolarophile	Product Cpd	M.p. (°C)	Yield (%)[g] Toluene; *p*-xylene
1	**3b**	Me	107–108[a]	DMAD	**6b**	88–89[d]	46;
2	**3c**	Me	238–239[b]	DMAD	**6c**	143–144[a]	79; 49[h]
3	**4a**	Ph	168–169[b]	DMAD	**7a**	158–159[a]	73; 17.5
4	**4c**	Ph	207–208[b]	DMAD	**7c**	174–175[a]	57.5; 46
5	**3b**	Me	107–108	DEAD	**8b**	*e*	41;
6	**3c**	Me	238–239	DEAD	**8c**	89–91[a]	38;
7	**4a**	Ph	168–169	DEAD	**9a**	129–130[c]	34;
8	**4c**	Ph	207–208	DEAD	**9c**	126–127[f]	47;
9	**3c**	Me	238–239	PMA	**10c**	214–215[c]	; 75
10	**5c**	$[CH_2]_4$	191–192[c]	PMA	**11c**	245–246[b]	; 80.5
11	**5a**	$[CH_2]_4$	93–94[a]	DMAD	**16**	oil[e]	10–15[i];

[a] From Et_2O. [b] From CH_2Cl_2. [c] From EtOAc. [d] From EtOH. [e] Isolated as an oily residue which did not solidify. [f] From aq. ethanol. [g] Recovered starting material was the only other compound encountered. [h] Yield in benzene, 41%. [i] Precise yield could not be determined. Recovered starting *N*-oxide, 85%.

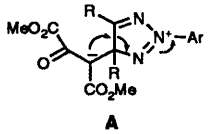


Scheme 2 *Reagent:* i, DMAD

thermal sigmatropic rearrangement to give the strained intermediate **14** which relieves strain by a disrotatory outward ring expansion to the triazine products **6** (Scheme 2).* If the 2,3-π-bond in compounds **13** were absent the sequence should then stop at that point. This was indeed observed with PMA as dipolarophile, when the products were the stable compounds **10** and **11** (Scheme 1) (Table 1). These compounds are derivatives of a new fused furo[2,3-*d*]-1,2,3-triazole system and compound **11** also represents a new oxa-aza-propellane ring system. Further support for the intermediate **14** was obtained when strain was introduced by linking of the bridgehead substituents. Thus, when RR was a chain of four methylene groups as in intermediate **15** from substrate **5a** (Scheme 3), the disrotatory outward ring expansion was inhibited and a 1,2-shift occurred to give the spiro-product **16** (Scheme 3). This type of 1,2-shift is a known feature of strained substituted cyclopropane systems.[2,11] Compound **16** was isolated with difficulty in low yield, the reaction being particularly sluggish. Its formaton, however, coupled with similar ring-contracting 1,2-shifts observed with nitrogen analogues[2] of these reactions is significant and supports the proposed mechanism. An alternative mechanism which we considered earlier,[4] involving oxygen transfer to the alkyne, thus generating an acyl carbene, is now disfavoured since we could find no support for it nor could we model the final steps with separately generated carbenes in the presence of triazoles.

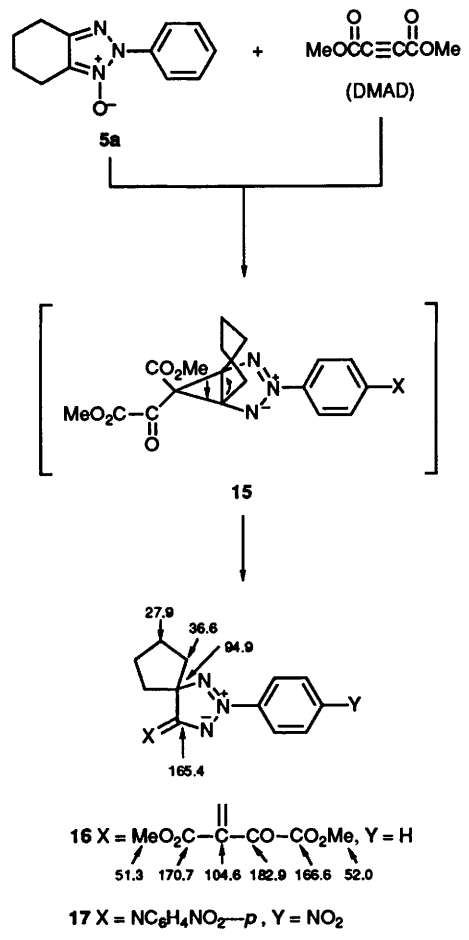
Structure of Products.—The structure of the products was established by IR and ^1H and ^{13}C NMR spectroscopy (Schemes 1–3). The compounds showed all of the expected signals. For the dihydrotriazines **6–9** the 4- and 6-carbons (sp^2) gave signals at δ_C 132–135, while the 5-carbon (sp^3) appeared at δ_C 61.4–61.7 in the carbon NMR spectrum. The X-ray crystal structure of compound **6b** is shown in Fig. 1. Of interest in the structure of the dihydrotriazine ring is the planar symmetrical nature of the atoms comprising the C–N–N–N–C system in which the

* Following comments from a referee, we acknowledge that another possible precursory intermediate to the triazines **6** could be a dipolar species **A**. However, for a number of reasons we favour the sigmatropic



A

route of Scheme 2; (i) the triazine synthesis is a general reaction (ref. 1–3) in which C-5 has been replaced by S, O and NR′ and an intermediate of type **A**, particularly with S^- replacing the carbanion site, is unlikely; (ii) the reactions occur readily in non-polar solvents such as benzene in all cases and also in cases where precursory products analogous to **13** have been isolated and separately heated; (iii) the reactions described herein were carried out using a 3–5 molar excess of DMAD (Experimental section). Owing to stabilisation by charge delocalisation in **A**, there should be time for a second molecule of DMAD to be trapped. In all cases only one mole of DMAD was found to cyclo add.



Scheme 3 ^{13}C NMR shifts are shown

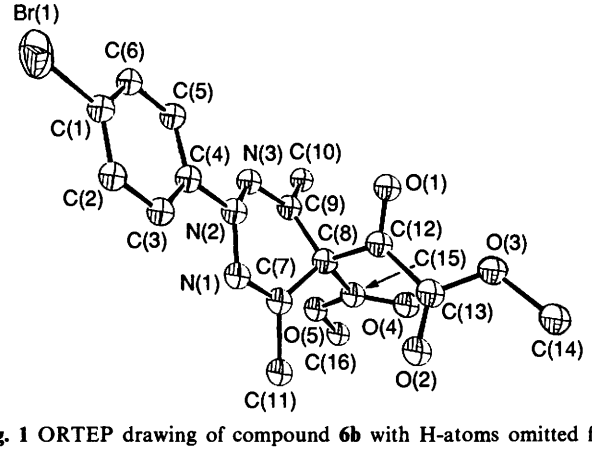
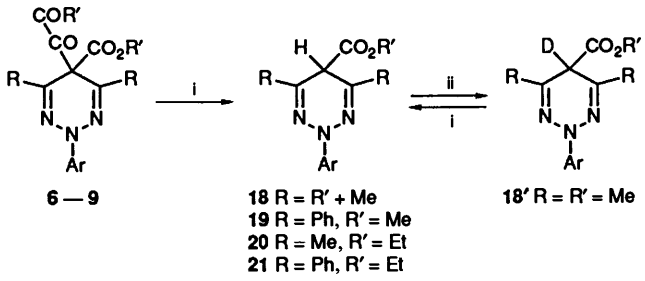


Fig. 1 ORTEP drawing of compound **6b** with H-atoms omitted for clarity

N(1)–N(2)–N(3) and C–N–N bond angles of 121° and 116°, respectively, contrast with the buckled saturated C–C–C region with almost normal C–C bond lengths and tetrahedral bond angles. The saturated carbon of the 2,5-dihydro-1,2,3-triazine compounds showed interesting reactivity involving both ready hydrolysis of the methoxalyl substituent and rapid hydrogen–deuterium exchange at this site (Scheme 4). Thus, simple heating of compounds **6–9** in aqueous ethanol gave the range of compounds **18–21** in high yield (Table 2) (Scheme 4). In these the NMR signals of the alkoxalyl moiety were absent and were replaced by that of a CH group which appeared at δ_H 3.92 (±0.1) for compounds **19** and **21**. These signals and the related



Scheme 4 *Reagents:* i, EtOH–water (1:1 v/v); ii, MeOD–D_2O (1:1 v/v)

carbon signals (Scheme 4) were easily identified by deuterium exchange, when it was found that the HC(5)-group readily underwent hydrogen–deuterium exchange on treatment with deuteriomethanol and D_2O (Scheme 4). This acidity of 5-H of the 2,5-dihydro-1,2,3-triazine ring has interesting synthetic potential which will be explored later. Compound **16** was characterised by ^1H and ^{13}C NMR spectra (Scheme 3). The chemical shifts of the triazaspiro[4.4]nonane moiety were known from nitrogen analogues such as compound **17** on which we have reported an X-ray crystal structure,[2] and the methoxalyl group signals were available from a comparison of the carbon NMR spectra of compounds **6a** and **18a**. The structures of the new furo[2,3-*d*]-1,2,3-triazole derivative **10** and the heteropropellane **11** were confirmed from microanalyses, and IR, ^1H NMR and ^{13}C NMR spectra, where all of the expected signals were observed. Particularly significant are the bridgehead carbon signals at δ_C 78–81 and 108–111.5. We have previously shown[3] from a combination of X-ray crystallography and ^{13}C NMR spectroscopy that these tertiary carbon signals are reliable indicators for structures of type **10** and **11** from cycloadditions of triazolium imide 1,3-dipoles.

Experimental

M.p.s were measured with an Electrothermal apparatus and are uncorrected. IR spectra were measured for KBr discs, and Nujol mulls with a Perkin-Elmer 983G spectrophotometer. ^1H and ^{13}C NMR spectra were measured with a JEOL JNM-GX 270 FT NMR spectrometer with tetramethylsilane as internal reference. All ^{13}C assignments were confirmed by off-resonance and selective-decoupling techniques. Elemental analyses were performed with a Perkin-Elmer model 240 CHN Analyser. The triazole *N*-oxide substrates (Table 1, Scheme 1) were prepared from known mono-oxime derivatives of 1,2-dicarbonyl compounds[12,13] which were converted into mono-oxime monohydrazone derivatives[14] and these were in turn oxidised to the triazole *N*-oxides (Table 1) by literature procedures. The following is a typical example: A solution of α-benzil monoxime[12] (2.0 g, 8.89 mmol) in 95% ethanol (10 cm^3) at 50–55 °C was treated with a warmed glacial acetic acid solution (20 cm^3) of *p*-nitrophenylhydrazine (1.36 g, 8.89 mmol) and the mixture was stirred at 80–85 °C for 2 h, during which *benzil mono-oxime mono-(p-nitrophenyl)hydrazone* separated out (67%); m.p. 212–214 °C (from MeOH) (Found: C, 66.45; H, 4.5; N, 15.5. $C_{20}H_{16}N_4O_3$ requires C, 66.7; H, 4.45; N, 15.55%). A solution of this compound (1 g, 2.78 mmol) in dichloromethane (50 cm^3) was treated with lead tetra-acetate (1.36 g; 3.07 mmol) [yellow mercury(II) oxide or lead dioxide may also be used] and the mixture was stirred under reflux for 30 min, cooled, filtered through a Celite bed to remove lead salts and evaporated under reduced pressure till crystals of 2-(p-*nitrophenyl*)-4,5-*diphenyl*-2H-1,2,3-*triazole* 1-*oxide* (**4c**) separated out (73%), m.p. 207–208 °C (from CH_2Cl_2) (Found: C, 67.1; H, 4.0; N, 15.4. $C_{20}H_{14}N_4O_3$ requires C, 67.05; H, 3.9; N, 15.65%); ν_{max}-

Table 2. Hydrolysis products of compounds **6–9**

Compound	M.p. (°C)	Yield (%)	5-H[b] δ_H	5-H[b] δ_C
18c	133–135	96	3.93	44.25
18b	*a*	23	3.92	43.44
19c	201–202	93	5.33	38.67
19a	195–196	69	5.33	38.42
20c	129–131	44	3.90	44.62
20b	106–107	82	5.0	50.75
21c	187–188	85	5.32	39.14
21a	99–101	69	5.28	38.90

[a] Compound was isolated as a yellow oil which did not crystallise. [b] NMR shifts from $SiMe_4$ in $CDCl_3$.

(mull)/cm^{-1} 1148 (=N^+O^-) and 1607 (C=N^+); $\delta_H(CDCl_3)$ 7.35–7.40 (10 H, m, 2 × Ph) and 8.28 (d) and 8.40 (d) (AA'BB', $J_{AB'}$ 6.97 Hz, $C_6H_4NO_2$); $\delta_C(CDCl_3)$ 122.55, 125.32, 125.49, 128.56, 129.48, 129.73, 130.05, 130.60, 130.68, 140.46, 145.20 and 146.66. All of the triazole *N*-oxides (Table 1) were similarly prepared. All compounds reported gave satisfactory CHN microanalyses and IR, ^1H NMR and ^{13}C NMR spectra.*

Cycloadditions.—The following are typical examples: (i) (No. 2, Table 1). A solution of 4,5-dimethyl-2-(*p*-nitrophenyl)-1,2,3-triazole 1-oxide **3c** (300 mg, 1.3 mmol) in toluene (10 cm^3) was treated with DMAD (0.79 cm^3, 6.4 mmol), stirred under reflux for 48 h, and cooled whereupon *5-methoxalyl-5-methoxycarbonyl-4,6-dimethyl-2-(*p*-nitrophenyl)-2,5-dihydro-2H-1,2,3-triazine* **6c** separated out. Successive crops were collected by fractional evaporation of the filtrate and treatment with diethyl ether and light petroleum (b.p. 40–60 °C) (total yield 380 mg, 79.2%); m.p. 143–144 °C (from diethyl ether, toluene or *p*-xylene) (Found: C, 50.65; H, 4.3; N, 14.7. $C_{16}H_{16}N_4O_7$ requires C, 51.05; H, 4.3; N, 14.9%); ν_{max}(mull)/cm^{-1} 1725 and 1744 (C=O); $\delta_H(CDCl_3)$ 2.32 (6 H, s, 4,6-dimethyl), 3.91 (6 H, s, 2 × MeO) and 7.74 (2 H, d) and 8.19 (2 H, d, $J_{AB'}$ 9.16 Hz, AA'BB') (*p*-nitrophenyl); $\delta_C(CDCl_3)$ 19.74, 53.56, 53.71, 61.46, 115.1, 124.86, 135.06, 143.02, 149.39, 160.16, 166.06 and 180.83. The final residue contained the recovered excess of DMAD and traces of a dark green oil.

(ii) (No. 3, Table 1). A solution of 2,4,5-triphenyl-2*H*-1,2,3-triazole 1-oxide **4a** (500 mg, 1.6 mmol) in toluene (10 cm^3) was treated with DMAD (0.98 cm^3, 8.0 mmol) and the mixture was stirred under reflux for 28 h and then evaporated under reduced pressure. The orange-coloured residue was taken up in diethyl ether (10 cm^3) and insoluble starting compound **4a** (220 mg) was removed. Slow evaporation of the ethereal filtrate caused separation of **7a** 5-methoxalyl-5-methoxycarbonyl-2,4,6-triphenyl-2,5-dihydro-1,2,3-triazine (total yield corrected for starting material recovered, 73.2%), m.p. 158–159 °C (from Et_2O); ν_{max}(mull)/cm^{-1} 1759 and 1735 (C=O); $\delta_H(CDCl_3)$ 3.12 (3 H, s, MeO), 3.84 (3 H, s, MeO), 7.13–7.68 (10 H, m, 4- and 6-Ph), 7.88–7.91 (3 H, m, $H_{m,p}$, 2-Ph) and 8.05–8.08 (2 H, m, H_o, 2-Ph); $\delta_C(CDCl_3)$ 51.76, 52.88, 60.50, 115.44, 122.19, 123.08, 126.08, 126.83, 127.57, 127.84, 128.03, 128.77, 128.84, 132.71, 133.27, 144.53, 156.91, 166.23 and 186.29. The final residue contained recovered DMAD and traces of a dark orange oil.

(iii) (No. 6, Table 1). A solution of 4,5-dimethyl-2-(*p*-nitrophenyl)-2*H*-1,2,3-triazole 1-oxide **3c** (500 mg, 2.1 mmol) in toluene (10 cm^3) was treated with DEAD (1.72 cm^3, 10.8 mmol), stirred under reflux for 30 h and evaporated. The green residue was taken up in diethyl ether and insoluble starting compound **3c** (10.7%) was removed. On evaporation of the ethereal solution and treatment of the residue with tetrahydrofuran (THF) (5 cm^3) some further insoluble brown scum was removed. Evaporation of the THF solution and crystallisation of the residue from diethyl ether gave *5-ethoxalyl-5-ethoxycarbonyl-4,6-dimethyl-2-(*p*-nitrophenyl)-2,5-dihydro-1,2,3-triazine* **8c** (total yield corrected for starting material recovered, 38%), m.p., 89–91 °C (from Et_2O) (Found: C, 53.5; H, 5.15; N, 13.9. $C_{18}H_{20}N_4O_7$ requires C, 53.45; H, 4.95; N, 13.85%); ν_{max}(mull)/cm^{-1}: 1729 and 1750 (C=O); $\delta_H(CDCl_3)$ 1.35–1.40 (6 H, overlapping ts, Me of both CO_2Et), 2.34 (6 H, s, 4-, 6-Me), 4.35–4.42 (4 H, overlapping qs, CH_2 of both CO_2Et) and 7.74 (2 H, d) and 8.18 (2 H, d, J_{AB} 8.61 Hz) (AA'BB' of *p*-$NO_2C_6H_4$); $\delta_C(CDCl_3)$ 13.85, 13.90, 19.8, 61.6, 63.2, 63.45, 115.1, 124.9, 135.35, 143.0, 149.5, 159.9, 165.6 and 181.3. The final residue contained an intractable orange gum.

(iv) (No. 10, Table 1). A solution of 2-(*p*-nitrophenyl)-4,6,7,8-tetrahydro-2*H*-benzo-1,2,3-triazole 1-oxide **5c** (1.0 g, 3.85 mmol) in *p*-xylene (30 .0 cm^3) was treated with PMA (1.33 g, 7.69 mmol) and the mixture was stirred under reflux for 40 h during which time the product **11c** began to separate out. Treatment of the filtrate of the early crop with diethyl ether and fractional evaporation gave *14-(*p*-nitrophenyl)-3,5-dioxo-4-phenyl-7-oxa-4,13,14,15-tetraazatetracyclo-[6.4:3.0^{1,8}.0^{2,6}]-pentadec-13-en-14-ium-15-ide* **11c** (80.5%), m.p. 245–246 °C (from CH_2Cl_2) (Found: C, 61.25; H, 4.6; N, 15.8. $C_{22}H_{19}N_5O_5$ requires C, 61.0; H, 4.4; N, 16.15%); ν_{max}(mull) 1713 cm^{-1} (C=O); $\delta_H[(CD_3)_2SO]$ 0.77–2.79 (8 H, m, $[CH_2]_4$), 4.03 (d, *J*, 7.7 Hz, 2-H), 4.97 (1 H, d, 6-H), 7.29–7.59 (5 H, m, NPh), 7.39 (2 H, d, AA', H_o of *p*-nitrophenyl) and 8.44 (2 H, d, $J_{AB'}$ 9.16 Hz, BB', H_m of *p*-nitrophenyl); $\delta_C[(CD_3)_2SO]$ 19.0, 20.6, 29.05, 30.8, 52.4, 75.5, 78.9, 108.5, 124.1, 124.85, 126.75, 128.9, 129.3, 131.7 and 173.95.

Hydrolyses (*Table* 2).—Typical examples: (a) A solution of

Table 3. Crystal data for compound **6b**

Crystal size (mm)	0.25 × 0.3 × 0.33
Formula	$C_{16}H_{16}BrN_3O_5$
M (amu)	410.224
Monoclinic, space group	$P2_1/c$
a (Å)	9.996(2)
b (Å)	12.851(2)
c (Å)	14.139(3)
β (°)	102.5(2)
V (Å^3)	1773.28
Z	4
D_c (g cm^{-3})	1.54
μ (cm^{-1})	22.51
F(000)	832
Radiation Mo-*Kα*	
Graphite monochromator	λ = 0.7093 Å
Diffractometer	Hilger Y290
Orienting reflections, range	12, 13 < θ < 20°
Temperature (°C)	22
Scan method	ω–2θ
Data collection range	2 < 2θ < 44°
No. unique data	1957
Total $I > 3\sigma(I)$	1432
No of parameters fitted	106
R[a], R_w[b]	8.28%, 8.99%
Largest shift/esd, final cycle	<0.001
Largest positive peak (e Å^{-3})	0.25
Largest negative peak (e Å^{-3})	−0.18

[a] $R = [\Sigma|F_o| - |F_c|]/\Sigma|F_o|$. [b] $R_w = \{[\Sigma w(|F_o - F_c|)^2]/[\Sigma w(|F_o|)^2]\}^{\frac{1}{2}}$; $w = 1/[(\sigma F_o)^2 - 0.000\,23 * F_o^2]$.

* *Supplementary data:* Microanalytical data and diagrammatic ^1H and ^{13}C NMR spectral data have been deposited at the British Library Lending Division, as Supplementary Publication SUP 56798 (16 pp.). See Instructions for Authors, January issue, section 4.4.

Table 4. Fractional atomic co-ordinates for compound **6b**

Atom	*x*	*y*	*z*
Br(1)	0.941 73(14)	0.244 63(9)	0.395 96(11)
O(1)	0.718 7(8)	−0.371 1(7)	0.483 3(6)
O(2)	0.874 2(9)	−0.415 8(6)	0.716 7(6)
O(3)	0.862 9(8)	−0.516 0(6)	0.587 1(6)
O(4)	0.557 6(8)	−0.483 0(6)	0.655 8(6)
O(5)	0.431 0(7)	−0.352 7(6)	0.687 6(5)
N(1)	0.719 4(8)	−0.145 8(6)	0.651 9(5)
N(2)	0.686 0(8)	−0.128 5(6)	0.553 7(5)
N(3)	0.567 2(8)	−0.166 1(6)	0.498 0(5)
C(1)	0.857 0(10)	0.130 7(8)	0.447 9(7)
C(2)	0.909 7(11)	0.100 2(8)	0.541 7(8)
C(3)	0.852 2(10)	0.013 2(8)	0.577 6(8)
C(4)	0.739 8(10)	−0.036 1(7)	0.519 5(7)
C(5)	0.686 1(10)	−0.001 0(8)	0.426 6(7)
C(6)	0.746 0(11)	0.085 6(8)	0.391 4(8)
C(7)	0.677 2(9)	−0.230 6(7)	0.680 5(7)
C(8)	0.610 5(10)	−0.312 7(7)	0.607 1(7)
C(9)	0.523 0(10)	−0.253 5(7)	0.526 2(7)
C(10)	0.391 3(11)	−0.295 7(9)	0.469 6(8)
C(11)	0.696 9(11)	−0.245 9(8)	0.788 2(7)
C(12)	0.716 9(10)	−0.373 7(7)	0.569 7(7)
C(13)	0.824 4(10)	−0.437 6(8)	0.632 6(8)
C(14)	0.969 6(14)	−0.582 0(11)	0.641 5(10)
C(15)	0.530 0(11)	−0.392 4(8)	0.653 2(7)
C(16)	0.344 1(12)	−0.424 3(9)	0.726 0(9)

Table 5. Bond lengths (Å)

Br(1)–C(1)	1.92(1)	O(1)–C(12)	1.23(1)
O(2)–C(13)	1.22(1)	O(3)–C(13)	1.30(1)
O(3)–C(14)	1.45(1)	O(4)–C(15)	1.20(1)
O(5)–C(15)	1.30(1)	O(5)–C(16)	1.45(1)
N(1)–N(2)	1.37(1)	N(1)–C(7)	1.27(1)
N(2)–N(3)	1.36(1)	N(2)–C(4)	1.43(1)
N(3)–C(9)	1.30(1)	C(1)–C(2)	1.37(1)
C(1)–C(6)	1.35(1)	C(2)–C(3)	1.40(1)
C(3)–C(4)	1.39(1)	C(4)–C(5)	1.38(1)
C(5)–C(6)	1.41(1)	C(7)–C(8)	1.53(1)
C(7)–C(11)	1.51(1)	C(8)–C(9)	1.49(1)
C(8)–C(12)	1.51(1)	C(8)–C(15)	1.53(1)
C(9)–C(10)	1.49(1)	C(12)–C(13)	1.49(1)

compound **6c** (0.3 g) in aqueous ethanol (1:1 v/v) (20.0 cm^3) was heated and stirred for 30 min, and then cooled to give crystals of *5-methoxycarbonyl-4,6-dimethyl-2-(p-nitrophenyl)-2,5-dihydro-1,2,3-triazine* **18c**, m.p. 133–135 °C (from EtOH) (96%) (Found: C, 54.15; H, 4.95; N, 19.0. $C_{13}H_{14}N_4O_4$ requires C, 53.8; H, 4.8; N, 19.3%); ν_{max}(mull) 1723 cm^{-1} (C=O); $\delta_H(CDCl_3)$ 2.23 (6 H, s, 4- and 6-Me), 3.75 (3 H, s, CO_2Me), 3.93 (1 H, s, 5-H), 7.72 (2 H, d, $J_{AB'}$ 9.34 Hz, AA', H_o of *p*-$NO_2C_6H_4$) and 8.18 (2 H, d, BB', H_m of *p*-$NO_2C_6H_4$); $\delta_C(CDCl_3)$ 21.9, 44.25, 53.15, 114.4, 125.05, 138.75, 142.5, 150.05 and 166.5. The 5-deuterio-derivative of this compound (**18c**) (m.p. 125 °C) was readily obtained by heating of a sample (0.10 g) under reflux in a 1:1 (v/v) mixture of D_2O and MeOD for 4 h.

(b) A solution of compound **7a** (73.3 mg) in aqueous ethanol (1:1 v/v) (20 cm^3) was stirred under reflux for six days and the solvent was removed under reduced pressure to give *5-methoxycarbonyl-2,4,6-triphenyl-2,5-dihydro-1,2,3-triazine* **19a**, m.p. 195–196 °C (from EtOH) (69%) (Found: C, 74.9; H, 5.4; N, 11.1. $C_{23}H_{19}N_3O_2$ requires C, 74.8; H, 5.15; N, 11.4%); ν_{max}(mull) 1742 cm^{-1} (C=O); $\delta_H(CDCl_3)$ 3.66 (3 H, s, CO_2Me), 5.33 (1 H, s, 5-H), 7.14–7.51 (10 H, m, 4- and 6-Ph), 7.96–7.99 (3 H, m, $H_{m,p}$ of 2-Ph), 8.03–8.06 (2 H, m, H_o of 2-Ph); $\delta_C(CDCl_3)$ 38.4, 52.25, 116.2, 123.6, 126.7, 128.75, 128.9, 129.8, 133.3, 134.8, 145.7 and 167.9.

Table 6. Bond angles (°)

C(14)–O(3)–C(13)	117.0(9)	C(16)–O(5)–C(15)	117.2(8)
C(7)–N(1)–N(2)	115.9(8)	N(3)–N(2)–N(1)	121.1(7)
C(4)–N(2)–N(1)	116.7(7)	C(4)–N(2)–N(3)	116.3(7)
C(9)–N(3)–N(2)	116.1(8)	C(2)–C(1)–Br(1)	118.6(8)
C(6)–C(1)–Br(1)	118.4(8)	C(6)–C(1)–C(2)	123.0(1)
C(3)–C(2)–C(1)	118.0(1)	C(4)–C(3)–C(2)	119.0(1)
C(3)–C(4)–N(2)	119.5(8)	C(5)–C(4)–N(2)	119.7(9)
C(5)–C(4)–C(3)	120.6(9)	C(6)–C(5)–C(4)	119.0(1)
C(5)–C(6)–C(1)	119.0(1)	C(8)–C(7)–N(1)	120.3(8)
C(11)–C(7)–N(1)	117.1(9)	C(11)–C(7)–C(8)	122.6(8)
C(9)–C(8)–C(7)	105.4(7)	C(12)–C(8)–C(7)	111.1(8)
C(12)–C(8)–C(9)	109.8(8)	C(15)–C(8)–C(7)	111.4(8)
C(15)–C(8)–C(9)	113.1(8)	C(15)–C(8)–C(12)	106.1(8)
C(8)–C(9)–N(3)	119.6(9)	C(10)–C(9)–N(3)	118.0(9)
C(10)–C(9)–C(8)	122.1(9)	C(8)–C(12)–O(1)	120.0(9)
C(13)–C(12)–O(1)	116.5(9)	C(13)–C(12)–C(8)	123.5(9)
O(3)–C(13)–O(2)	124.0(1)	C(12)–C(13)–O(2)	123.0(1)
C(12)–C(13)–O(3)	112.7(9)	O(5)–C(15)–O(4)	124.0(1)
C(8)–C(15)–O(4)	122.0(1)	C(8)–C(15)–O(5)	114.2(9)

X-Ray Crystal Structure.—The structure of compound **6b** was solved by direct methods, MULTAN,[15] and refined by full-matrix least-squares using SHELX76.[16] Data were corrected for Lorentz and polarisation effects but not for absorption. Hydrogen atoms were included in calculated positions with fixed thermal parameters. The bromine atom was refined anisotropically. The thermal parameters were terms U_{ij} of exp $[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. The atomic scattering factors for non-hydrogen and hydrogen atoms and the anomalous dispersion correction factors for non-hydrogen atoms were taken from the literature.[17–19] All calculations were performed on a VAX 8700 computer. The ORTEP program was used to obtain the drawings.[20] Tables 3–6 present crystal data, fractional atomic co-ordinates, bond lengths and bond angles.†

† *Supplementary data* (section 5.6.3 of Instructions for Authors, January issue). Tables of H-atom co-ordinates and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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