Photochemistry of *N*-Heterocycles. Part 3.[1] Synthesis and Photochemistry of some New Dihydro-1,2,4-triazines and their Quaternary Salts

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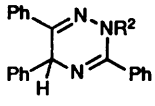
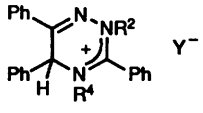
Several new dihydro-1,2,4-triazines, **1b**, **4**, **5**, **16** and **19**, have been synthesized and their structures unambiguously determined. The existence of 1,2- and 1,4-dihydrotriazines, **20** and **22**, described in the literature was ruled out. Irradiation of the aromatic triazines **6** and **15** and the novel quaternary dihydro-1,2,4-triazinium salts **4**, **5**, **19** furnished new evidence for both the reduction pathways and the mechanism of ring-contraction reactions.

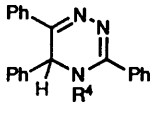
In line with our earlier papers[1,2] we have continued our studies on the photochemically induced ring contractions of 1,2,4-triazines. Irradiation of the 2(4),5-dihydro-1,2,4-triazinium salt **1a** in propan-2-ol furnished the pyrazole **7** and the phenanthroimidazole **12** in the ratio ~2:1 in 91% yield. The HPLC studies[1,3] showed that the aromatic triazine **6** appeared at the beginning of the reaction but also that it had been subsequently reduced and consumed by the end of the reaction.



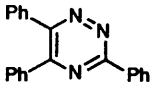
1 R^2 = H
2 R^2 = Me



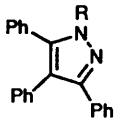
1a R^2 = R^4 = H, Y = Cl
1b R^2 = R^4 = H, Y = I
2a R^2 = Me, R^4 = H, Y = Cl
3a R^2 = H, R^4 = Me, Y = Cl
4 R^2 = R^4 = Me, Y = I
5 R^2 = Me, R^4 = Et, Y = I



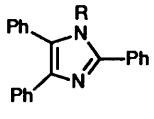
3 R^4 = Me



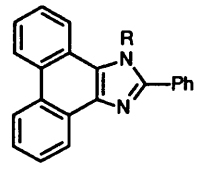
6



7 R = H
8 R = Me



9 R = H
10 R = Me
11 R = Et



12 R = H
13 R = Me

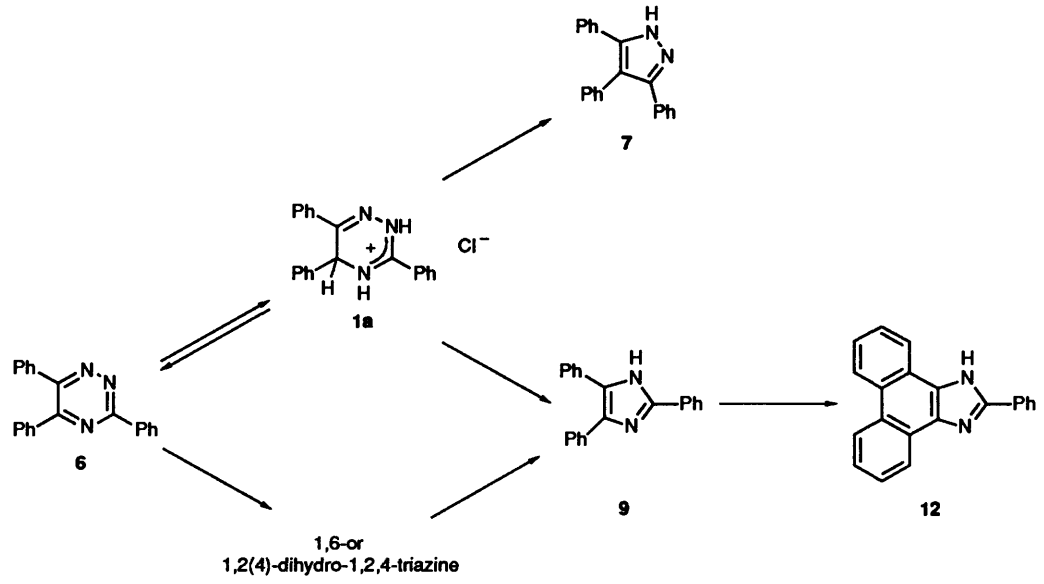
When irradiated in propan-2-ol in the presence of HCl the aromatic triazine **6** is also reduced to the ring-contraction products **7** and **12**, but the ratio of products is shifted in favour of the imidazole **12** (4:1, 79%). This means that a further intermediate dihydro-1,2,4-triazine must be involved in the latter pathway (Scheme 1).

This assumption is supported by the irradiation of the aromatic triazine **6** in absence of HCl. In this case dihydrotriazine **1** was formed (25%) as well as the imidazoles **9** (14.5%) and **12** (3%) and the tetrahydro derivative **21** (41%). The latter could not be separated by preparative methods from compound **1**, and it could be detected only by analytical HPLC. As had been ascertained earlier,[2] the 2,5-dihydrotriazine **1** was found to be stable to irradiation in absence of acid. This means that all of the further photoproducts, **9**, **12** and **21** must be formed *via* another dihydrotriazine. The tetrahydrotriazine **21** is not an intermediate of the ring contraction. It was separately irradiated but proved to be stable to irradiation. The UV spectrum of compound **6** shows no change on addition of up to 10 mole equivalents of HCl in propan-2-ol. This means that the neutral aromatic triazine **6**, rather than its protonated form, is photoreduced. The acid promotes only the subsequent ring contractions of dihydro compounds **1** to give the pyrazole **7** and the imidazoles **9** and **12**.

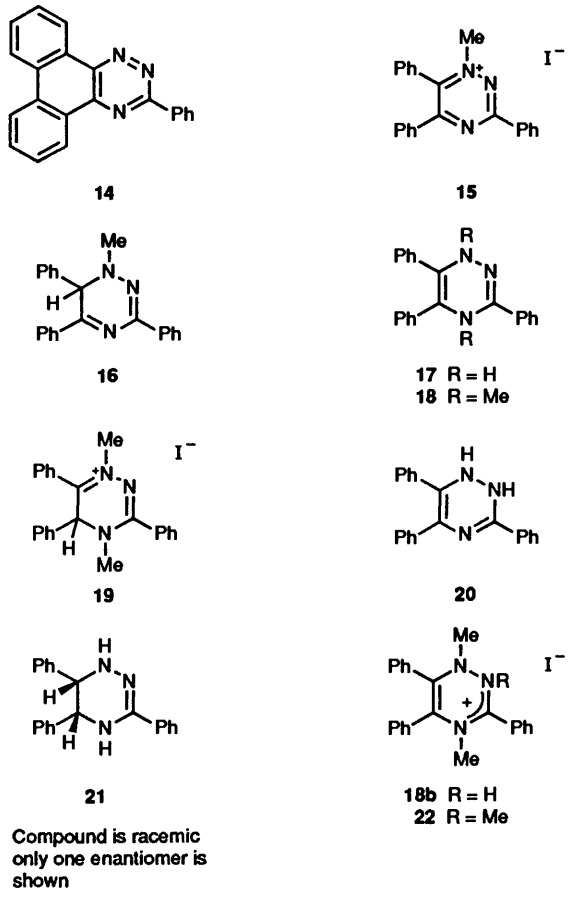
One of the possible intermediates of the ring contraction starting from the aromatic triazine **6** may be the 1,6-dihydro-1,2,4-triazine. Accordingly, *via* the method of *Atkinson* and *Cossey*,[4] 1-methyl-3,5,6-triphenyl-1,6-dihydro-1,2,4-triazine **16** was prepared, and its structure unambiguously determined by NMR and MS spectroscopy. Compound **16** was then irradiated, in the presence of an equimolar amount of hydrogen chloride. The starting material decomposed completely but none of the expected photoproducts were formed. 1-Methyl-3,5,6-triphenyl-1,2,4-triazinium iodide **15** was also irradiated, in acetonitrile. A similar disproportionation took place as in the case of triazinium salt **1a**[2] and furnished the imidazole **9** and the phenylphenanthrotriazine **14**. These experiments ruled out the 1,6-dihydro-1,2,4-triazine as being a possible intermediate of the photochemical ring contraction of the aromatic triazine **6**.

The only hints on the existence of 1,4-dihydro-3,5,6-triphenyl-1,2,4-triazine **17** are found in *Pinson*'s work.[5] It was claimed that compound **17** is an intermediate in the electrochemical reduction of the aromatic triazine **6**, and that it rearranges into the stable 1,2-dihydro derivative **20** and 2(4),5-dihydro compound **1**. We therefore reproduced the electrochemical reduction of the aromatic triazine **6**. Reduction on the first plateau at pH 3.60 (E − 0.70 V) furnished the 2,5-dihydro-1,2,4-triazine **1**, and the pyrazole **7** rather than the 1,2-dihydro compound **20** † In the second step (pH 3.60; E − 1.20 V) the

† The reduction of the aromatic triazine **6** with zinc/acetic acid has also been described.[4,6] *Metze* and *Scherowsky* proposed that the product had the 1,2-dihydro structure **20**.[6] We repeated the reduction, but the products were the 2(4),5-dihydrotriazine **1**, the imidazole **9** and the pyrazole **7**.



Scheme 1 Irradiation of 2(4),5-dihydro-1,2,4-triazine **1a** and aromatic 1,2,4-triazine **6** in propan-2-ol in the presence of an equimolar amount of HCl



2(4),5-dihydrotriazine **1** was reduced, resulting in *cis*-3,5,6-triphenyl-1,4,5,6-tetrahydro-1,2,4-triazine **21** and in the corresponding imidazole **9**. Our aim was to synthesize compound **18** containing the 1,4-dihydro structure fixed by methyl groups. According to *Shvaika* and *Fomenko*'s [7] method, 3-methyl-2,4,5-triphenyloxazolium iodide was treated with methylhydrazine to give the dihydro-1,2,4-triazinium iodide **19**. The structure assignment will be discussed later, together with that of the isomeric triazinium iodide **4**. Irradiation of compound **19** furnished only the 1-methylphenanthroimidazole **13**, in excellent yield (90%), but no trace of the 1-methylpyrazole **8** could be detected. The ring contraction must proceed with high probability *via* the 1,4-dihydro compound **18**. In order to confirm this assumption some attempts were made to synthesize compound **18** starting with the quaternary salt **19**. When compound **19** was treated with a catalytic amount of silver carbonate in tetrahydrofuran (THF)–acetonitrile mixture the isomeric iodide **18b** was formed, as seen from the ^{1}H NMR and mass spectra of the crude product. We were unable to purify compound **18b** without decomposition.

Compound **1** was heated with excess of methyl iodide in a sealed tube. In contrast to the literature report [6] the product proved to be the 2,4-dimethyl-2,5-dihydrotriazinium iodide **4** rather than a trimethyltriazinium derivative **22**. The same product was obtained starting from both compounds **2** and **3**.

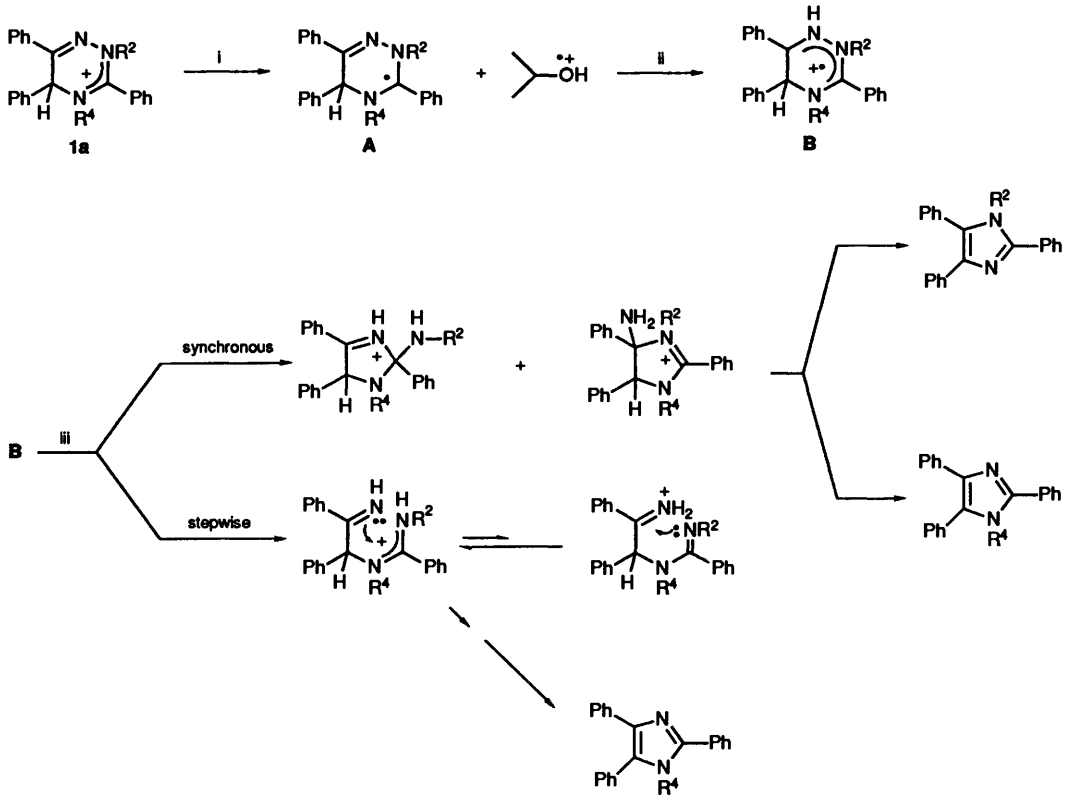
Table 1 shows the ^{1}H and ^{13}C NMR data of various dihydrotriazines **1b**, **2**–**4**, **16** and **19**. According to the chemical shift of the methyl carbon atom in compound **16** it could be in position 1 or 2. From its characteristic chemical shift [2] (δ_C 145.9) the ring carbon C-3 is an sp^2 carbon atom which rules out the 2,3-dihydro structure. The methyl group must be in position 1. The indicated hydrogen must be on a ring carbon, which means that the correct structure for compound **16** is the 1,6-dihydro structure. The significant deshielding effect on the methyl carbon in compound **19** makes its position on a charged nitrogen (N-1) probable. The fragmentation pattern in the mass spectra of compounds **19** and **4** supports their structures. The fragmentation of compound **19** starts with the loss of HI to furnish the radical cation with *m*/*z* 339, which is followed by a methyl radical cleavage. On the other hand the main fragmentation route of compound **4** begins with the loss of methyl iodide, and the subsequent loss of a hydrogen atom [metastable peak *m*/*z* = 323 (325 ⟶ 324)].

Irradiation of compound **3a** in propan-2-ol furnished the 1-methylpyrazole **8** and both of the expected phenanthroimidazoles **12** and **13**.[2] The imidazoles **9** and **10** were formed by the loss of N(2) and N(1), respectively. The irradiation of 2,4-dimethyldihydrotriazinium iodide **4** under the same conditions gave, as expected, the pyrazole **8** and the imidazole **13**. The formation of the imidazole **10** could proceed either by the loss of N(1) or N(2) of the triazine ring. The asymmetrically substituted 4-ethyl-2-methyl-2,5-dihydro-1,2,4-triazinium iodide **5** was also synthesized and irradiated. In this

Table 1 Characteristic ^1H and ^{13}C NMR data for various dihydrotriazines, **1b**, **2–4**, **16** and **19**

	^1H NMR			^{13}C NMR				
Compound	1/2-Me	4-Me	CH	1/2-Me	4-Me	C-3	C-5	C-6
2[a]	3.4		5.9	41.6		143.4	56.7	154.0
3[a]		3.1	5.3		39.5	148.2	57.6	153.1
3[b]		3.1	5.8		39.1	148.5	55.2	152.8
16[b]	3.3		5.5	42.3		145.9	153.1	56.2
19[b]	3.91	3.17	6.31	47.66	39.11	159.21	62.45	155.66
4[b]	3.54	3.11	6.57	43.48	40.34	150.23	57.17	154.83
1b[b]			6.45			150.47	50.49	153.05

[a] In $CDCl_3$. [b] In $(CD_3)_2SO$.



Scheme 2 Only routes leading to imidazoles are shown. *Reagents and conditions:* i, propan-2-ol, *hv* (single-electron transfer); ii, H^+; iii, $H^+ + e^-$, or $H^\bullet$

case the only imidazole product was compound **11**. Owing to the long reaction time the photo-oxidation product **14** also appeared in the reaction mixture. The exclusive formation of compound **11** as an imidazole product supports our concept for the stepwise manner of the electron, proton (or atomic hydrogen) uptake and ring opening of common key intermediate **B**[1] of the ring-contraction products and seems to rule out the synchronous formation of ring-contraction intermediates (Scheme 2).

The equilibrium between the protonated intermediates must be shifted in favour of the amidinium structure whose ring closure furnishes only one of the imidazole-type products containing the R^4 substituent. With this concept of the mechanism the exclusive formation of compound **11** could be well explained by the irradiation of compound **5**.

Experimental

M.p.s were measured on a hot-stage melting point apparatus and are uncorrected. UV spectra were measured on a Perkin-Elmer 554 spectrophotometer for samples in ethanol, unless otherwise stated. IR spectra were obtained with a Zeiss Specord 75 or a Perkin-Elmer 397 spectrometer. 1H and ^{13}C NMR spectra were recorded on a JEOL FX-100, Bruker WP80, or Bruker WM 300 spectrometer, with $SiMe_4$ as internal reference. *J* Values are given in Hz. Mass spectra were obtained with a Varian MAT CH5, a Finnigan MAT 90, or a Varian MAT 311A spectrometer. All spectra were measured in an EI mode.

Column and analytical TLC were carried out on Merck Kieselgel 60 (0.063–0.2 mm) and Merck Kieselgel 60 F_{254} Alufolien, respectively. For preparative TLC (PLC) Merck PSC-ready plates (20 × 20 cm, 2 mm) were used.

Synthesis of 1,2,4-*Triazine Derivatives.*—1-*Methyl*-3,5,6-*triphenyl*-1,2,4-*triazinium iodide* **15**. A mixture of 3,5,6-triphenyl-1,2,4-triazine **6**[8] (4.0 g, 13 mmol), methyl iodide (20 cm^3, 0.32 mol) and dry nitromethane (200 cm^3) was heated at 60 °C for 12 h. The solution was evaporated and the residue was triturated with dry diethyl ether, and the crystalline product was filtered off, washed successively with nitromethane and diethyl ether, and dried over P_2O_5 in a vacuum desiccator to give compound **15** (2.40 g, 41.2%), m.p. 183 °C, (lit.,[4] 184 °C)

(Found: N, 8.95; I, 27.0. Calc. for $C_{22}H_{18}IN_2 \cdot H_2O$; N, 8.7; I, 27.3%); λ_{max}(1g ε) (MeCN)/nm 220 (4.45), 273 (4.35) and 392 (3.66); ν_{max}(KBr)/cm^{-1} 3085, 1530, 1430, 1385, 665 and 530; δ_H($CDCl_3$) 4.38 (3 H, s, Me), 7.30 (2 H, m, ArH), 7.4–7.7 (9 H, m, ArH), 8.0 (2 H, m, ArH) and 8.55 (2 H, m, ArH); *m/z* (70 eV; 200 °C) 309 (4.5%, M − MeI), 179 (16.8, PhCH=CPh), 178 (100, C_2Ph_2), 152 (6.2, 178 − C_2H_2), 142 (11.2), 128 (11.2), 127 (7.9), 103 (6.7, PhCN) and 76 (4.5); *m** 307 (309 ⟶ 308), 294 (296 ⟶ 295), 102.8 (309 ⟶ 178), 129.5 (178 ⟶ 152), 56.2 (103 ⟶ 76) and 33.8 (77 ⟶ 51).

1-*Methyl*-3,5,6-*triphenyl*-1,6-*dihydro*-1,2,4-*triazine* **16**. $NaBH_4$ (1.0 g, 22.2 mmol) was added to a stirred mixture of compound **15** (1.0 g, 2.2 mmol) in methanol (25 cm^3) at ambient temperature. The mixture was stirred for 2 h, and then was acidified with glacial acetic acid. The product was filtered off, and recrystallised from ethanol to obtain compound **16** (0.5 g, 69.4%), m.p. 143–144 °C (lit.,[4] 142–144 °C) (Found: C, 80.9; H, 6.0; N, 13.2. Calc. for $C_{22}H_{19}N_3$; C, 81.2; H, 5.9; N, 12.9%); λ_{max}(1g ε)/nm 275 (4.36) and 421 (3.56); ν_{max}(KBr)/cm^{-1} 3030, 2930, 1465, 1270, 1215, 1025, 780, 755 and 700; δ_H($CDCl_3$) 3.31 (3 H, s, NMe), 5.48 (1 H, s, C*H*Ph), 7.18–7.47 (11 H, m, ArH) and 8.06–8.13 (4 H, m, ArH); δ_C($CDCl_3$) 42.27 (Me), 56.21 (CH), 125.01, 127.76, 127.86, 128.18, 128.23, 128.66, 128.87, 131.29, 133.73, 135.89 and 135.92 (PhCs), 145.9 (C-3) and 153.15 (C-5); *m/z* (70 eV; 200 °C) 326 (9.0%, M + 1), 325 (36.0, M$^+$), 324 (7.3, M − H), 283 (8.4, M − CH_2N_2), 282 (33.7, M − MeN_2), 249 (5.6, M − Ph + H), 248 (28.9, M − Ph), 180 (15.7, PhCH=CHPh), 179 (100, PhCH=CPh), 178 (38.2, C_2Ph_2), 177 (4.5, 178 − H), 152 (4.5, 178 − C_2H_2), 118 (29.2, PhCNMe), 104 (6.7, PhCNH), 103 (6.8, PhCN), 77 (10.7), 76 (5.1), 51 (5.6) and 42 (10.1, CH_2N_2); *m** 323 (325 ⟶ 324), 244.8 (325 ⟶ 282), 189.2 (325 ⟶ 248), 113.5 (282 ⟶ 179), 56.2 (248 ⟶ 118), 177 (179 ⟶ 178), 130 (178 ⟶ 152), 50.2 (118 ⟶ 77), 56.2 (103 ⟶ 76) and 33.8 (77 ⟶ 51).

1,4-*Dimethyl*-3,5,6-*triphenyl*-4,5-*dihydro*-1,2,4-*triazinium iodide* **19**. A mixture of 2,4,5-triphenyloxazole[9] (4.4 g, 14.8 mmol) and methyl iodide (4.5 cm^3, 72 mmol) was heated in a sealed tube for 10 h at 100–120 °C. The crystalline product was filtered off, washed with diethyl ether, and dried over P_2O_5 in a vacuum desiccator to give 3-*methyl*-2,4,5-*triphenyloxazolium iodide* (2.8 g, 43.1%), m.p. 198–205 °C (decomp.) (Found: C, 59.9; H, 4.0; I, 28.85. $C_{22}H_{18}INO$ requires C, 60.15; H, 4.1; I, 28.9%); ν_{max}(KBr)/cm^{-1} 3050, 1600, 1560, 1470, 1425, 1400, 1350, 735 and 650; δ_H[$(CD_3)_2SO$] 3.54 (3 H, s, Me), 7.2–7.8 (13 H, m, ArH) and 7.8–8.2 (2 H, m, ArH).

The mixture of 3-methyl-2,4,5-triphenyloxazolium iodide (2.2 g, 5 mmol), toluene-*p*-sulfonic acid (0.38 g, 2 mmol), methylhydrazine (0.5 cm^3, 10 mmol) and ethanol (10 cm^3) was stirred for 4 h at ambient temperature. The product was filtered off, and crystallised from ethanol–diethyl ether to give *compound* **19** (0.9 g, 38.5%), m.p. 183 °C (Found: C, 56.85; H, 4.4; I, 26.6; N, 8.5. $C_{23}H_{22}IN_3 \cdot H_2O$ requires C, 56.9; H, 4.6; I, 26.15; N, 8.5%); λ_{max}(1g ε)/nm 259 (3.7); ν_{max}(KBr)/cm^{-1} 3036, 1560, 1470, 1375, 1185, 760 and 700; δ_H[$(CD_3)_2SO$] 3.17 (3 H, s, NMe), 3.91 (3 H, s, N^+Me), 6.31 (1 H, s, 5-H) and 7.48–7.74 (15 H, m, ArH); δ_C[$(CD_3)_2SO$] 39.11 (NMe), 47.66 (N^+Me), 62.45 (C-5), 127.82, 128.67, 128.99, 129.10, 129.68, 130.31, 132.21, 132.64 and 134.81 (ArCs), 155.66 (C-6) and 159.21 (C-3); *m/z* (70 eV; 200 °C) 340 (16.3%, M$^+$ − I), 339 (56.1, M − HI), 325 (27.0, M − MeI), 324 (100, 339 − Me), 311 (10.7), 310 (44.4), 309 (24.7), 294 (3.9, $C_{21}H_{14}N_2$), 235 (11.2), 179 (6.7), 178 (31.5, C_2Ph_2), 169 (10.1), 165 (7.9, $C_{13}H_9$), 142 (14.6), 132 (6.7), 128 (28.0), 127 (15.7), 119 (6.7), 118 (69.7, PhCNMe), 105 (18.5), 104 (8.4), 103 (22.5, PhCN), 91 (7.3, C_7H_7), 77 (39.3), 76 (6.7) and 43 (7.9); *m** 309.5 (339 ⟶ 324), 43.1 (324 ⟶ 118), 308 (310 ⟶ 309), 280 (309 ⟶ 294), 176 (178 ⟶ 177), 46.5 (178 ⟶ 91), 50.2 (118 ⟶ 77) and 56.2 (103 ⟶ 77).

1,4-*Dimethyl*-3,5,6-*triphenyl*-1,4-*dihydro*-1,2,4-*triazinium iodide* **18b**. Compound **19** (581.4 mg, 1.24 mmol) was dissolved in a mixture of acetonitrile (5 cm^3) and THF (8 cm^3). Silver carbonate (56 mg, 0.2 mmol) was added to the solution and the mixture was stirred for 7 h at ambient temperature. The product was filtered off, washed with THF, and dried over P_2O_5 in a vacuum desiccator to give the crude title compound **18b**, δ_H($CDCl_3$) 4.04 (3 H, s, NMe), 4.16 (3 H, s, NMe) and 7.18–7.52 (15 H, m, ArH); *m/z* (70 eV; 200 °C), 339 (21%, M$^+$ − HI), 310 (100), 309 (39.0), 234 (21.0), 178 (54.5), 118 (23.0) and 77 (12.0).

2,4-*Dimethyl*-3,5,6-*triphenyl*-2,5-*dihydro*-1,2,4-*triazinium iodide* **4**. (*a*) A mixture of compound **1**[2] (1.0 g, 3.2 mmol) and methyl iodide (1 cm^3, 16 mmol) was heated in a sealed tube for 10 h at 140 °C. The precipitate was filtered off, washed with diethyl ether, and crystallised from acetone to furnish *compound* **4** (0.70 g, 46.0%), m.p. 242 °C (Found: C, 59.0; H, 4.85; I, 27.5; N, 8.8. $C_{23}H_{22}IN_3$ requires C, 59.0; H, 4.75; I, 27.2; N, 9.0%); ν_{max}(KBr)/cm^{-1} 3040, 1575, 1500, 1470, 1430, 725 and 660; δ_H[$(CD_3)_2SO$] 3.11 (3 H, s, NMe), 3.54 (3 H, s, NMe), 6.75 (1 H, s, 5-H) and 7.34–8.04 (15 H, m, ArH); δ_C[$(CD_3)_2SO$] 40.34 (NMe), 43.48 (NMe), 57.17 (C-5); 124.89, 127.21, 127.91, 128.05, 128.27, 129.02, 129.89, 129.96, 130.15, 130.61, 132.23, 132.81 and 134.91 (PhCs), 150.23 (C-3) and 154.83 (C-6); *m/z* (70 eV; 200 °C) 339 (6.7%, M$^+$ − HI), 326 (20.2, M − CH_2I), 325 (80.8, M − MeI), 324 (73.2), 311 (11.1), 310 (43.0), 309 (17.8), 248 (37.7), 221 (19), 179 (46.6, PhCH=CPh) 178 (40.8, C_2Ph_2), 165 (8.6, $C_{13}H_9$), 142 (31.4), 127 (10.7), 119 (14.4), 118 (100, PhCNMe), 103 (12.4 PhCN) and 77 (12.3); *m** 323 (325 ⟶ 324), 308 (310 ⟶ 309), 176 (178 ⟶ 177), 129.5 (177 ⟶ 152), 70.2 (118 ⟶ 91), 50.2 (118 ⟶ 77), 57 (104 ⟶ 77), 56.2 (103 ⟶ 76) and 33.8 (77 ⟶ 51).

(*b*) Compound **4** was similarly obtained as described under method (*a*) starting with a mixture of compound **2** (1.1 g, 3.4 mmol) and methyl iodide (1.5 cm^3, 16.9 mmol) in 82.3% yield. The product was completely identical (m.p., IR, ^1H and ^{13}C NMR spectra) with the sample prepared as described in method (*a*).

(*c*) Compound **4** was similarly obtained by reaction of compound **3** (0.2 g, 0.6 mmol) and methyl iodide (0.2 cm^3, 3.1 mmol) in 63.1% yield and proved to be identical with the sample prepared as described in method (*a*).

4-*Ethyl*-2-*methyl*-3,5,6-*triphenyl*-2,5-*dihydro*-1,2,4-*triazinium iodide* **5**. A mixture of 2-methyl-3,5,6-triphenyl-2,5-dihydrotriazine **2** (0.8 g, 2.45 mmol) and ethyl iodide (0.97 cm^3, 12.3 mmol) was heated in a sealed tube for 6 h at 140 °C. The precipitate was filtered off, washed with dry diethyl ether, and crystallised from acetone to obtain *compound* **5** (0.81 g, 68.7%), m.p. 280–282 °C (Found: C, 59.7; H, 5.15; I, 26.2; N, 8.6. $C_{24}H_{24}IN_3$ requires C, 59.9; H, 5.03; I, 26.4; N, 8.7%); δ_H($CDCl_3$) 1.17 (3 H, t, *J* 7, CH_2*Me*), 3.57 (3 H, s, NMe), 3.86 (2 H, q, *J* 7, C*H*$_2$Me), 6.82 (1 H, s, 5-H) and 7.28–8.16 (15 H, m, Ph); *m/z* (70 eV; 210 °C) 353 (23%, M$^+$ − HI), 324 (100, M − HI − Et), 310 (14.0), 254 (5.0), 193 (10.0), 178 (20.0, C_2Ph_2), 132 (25.5), 118 (62.5, PhCNMe), 105 (51.5, PhCHNH) and 77 (33.0).

Reduction of 3,5,6-*Triphenyl*-1,2,4-*triazine* **6**.—A mixture of the aromatic triazine **6** (1.0 g, 3.2 mmol), acetic acid (15 cm^3) and zinc dust (1.5 g) was refluxed for 1 h. The solution was decanted from the unchanged zinc dust and evaporated under reduced pressure. The residue was triturated with 10% aq. ammonia and the product was filtered off, and washed with water. The crude product was chromatographed on a column (10 g; CH_2Cl_2) to furnish the imidazole **9**[9] (0.25 g, 26.4%), the pyrazole **7**[10] (50 mg, 5.3%) and 3,5,6-triphenyl-2(4),5-dihydro-1,2,4-triazine **1** (0.15 g, 15.1%). The latter was completely identical (m.p., IR, NMR) with the sample prepared earlier.[1]

Electrochemical Experiments.—The following instruments

were used: Standard Potentiostat Wenking ST72, Voltage Scan Generator Wenking Model VSG 72 (Bank Electronic Instruments Gottingen, G), and Omnigraphic XY-recorder 2000 (Houston Instruments). A calomel electrode was applied as the reference electrode.

The cyclic voltammetric measurements were carried out under argon in acetonitrile solutions with lithium perchlorate as conducting salt in a 35 cm^3 polarographic cell at ambient temperature and a platinum working electrode.

(±)-cis-3,5,6-*Triphenyl*-1,4,5,6-*tetrahydro*-1,2,4-*triazine* **21**. In an electrolytic cell (volume 180 cm^3) compound **1** (600 mg, 1.93 mmol) was reduced in a manner similar to that described by Pinson *et al.*[5] – mercury was used as working electrode and the reaction was carried out in buffer solution [citric acid (5.3 g), 1 mol dm^{-3} NaOH (14 cm^3), water (110 cm^3), acetonitrile (125 cm^3), sodium perchlorate (2.0 g), pH 3.6] under argon within a period of 1.5 h at −1.2 V. The crude product was precipitated by addition of sodium hydrogen carbonate and crystallised from ethanol to furnish the title *compound* **21** (205 mg, 34%), m.p. 225–227 °C; λ_{max}(lg ε)/nm 292 (3.65); ν_{max}(KBr)/cm^{-1} 3430, 3270 (NH), 1620, 1595, 1450, 770 and 695; δ_H[$(CD_3)_2SO$] 4.30 (1 H, d, *J* 3.5, 5-H), 4.66–4.80 (1 H, m, 6-H), 6.20 (1 H, br s, NH), 6.6–7.23 (10 H, m, Ph), 7.27–7.50 (3 H, m, Ph) and 7.67–7.90 (2 H, m, Ph). Upon addition of D_2O, the multiplet at 4.66–4.80 (6-H) narrows to a doublet (*J* 3.5); *m/z* (70 eV; 184 °C) 313 (26%, M^+), 209 (14), 180 (15), 106 (100), 105 (52), 104 (74) and 77 (38).

Electrolytic reduction of 3,5,6-*triphenyl*-1,2,4-*triazine* **6**. The aromatic triazine **6** (150 mg, 0.48 mmol) was reduced similarly to compound **1** but at 10 °C with a −0.7 V electrode potential. The pyrazole **7** (10 mg, 7%) precipitated from the reaction mixture, and the pyrazole **7** and dihydrotriazine **1** could be detected in solution by HPLC.

Irradiations.—Solutions of triazine derivatives in solvent (150 cm^3) were irradiated under nitrogen at ambient temperature in Pyrex immersion-well reactors, using high-pressure mercury lamps (Philips HPK 125). The photoreactions were monitored by TLC [toluene–methanol (10:2); hexane–dioxane–triethylamine (8:4:2)] or analysed with HPLC. HPLC was carried out on a column (Nucleosil C_{18}, 250 × 4.6 mm), using a Waters 6000A multisolvent delivery system, a Rheodyne 7125 injection valve (20 mm^3), a Biotronik BT 3030 UV detector working at 254 nm, a Biorad two-pen chart recorder, and methanol–water (80:20) as eluant.

(*a*) 3,5,6-Triphenyl-1,2,4-triazine **6** (310.1 mg, 1 mmol) was irradiated for 57 h in propan-2-ol. The precipitate was filtered off and was shown to be identical with the 2,5-dihydrotriazine **1**. The solution was evaporated and an aliquot of the residue was analysed by HPLC. From these results the yield of products was calculated: the 2,5-dihydrotriazine **1** (79 mg, 25.4%), the 1,4,5,6-tetrahydrotriazine **21** (128 mg, 41.2%), the triphenylimidazole **9** (43 mg, 14.5%) and the phenylphenanthroimidazole **12**[11] (9 mg, 3.1%).

(*b*) 1-Methyl-3,5,6-triphenyl-1,2,4-triazinium iodide **15** (467.4 mg, 1.04 mmol) was irradiated in acetonitrile for 84 h. The solution was evaporated and the residue was separated on PLC plates, with toluene–methanol (8:2) as eluant, to yield the imidazole **9** (98.5 mg, 32.1%) and the phenanthrotriazine **14**[2] (108.8 mg, 34.2%).

(*c*) 1,4-Dimethyl-3,5,6-triphenyl-4,5-dihydro-1,2,4-triazinium iodide **19** (419.2 mg, 0.9 mmol) was irradiated in propan-2-ol for 10 h. The reaction mixture was evaporated, and the residue was crystallised from acetone to furnish the 1-methylphenanthroimidazole **13**[2] (250 mg, 90.4%).

(*d*) 2,4-Dimethyl-3,5,6-triphenyl-2,5-dihydro-1,2,4-triazinium iodide **4** (462.5 mg, 0.99 mmol) was irradiated in propan-2-ol for 96 h. The reaction mixture was evaporated, the residue was taken up in acetone (10 cm^3), and the insoluble material was filtered off. The latter proved to be unchanged starting material **4** (18.1 mg, 3.9% recovery). The products in the filtrate were separated by PLC, with toluene–methanol (8:2) as eluant, to give the 1-methylpyrazole **8**[12] (34.2 mg, 11%), the 1-methylphenanthroimidazole **13** (31.4 mg, 10.3%) and the starting material **4** (131 mg, 28.3% recovery).

(*e*) 4-Ethyl-2-methyl-3,5,6-triphenyl-2,5-dihydro-1,2,4-triazinium iodide **5** (485.1 mg, 0.96 mmol) was irradiated in propan-2-ol for 100 h. The insoluble material was filtered off and identified as starting material **5** (135 mg, 27.8% recovery). The filtrate was evaporated and the residue was chromatographed on PLC to obtain 1-ethyl-2,4,5-triphenylimidazole **11** (46.9 mg, 15.2%), m.p. 119 °C (lit.,[13] 119.5–120 °C); $\delta_H(C_5D_5N)$ 1.40 (3 H, t, *J* ~ 7, CH_2*Me*), 4.56 (2 H, q, *J* ~ 7, CH_2Me), 7.1–7.35 (9 H, m, Ph), 7.60–7.80 (4 H, m, Ph) and 7.95 (2 H, m, Ph); the pyrazole **7** (21.5 mg, 7.3%) and the phenanthrotriazine **14** (70.1 mg, 24%). In addition, starting material (58.7 mg, 20.3%) was recovered.

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