Photochemistry of *N*-Heterocycles. Part 1.† Synthesis and Photochemistry of some 2(4),5-Dihydro-1,2,4-triazines. *X*-Ray Molecular Structure of 1-(4-Methyl-3,5,6-triphenyl-1,4,5,6-tetrahydro-1,2,4-triazin-6-yl)ethanol

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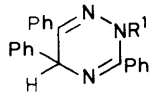
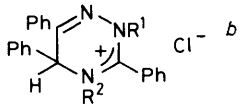
Ethanolic solutions of the hydrochlorides of the mostly new 2(4),5-dihydro-1,2,4-triazines (**1**)—(**4**) were irradiated with a high-pressure mercury immersion lamp ($\lambda \geqslant 300$ nm). The salts (**1a**)—(**3a**) underwent reductions, ring contractions, and dehydrogenations upon irradiation to yield pyrazoles (**5**) and (**6**) along with phenanthroimidazoles (**9**) and (**10**). In addition, the 4-methyl-3,5,6-triphenyl-4,5-dihydro-1,2,4-triazinium chloride (**3a**) furnished the 6-(1-hydroxyethyl) adduct (**11**) whose structure was assigned on the basis of its ^{1}H and ^{13}C n.m.r. spectra, and an *X*-ray diffraction study. The 4-(3-hydroxypropyl)dihydrotriazinium chloride (**4a**) led, in addition to the expected pyrazole (**5**), to two new products: the aromatic triazine (**15**) and the oxazinotriazine (**21**) by photoelimination and intramolecular photosubstitution, respectively.

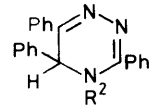
The study of the photochemistry of nitrogen heterocycles has attracted continued interest during the past two decades.[2-5] In order to establish whether aza-di-π-methane rearrangements are feasible in the 2(4),5-dihydro-1,2,4-triazine series, compounds (1)—(3) were prepared and irradiated under various conditions.‡



(1) [a] R^1 = H
(2) R^1 = Me



(**1a**) $R^1 = R^2$ = H
(**2a**) R^1 = Me, R^2 = H
(**3a**) R^1 = H, R^2 = Me
(**4a**) R^1 = H, R^2 = $[CH_2]_3OH$



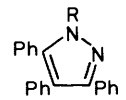
(3) R^2 = Me
(4) R^2 = $[CH_2]_3OH$

[a] The predominant tautomeric form in ethanolic solution[1] is shown. For details see the Experimental section. [b] The u.v. spectra of ethanolic solutions of the 2(4),5-dihydrotriazines (1)—(4) did not change after addition of more than 1 mol equiv. of aqueous hydrogen chloride; *i.e.* only monoprotonation takes place. All four compounds exhibit identical u.v. spectra after monoprotonation, which demonstrates that the imine nitrogen atoms of the amidine moieties have been protonated.

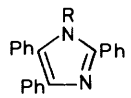
† For a preliminary communication, see ref. 1.
‡ For similar studies in the related diazine series, see ref. 6.

At the very beginning[1] of our studies the dihydro-1,2,4-triazines (**1**)—(**3**) were found to be stable in ethanolic solution to irradiation with a high-pressure mercury lamp ($\lambda \geqslant 300$ nm). In contrast, the salts (**1a**)—(**3a**) gave, on irradiation under the same conditions, the corresponding pyrazoles (**5**) and (**6**) as the main products; *i.e.* a novel photochemical ring contraction took place rather than an aza-di-π-methane rearrangement.

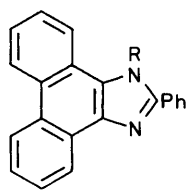
In the preliminary phase of our studies it was also shown that formation of the pyrazoles (**5**) and (**6**) takes place with loss of the nitrogen atom from position 4 of the dihydro-1,2-4-triazine ring. In addition to pyrazoles (**5**) and (**6**) phenanthroimidazoles (**9**) and (**10**), respectively, were also isolated. Irradiation of the salt (**2a**) furnished both the non-methylated (**9**) and the methylated phenanthroimidazole (**10**), demonstrating that, during formation of the imidazole ring, either of the nitrogen atoms in positions 1 and 2 of the dihydro-1,2,4-triazine ring may be lost.



(**5**) R = H
(**6**) R = Me



(**7**) R = H
(**8**) R = Me



(**9**) R = H
(**10**) R = Me

The loss of the nitrogen atom occurs in the form of ammonium and alkylammonium ions, respectively, *i.e.* all ring contractions are reductions. This observation suggests an

explanation of why only the salts (**1a**)—(**3a**) but not the parent triazines (**1**)—(**3**) are photoactive: only the excited salts are able to be reduced but not the parent triazines. 1,2- and 1,3-Azoles are known to rearrange into each other upon irradiation.[7] The above conclusions are therefore correct provided that no pryazole → imidazole interconversions take place in our cases. The occurrence of such rearrangements under our reaction conditions was ruled out by separate irradiations of both types of compounds.

The triphenylpyrazole (**5**) proved to be photoinactive in ethanol even in the presence of hydrogen chloride. Neither did the triphenylimidazole (**7**) rearrange under the same conditions into the corresponding pyrazole (**5**), but it was quantitatively dehydrogenated to the phenanthroimidazole (**9**).* Consequently, the phenanthroimidazoles (**9**) and (**10**), and the pyrazoles (**5**) and (**6**) are both formed by mutually independent routes from the corresponding salts (**1a**)—(**3a**) of dihydro-1,2,4-triazines, the triphenylimidazoles (**7**) and (**8**) being the precursors of the phenanthro derivatives. A further product was obtained from salt (**3a**) in addition to the expected pyrazole (**5**) and phenanthroimidazole (**9**) on irradiation in ethanolic solution in the presence of excess hydrochloric acid. The i.r. and ^{1}H n.m.r. spectra of the product are consistent with either of the structures (**11**) or (**12**). In Table 1 the chemical shifts of C-3 and C-6 in the ^{13}C n.m.r. spectra of the starting material (**3**) are shown as well as those of the photoaddition product (**11**) or (**12**) and of two model compounds (**13**) and (**14**). These data seem to support structure (**11**). An *X*-ray diffraction study of the adduct furnished the final unambiguous proof of its structure.† The Figure shows the computer drawing and contains three chiral centres, but only one racemic mixture (67*RS*, 6*RS*, 5*SR*) could be isolated. The formation of other epimers is not ruled out,

(**11**) (**12**) (**13**) (**14**)

Table 1. Some characteristic ^{13}C n.m.r. values of compounds (**3**) and (**11**)—(**14**)

	δ_C[(CD$_3$)$_2$SO]/p.p.m.				
Carbon	(**3**)	(**11**) or (**12**)		(**13**)	(**14**)
3	148.54	145.53			148.22
6	152.76		145.53		148.22
2				157.47	

Table 2. Atomic fractional co-ordinates for the non-hydrogen atoms of compound (**11**) with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
O(69)	0.466 5(1)	−0.159 6(1)	0.576 3(1)
N(1)	0.566 6(1)	0.009 6(1)	0.623 0(1)
N(2)	0.433 3(2)	0.054 9(1)	0.584 9(1)
N(4)	0.356 5(2)	0.050 2(1)	0.743 3(1)
C(3)	0.340 8(2)	0.075 1(1)	0.647 6(1)
C(5)	0.489 8(2)	0.000 5(1)	0.783 5(1)
C(6)	0.540 9(2)	−0.051 4(1)	0.698 5(1)
C(31)	0.200 5(2)	0.121 3(1)	0.606 5(1)
C(32)	0.210 9(2)	0.191 7(1)	0.552 0(1)
C(33)	0.079 9(3)	0.232 4(1)	0.510 5(1)
C(34)	−0.062 8(2)	0.202 3(1)	0.523 4(2)
C(35)	−0.075 0(2)	0.133 1(1)	0.577 2(2)
C(36)	0.054 7(2)	0.092 6(1)	0.619 0(2)
C(41)	0.278 9(3)	0.091 8(1)	0.817 2(1)
C(51)	0.620 1(2)	0.051 3(1)	0.836 5(1)
C(52)	0.690 1(3)	0.028 1(1)	0.928 8(1)
C(53)	0.817 8(3)	0.069 8(1)	0.973 9(2)
C(54)	0.873 8(3)	0.136 4(1)	0.928 3(2)
C(55)	0.800 6(3)	0.162 0(1)	0.839 4(2)
C(56)	0.674 1(2)	0.119 8(1)	0.793 6(1)
C(61)	0.692 5(2)	−0.095 3(1)	0.733 0(1)
C(62)	0.707 8(2)	−0.144 9(1)	0.815 4(1)
C(63)	0.844 6(2)	−0.185 1(1)	0.847 2(1)
C(64)	0.969 5(2)	−0.175 4(1)	0.796 4(1)
C(65)	0.955 9(2)	−0.126 8(1)	0.715 2(1)
C(66)	0.818 4(2)	−0.086 9(1)	0.682 5(1)
C(67)	0.414 9(2)	−0.113 4(1)	0.654 0(1)
C(68)	0.361 2(2)	−0.176 0(1)	0.723 4(2)

Table 3. Selected bond lengths (Å) for compound (**11**) with e.s.d.s in parentheses

O(69)–C(67)	1.426(3)	N(4)–C(41)	1.459(3)
N(1)–N(2)	1.422(2)	C(3)–C(31)	1.488(3)
N(1)–C(6)	1.475(3)	C(5)–C(6)	1.552(3)
N(2)–C(3)	1.299(3)	C(5)–C(51)	1.517(3)
N(4)–C(3)	1.365(3)	C(6)–C(61)	1.528(3)
N(4)–C(5)	1.468(3)	C(6)–C(67)	1.562(3)

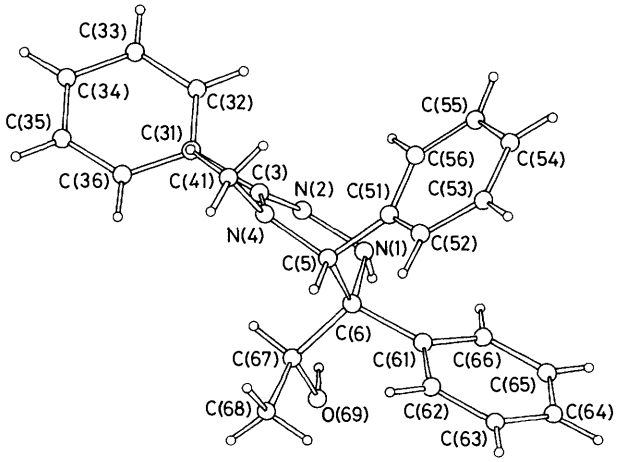


Figure. Perspective view of the molecule (11) showing the crystallographic numbering. The H atoms are shown but not labelled. Only one enantiomer is shown

* Photodehydrogenation of the triphenylimidazole (**7**) is known to take place in the presence of iodine;[8] analogous reactions have been observed on irradiation of iminium salts.[9]

† In a preliminary communication[1] the structure of the adduct was erroneously given as (**12**). This structure assignment was mainly based on the appearance of a mass spectral peak at *m/z* 208 and on the metastable transition m* 152.4 (208 → 178).

Table 4. Selected bond angles (°) for compound (11) with e.s.d.s in parentheses

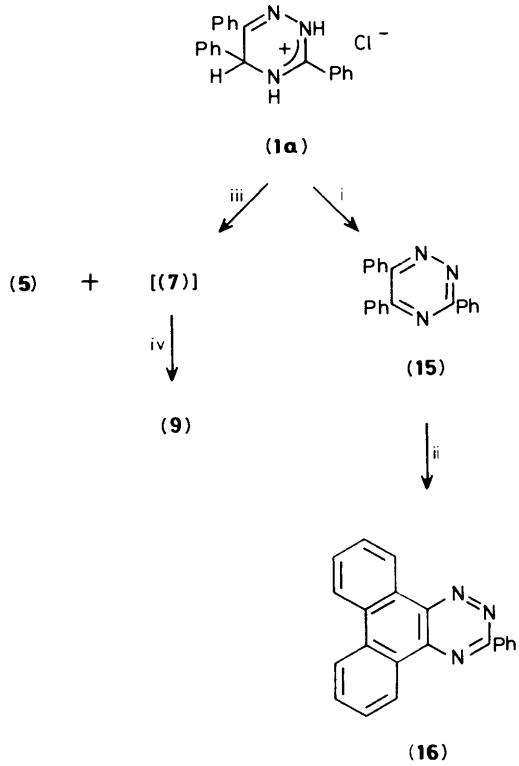
N(2)–N(1)–C(6)	114.5(3)	C(6)–C(5)–C(51)	112.6(3)
N(1)–N(2)–C(3)	116.3(3)	N(1)–C(6)–C(5)	104.2(3)
C(3)–N(4)–C(5)	120.0(3)	N(1)–C(6)–C(61)	109.1(3)
C(3)–N(4)–C(41)	122.2(3)	N(1)–C(6)–C(67)	109.1(3)
C(5)–N(4)–C(41)	114.6(3)	C(5)–C(6)–C(61)	110.4(3)
N(2)–C(3)–N(4)	124.6(3)	C(5)–C(6)–C(67)	112.8(3)
N(2)–C(3)–C(31)	115.8(3)	C(61)–C(6)–C(67)	111.0(3)
N(4)–C(3)–C(31)	119.3(3)	O(69)–C(67)–C(6)	111.0(3)
N(4)–C(5)–C(6)	108.2(3)	O(69)–C(67)–C(68)	105.6(3)
N(4)–C(5)–C(51)	112.9(3)	C(6)–C(67)–C(68)	117.0(3)

because the sum of the yields of the compounds isolated after irradiation of compound (**3a**) comes only to 65.5%.

The molecular structure was computed from the final fractional co-ordinates which are given with their e.s.d.s in Table 2. Selected bond lengths and angles are listed in Tables 3 and 4. The endocyclic bond lengths of the triazine ring agree well with the corresponding values found in the literature. The N(2)–C(3) double bond [1.299(3) Å] and the adjoining C(3)–N(4) multiple bond [1.365(3) Å] account for an almost perfect envelope shape assumed by the triazine ring [the puckering parameters[10] Q 0.519(2) Å, φ 123.3(3)°, θ 129.8(3)° and the corresponding asymmetry factor[11] fC_s(C3) 2.3 pm] with C(6) on the flap. The 1-hydroxyethyl group is bound axially to C(6) [C(67)–C(6)–C(5)–N(4) − 63.1(3)°] and it is *trans*-diaxial with the phenyl ring attached to C(5). Their antiperiplanar[12] orientation is shown by the torsion angle C(67)–C(6)–C(5)–C(51) 171.4(4)°. The C(3)–phenyl ring is tilted by *ca.* 51° to the best plane of the sofa around the C(3)–C(31) bond. The out-of-plane bending of the N(4)–methyl group calculated as suggested by Dunitz and Winkler[13] (χ_N 0.34 rad) indicates a low, but retained pyramidality at N(4). The bulky molecules of compound (**11**) are linked by centre-of-symmetry-related hydrogen-bond pairs between N(1) as donor and N(2) as acceptor with the parameters N(1)–H(N1) x,y,z ··· N(2)[1 − $x,-y$, 1 − z] N ··· N 3.040(2), H ··· N 2.08(2) Å NH ··· N 160.6(2)°. These molecular dimers are strengthened by another pair of centre-of-symmetry-related hydrogen bonds in which O(69) acts as donor while the acceptor is invariably N(2): 0(69)–H(O)[x,y,z] ··· N(2)[1 − $x,-y$, 1 − z] O ··· N 3.015(3), H ··· N 2.11(3) Å, OH ··· N 160.4(2)°. From this it follows that the dimers possessing hydrophobic surfaces are isolated from each other.

Both photochemical ring contractions [the formation of the pyrazoles (**5**) and (**6**), and of the intermediate imidazoles (**7**) and (**8**)] are reductions. It has therefore to be assumed that the solvent ethanol is oxidised by the excited cations of the salts (**1a**)—(**3a**). The formation of adduct (**11**) supports this assumption. When a solvent (*e.g.* acetonitrile) is used which is incapable of being oxidised, a complex series of oxidations and reductions. leading to the formation of two new products (**15**) and (**16**) in addition to the known products (**5**), (**7**), and (**9**), takes place upon irradiation of the salt (**1a**) (Scheme 1). The sum of the yields of the two oxidation products (**15**) and (**16**) (14.8 + 2 × 6.3* = 27.4%) is practically equal to the yield of the reduction product (**5**) (27%, see Scheme 1). [Since compound (**9**) is formed in two steps *via* successive reduction and oxidation, its yield (31.9%) is not taken into account in this calculation.]

In compound (**4**) an alcoholic function is incorporated into



Scheme 1. *Conditions:* i, ii, iii, iv: *hν*–CH_3CN. Types of reaction: i, ii, iv, oxidation; iii, reduction

the dihydrotriazine molecule. For the synthesis of compound (**4**), see Scheme 2. The length of the chain separating the two moieties was chosen so as to permit an intramolecular version of the adduct formation (**3a**) ⟶ (**11**) to take place. Salt (**4a**) was irradiated in acetonitrile. Instead of formation of the expected bicyclic analogue of compound (**11**) a different product, (**21**), was formed in addition to the pyrazole (**5**) and the aromatic triazine (**15**). The structure of compound (**21**) was deduced from its ^1H and ^{13}C n.m.r. and mass spectra.

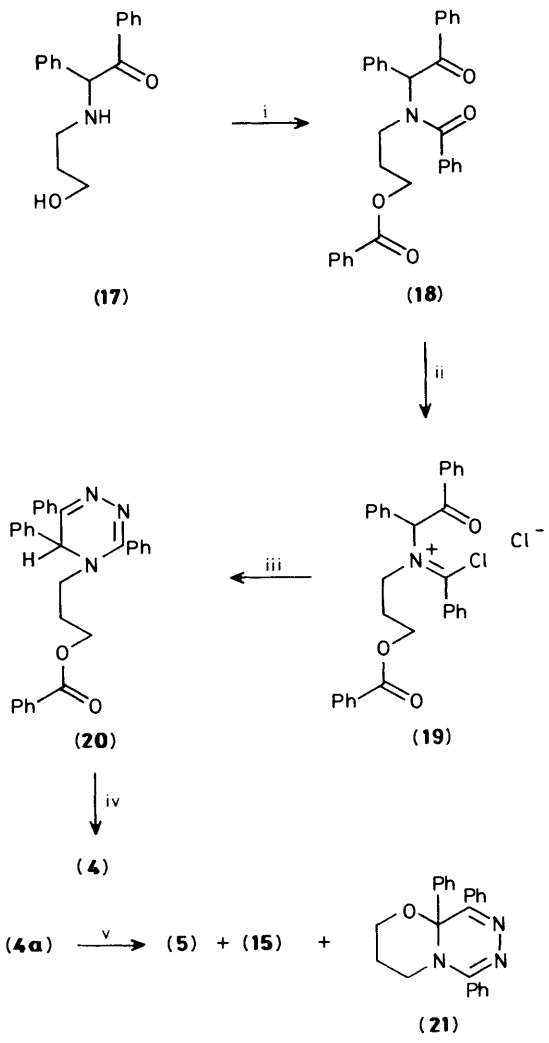
Experimental

M.p.s were measured on a hot-stage melting point apparatus and are uncorrected. I.r. spectra were obtained with a Spectromom 2000 instrument (Hungarian Optical Works, Budapest). ^1H and ^{13}C n.m.r. spectra were recorded on a JEOL FX-100 spectrometer, with $SiMe_4$ as internal reference. Mass spectra were obtained with a JEOL JMS-01SG-2 double-focussing instrument at 75 eV. Metastable peaks were measured on an AEI MS 902 instrument at 70 eV, using the direct insertion system at 150—160 °C.

3,5,6-*Triphenyl*-2,5-*dihydro*-1,2,4-*triazine* (**1**).—A solution of *N*-desylbenzamide[14]† (3.15 g, 10 mmol), hydrazine hydrate (0.5 ml, 10 mmol), and conc. hydrochloric acid (1.75 ml) in ethanol (25 ml) was refluxed for 8 h. The hot mixture was poured into water (100 ml) and made alkaline by addition of aqueous ammonium hydroxide. The resulting crystalline product was filtered off to obtain the title compound (**1**) (2 g, 64%), m.p. 240—244 °C [from aqueous *N*,*N*-dimethylformamide (DMF)] (lit.,[15] 249.5 °C) (Found: C, 80.85; H, 5.4; N, 13.6. Calc. for $C_{21}H_{17}N_3$: C, 81.0; H, 5.5; N, 13.5%); $\lambda_{max.}$(EtOH) 244 (lg ε

* Since compound (**16**) is formed by a succession of two oxidation steps its yield counts double.

† Desyl is 2-oxo-1,2-diphenylethyl.



Scheme 2. *Reagents:* i, PhCOCl–pyridine; ii, PCl_5–$CHCl_3$–N_2; iii, $NH_2NH_2 \cdot H_2O$–$MgSO_4$–N_2; iv, KOH–H_2O–EtOH; v, *hν*–CH_3CN

4.27) and 319 nm (3.77); $\nu_{max.}$ (KBr) 3 305br (NH), 1 605, 1 485, 1 455, and 1 345 cm^{-1}; δ_H [$(CD_3)_2SO$] 6.0 (1 H, s, 5-H), 7.2—7.5 (13 H, m, ArH), and 7.7—8.0 (2 H, m, ArH); δ_H (CF_3CO_2H–C_6D_6, 10:1) 6.01 (1 H, d, *J* 4 Hz, 5-H), 7.2—7.8 (15 H, m, Ph), and 9.02 (1 H, d, *J* 4 Hz, NH); δ_C [$(CD_3)_2SO$] 55.38 (C-5), 125.93, 126.58, 127.16, 127.34, 128.39, 128.62, 129.21, 129.56 (Ph Cs), 132.60 (C-1, 5-Ph), 135.06 (C-1, 3-Ph), 141.55 (C-1, 6-Ph), 141.96 (C-3), and 150.56 (C-6); *m/z* 311 (M^+, 50.9%), 310 (23.7), 178 (Ph_2C_2, 20.8), 104 (PhCNH, 100), and 77 (Ph, 25.9).

2-*Methyl*-3,5,6-*triphenyl*-2,5-*dihydro*-1,2,4-*triazine* (**2**).—(*a*) A solution of *N*-desylbenzamide[14] (3.15 g, 10 mmol), methylhydrazine (0.68 g, 15 mmol), and acetic acid (0.1 ml) in butan-1-ol (30 ml) was refluxed under nitrogen for 16 h. The mixture was evaporated to dryness under reduced pressure and the residue was triturated with excess of ammonium hydroxide (5 ml), and extracted with CH_2Cl_2 (3 × 15 ml); the extract was dried ($MgSO_4$) and evaporated to dryness to give *compound* (**2**) (1.0 g, 30%), m.p. 121—123 °C (from aqueous EtOH) (Found: C, 81.0; H, 5.7; N, 12.9. $C_{22}H_{19}N_3$ requires C, 81.2; H, 5.9; N, 12.9%); $\lambda_{max.}$(EtOH) 234 (log ε 4.31) and 327 nm (3.89); $\nu_{max.}$ (KBr) 1 600, 1 490, 1 445, 1 325, and 770 cm^{-1}; δ_H ($CDCl_3$) 3.36 (3 H, s, Me), 5.94 (1 H, s, 5-H), 7.3—7.5 (13 H, m, ArH), and 7.7—7.8 (2 H, m, ArH); δ_C ($CDCl_3$) 41.60 (Me), 56.69 (C-5), 126.51, 127.10, 127.54, 128.33, 128.47, 128.68, 129.47, 129.55 (Ph Cs), 134.23 (C-1, 5-Ph), 134.85 (C-1, 3-Ph), 140.70 (C-1, 6-Ph), 143.42 (C-3), and 154.01 (C-6); *m/z* 325 (M^+, 84.6%), 324 (55.3), 249 (36.8), 220 (17.5), 178 (Ph_2C_2 57.1), 118 ($PhCNCH_3$, 100), and 77 (Ph, 12.4).

(*b*) Sodium hydride (80% dispersion in oil; 0.4 g, 13 mmol) was added to a mixture of compound (**1**) (3.1 g, 10 mmol), and DMF (40 ml) under nitrogen. Methyl iodide (0.8 ml, 13 mmol) was added dropwise to the homogeneous solution. The mixture was stirred for 5 h, then evaporated to dryness under reduced pressure, and the residue was taken up in ethyl acetate (50 ml). The insoluble salts were filtered off and the resulting solution was evaporated to obtain compound (**2**) (0.8 g, 25%), identical with the sample obtained as described in (*a*).

4-*Methyl*-3,5,6-*triphenyl*-4,5-*dihydro*-1,2,4-*triazine* (**3**).—A mixture of desylmethylammonium chloride[16] (2.65 g, 10 mmol), dry pyridine (10 ml), and benzoyl chloride (1.2 ml, 10 mmol) was stirred for 1 day. The solution was poured onto a 1:1 mixture of ice and hydrochloric acid (10 ml). The oily product was triturated with 10% aqueous Na_2CO_3 to yield N-*desyl*-N-*methylbenzamide* (1.60 g, 45%), m.p. 108 °C (from EtOH) (Found: C, 80.15; H, 6.0; N, 4.4. $C_{22}H_{19}NO_2$ requires C, 80.2; H, 5.8; N, 4.25%); $\nu_{max.}$(KBr) 1 695 (CO) and 1 625 cm^{-1}; δ_H($CDCl_3$) 2.82 (3 H, s, Me), 6.44 (1 H, br, CH), 7.0—7.6 (13 H, m, ArH), and 7.9—8.1 (2 H, m, ArH); δ_C ($CDCl_3$) 35.10 (br, Me), 63.48 (br, Ph*C*HCO), 127.13, 128.47, 128.65, 128.76, 129.17, 129.70, 129.99, 133.27 (Ph Cs), 134.79 (C-1, in PhCON), 135.78 (C-1, in PhCOC), 136.37 (C-1, in PhCH), 172.17 (CON), and 197.10 (*C*OC); *m/z* 329 (M^+, 1.9%), 224 (52.4), 105 (PhCO, 100.0), and 77 (Ph, 28.1).

A mixture of *N*-desyl-*N*-methylbenzamide (3.3 g, 10 mmol), PCl_5 (2.1 g, 10 mmol), and dry $CHCl_3$ (30 ml) was refluxed under nitrogen until a homogeneous solution was formed. The cold solution was diluted with dry Et_2O (200 ml) whereupon the imidoyl chloride crystallised. The latter was washed by decantation with dry Et_2O (3 × 100 ml) and the crude product (2.7 g, 7 mmol) was treated with hydrazine hydrate (1.05 g, 21 mmol) in $CHCl_3$ (21 ml) in the presence of dry $MgSO_4$ (7 g). After being stirred for 3 h the mixture was filtered to remove $MgSO_4$ and the organic solution was washed with water (3 × 10 ml), dried, and evaporated to give *compound* (**3**) (1.23 g, 53.9%), m.p. 185—186 °C (from aqueous EtOH) (Found: C, 81.2; H, 5.8; N, 13.0. $C_{22}H_{19}N_3$ requires C, 81.2; H, 5.9; N, 12.9%); $\lambda_{max.}$(EtOH) 246 (lg ε 4.26) and 345 nm (4.05); $\nu_{max.}$(KBr) 1 495, 1 440, 765, and 695 cm^{-1}; δ_H($CDCl_3$) 3.11 (3 H, s, Me), 5.27 (1 H, s, 5-H), 7.2—7.6 (13 H, m, ArH), and 7.9—8.0 (2 H, m, ArH); δ_C ($CDCl_3$) 39.52 (Me), 57.63 (C-5), 126.48, 127.45, 128.35, 128.50, 128.91, 129.09, 129.26, 129.76, 130.31 (Ph Cs), 133.18 (C-1, 3-Ph), 134.99 (C-1, 5-Ph), 137.31 (C-1, 6-Ph), 148.22 (C-3), and 153.10 (C-6); δ_C [$(CD_3)_2SO$] 39.14 (Me), 55.23 (C-5), 126.50, 127.34, 128.65, 128.77, 128.89, 129.18, 129.88, 130.47 (Ph Cs), 133.30 (C-1, 3-Ph), 135.03 (C-1, 5-Ph), 138.19 (C-1, 6-Ph), 148.54 (C-3), and 152.76 (C-6); *m/z* 325 (M^+, 37.8%), 324 (3.9), 310 ($M - CH_3$, 2.1), 249 (4.9), 221 (10.8), 178 (Ph_2C_2, 4.9), 118 (PhCNMe, 100), and 77 (Ph, 17.8); *m** 323.1 (325 → 324), 296.0 (325 → 310), 220.1 (222 → 221), and 117.0 (119 → 118).

α-(3-*Hydroxypropylamino*)*benzyl Phenyl Ketone* (**17**).—3-Aminopropan-1-ol (2 ml, 25 mmol) was added to a melt of neat benzoin (5.3 g, 25 mmol). The mixture was stirred at 140 °C for 1 h, cooled to room temperature, and triturated with Et_2O to obtain the *title compound* (**17**) (5.3 g, 78.7%), m.p. 74 °C (from EtOH–Et_2O) (Found: C, 76.0; H, 7.0; N, 5.0. $C_{17}H_{19}NO_2$ requires C, 75.8; H, 7.1; N, 5.2%); $\nu_{max.}$(KBr) 3 280 and 3 125br (NH + OH), 1 680 (CO), and 1 080 cm^{-1}; δ_H($CDCl_3$) 1.71 (2 H, m, CCH_2C), 2.74 (2 H, m, NCH_2), 3.56 (2 H, br, NH + OH),

3.74 (2 H, t, *J* 5.5 Hz, OCH_2), 5.34 (1 H, s, CHCO), 7.1—7.5 (8 H, m, ArH), and 7.8—8.0 (2 H, m, ArH); $\delta_C(CDCl_3)$ 31.27 (CCH_2C), 46.71 (NCH_2), 63.18 (OCH_2), 67.22 (CH), 128.03, 128.56, 129.09, 133.24 (Ph Cs), 135.49 (C-1, in PhCO), 137.80 (C-1, in PhCH), and 198.44 (CO).

3-(N-*Benzoyl*-N-*desylamino*)*propyl Benzoate* (**18**).—Benzoyl chloride (2.4 ml, 20 mmol) was added dropwise to a stirred solution of compound (**17**) (2.7 g, 10 mmol) in dry pyridine (20 ml). The mixture was kept overnight and poured onto a 1:1 mixture of ice and hydrochloric acid (100 ml). The aqueous layer was discarded; the thick oily product was taken up in EtOAc (30 ml), and the solution was washed with water, dried ($MgSO_4$), and diluted with Et_2O (200 ml) to precipitate *compound* (**18**) (3.2 g, 67%), m.p. 114.5 °C (from EtOH) (Found: C, 77.8; H, 5.8; N, 3.1. $C_{31}H_{27}NO_4$ requires C, 77.8; H, 5.7; N, 2.9%); $\nu_{max.}$(KBr) 1 710 (CO), 1 695 (CO), 1 625 (CO), 1 260, and 1 050 cm^{-1} (C–O–C); $\delta_H[(CD_3)_2SO$; 100 °C] 1.6 (2 H, m, CCH_2C), 3.46 (2 H, m, NCH_2), 3.91 (2 H, t, *J* 6 Hz, OCH_2), 6.7 (1 H, s, CH), and 7.1—8.0 (20 H, m, Ph); $\delta_C[(CD_3)_2SO$; 100 °C] 28.23 (CCH_2C), 43.97 (NCH_2), 61.76 (OCH_2), 65.35 (CH), 125.73, 127.63, 128.10, 128.54, 128.62, 128.92, 129.76, 132.49, 132.60 (Ph Cs), 129.50 (C-1, in $PhCO_2$), 134.06 (C-1, in PhCON), 135.85 (C-1, in PhCOC), 136.23 (C-1, in PhCH), 165.07 (CO_2), 171.18 (CON), and 195.84 (CO); *m/z* 477 (M^+, < 0.1%), 372 (16.9), 266 (3.0), 160 ($C_{10}H_{10}NO$, 3.6), 105 (PhCO, 100), and 77 (Ph, 39.9).

N-(3-*Benzoyloxypropyl*)-N-(α-*chlorobenzylidene*)-N-*desylammonium Chloride* (**19**).—PCl_5 (2.1 g, 10 mmol) was added to a solution of compound (**18**) (4.8 g, 10 mmol) in dry $CHCl_3$ (30 ml) under argon. The mixture was refluxed until a homogeneous solution was formed. The solvent was removed under reduced pressure and the residue was successively triturated with Et_2O and pentane under argon to yield the hygroscopic crystalline product (**19**) (4.2 g, 79%); $\nu_{max.}$ 1 715 (CO), 1 700 (CON), 1 625 (C=N), 1 275, and 1 050 cm^{-1} (COC).

3-(3,5,6-*Triphenyl*-4,5-*dihydro*-1,2,4-*triazin*-4-*yl*)*propyl Benzoate* (**20**).—Hydrazine hydrate (1.5 g, 30 mmol) was added dropwise to a solution of the crude salt (**19**) (4.2 g, 7.9 mmol) in $CHCl_3$ (30 ml) in the presence of dry $MgSO_4$ (10 g). The mixture was kept overnight, the $MgSO_4$ was then filtered off, and the organic solution was washed with water (3 × 10 ml), dried ($MgSO_4$), and evaporated to dryness to obtain the oily crude *product* (**20**) (1.30 g, 35%) which gradually solidified when taken up in ethanol, m.p. 195 °C (from EtOH) (Found: C, 78.5; H, 5.9; N, 9.05. $C_{31}H_{27}N_3O_2$ requires C, 78.6; H, 5.75; N, 8.9%); $\nu_{max.}$(KBr) 1 725 (CO), 1 500, 1 440, 1 285, and 1 125 cm^{-1} (C–O–C); $\delta_H[(CD_3)_2SO$; 80 °C] 1.92 (2 H, m, CCH_2C), 3.70 (2 H, m, NCH_2), 4.05 (2 H, m, OCH_2), 5.93 (1 H, s, 5-H), 7.2—7.7 (18 H, m, ArH), and 7.9—8.1 (2 H, m, ArH); $\delta_C[(CD_3)_2SO$; 80 °C] 28.29 (CCH_2C), 47.63 (NCH_2), 52.69 (C-5), 61.08 (OCH_2), 126.17, 126.61, 127.92, 128.04, 128.30, 128.39, 128.45, 128.59, 129.38, 129.85, 132.60 (Ph Cs), 129.44 (C-1 in $PhCO_2$), 133.01 (C-1, 3-Ph), 134.80 (C-1, 5-Ph), 138.16 (C-1, 6-Ph), 149.30 (C-3), 152.35 (C-6), and 165.13 (CO).

3-(3,5,6-*Triphenyl*-4,5-*dihydro*-1,2,4-*triazin*-4-*yl*)*propan*-1-*ol* (**4**).—Compound (**20**) (4.7 g, 10 mmol) was added to a solution of KOH (2.2 g, 40 mmol) in a mixture of water (20 ml) and ethanol (40 ml), and the mixture was stirred until a homogeneous solution was formed (2 days). The solution was poured into water (800 ml), and the resulting crystalline *title compound* (**4**) was filtered off (3.6 g, 97%), m.p. 199—200 °C (from EtOH) (Found: C, 77.7; H, 6.05; N, 11.3. $C_{24}H_{23}N_3O$ requires C, 78.0; H, 6.3; N, 11.4%); $\lambda_{max.}$(EtOH) 247 (lg ε 4.21) and 339 nm (4.03); $\nu_{max.}$(KBr) 3 105br (OH), 1 445, and 645 cm^{-1}; $\delta_H[(CD_3)_2SO]$ 1.59 (2 H, qui, *J* 6.5 Hz, CCH_2C), 3.22 (2 H, t, *J* 6.5 Hz, NCH_2), 3.57 (2 H, sx, *J* 6.5 Hz, OCH_2), 5.86 (1 H, s, 5-H), 7.2—7.6 (13 H, m, ArH), and 7.9—8.1 (2 H, m, ArH); $\delta_C[(CD_3)_2SO]$ 32.65 (CCH_2C), 48.68 (NCH_2), 52.34 (C-5), 57.66 (OCH_2), 126.58, 126.96, 128.42, 128.71, 128.95, 129.09, 130.03, 130.67, (Ph Cs), 133.22 (C-1, 3-Ph), 134.91 (C-1, 5-Ph), 138.69 (C-1, 6-Ph), 149.45 (C-3), and 152.99 (C-6); *m/z* 369 (M^+, 3.7%), 310 (7.1), 265 (5.8), 178 (Ph_2C_2, 58.4), 176 (13.2), 118 (PhCNMe, 32.8), 104 (PhCNH, 100), and 77 (Ph, 57.6).

Dihydro-1,2,4-*triazinium Chlorides* (**1a**)—(**4a**).—Dry HCl was bubbled into solutions of the dihydrotriazines (**1**)—(**4**) (10 mmol) in dry methanol (80 ml) at 0 °C for *ca.* 2 h. The solvent was removed under reduced pressure, and the residues were triturated with dry Et_2O–acetone (10:0.5) to give the title compounds (**1a**)—(**4a**) in 90—94% yield.

3,5,6-*Triphenyl*-2(4),5-*dihydro*-1,2,4-*triazinium chloride* (**1a**), m.p. 210—211 °C (from EtOH–Et_2O) (Found: N, 11.9; Cl, 10.4. $C_{21}H_{18}ClN_3$ requires N, 12.1; Cl, 10.2%); $\lambda_{max.}$(EtOH) 249 (lg ε 4.22) and 320 nm (4.06); $\nu_{max.}$(KBr) 3 335, 2 865, 2 585, 1 625, 1 545, 1 445, 710, and 695 cm^{-1}.

2-*Methyl*-3,5,6-*triphenyl*-2,5-*dihydro*-1,2,4-*triazinium chloride* (**2a**), m.p. 215—217 °C (from EtOH–Et_2O) (Found: N, 11.5; Cl, 9.45. $C_{22}H_{20}ClN_3$ requires N, 11.6; Cl, 9.8%); $\lambda_{max.}$(EtOH) 247 (lg ε 4.21) and 321 nm (4.05); $\nu_{max.}$(KBr) 3 400, 2 500, 1 615, 1 600, 1 570, 1 535, 1 345, and 700 cm^{-1}.

4-*Methyl*-3,5,6-*triphenyl*-4,5,-*dihydro*-1,2,4-*triazinium chloride* (**3a**), m.p. 198—200 °C (from EtOH–Et_2O) (Found: N, 11.2; Cl, 9.8. $C_{22}H_{20}ClN_3$ requires N, 11.6; Cl, 9.8%); $\lambda_{max.}$(EtOH) 249 (log ε 4.19) and 325 nm (4.09); $\nu_{max.}$(KBr) 3 350, 2 550, 1 610, 1 590, 1 530, 1 445, 1 385, and 690 cm^{-1}.

4-(3-*Hydroxypropyl*)-3,5,6-*triphenyl*-4,5-*dihydro*-1,2,4-*triazinium chloride* (**4a**), m.p. 229—232 °C (from EtOH–Et_2O) (Found: N, 10.0; Cl, 8.4. $C_{24}H_{24}ClN_3O$ requires N, 10.35; Cl 8.7%); $\nu_{max.}$(KBr) 3 380, 2 700, 1 515, 1 485, 1 385, 1 165, 760, and 685 cm^{-1}.

Irradiations.—Solutions of the dihydrotriazinium salts (**1a**)—(**4a**) (1.1 mmol in 150 ml of solvent) 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 t.l.c. (for details see Table 5).

Unless otherwise stated the reaction mixtures were worked up as follows. When the starting triazinium salts were consumed

Table 5. R_F Values of the dihydrotriazines (1)—(4) and of their photoproducts on Merck DC Plastik or Alufolien (Kieselgel 60 PF_{254})

	Solvent		
Compd.	Hexane–dioxane–triethylamine (8:4:2)	Toluene–methanol (10:2)	Methylene dichloride–methanol (10:0.5)
(1)	0.58	0.48	0.55
(2)	0.66	0.58	0.59
(3)	0.39	0.42	0.22
(4)	0.15	0.31	0.08
(5)	0.45	0.53	0.52
(6)	0.67	0.70	0.80
(7)	0.46	0.46	0.68
(8)	0.66	0.64	0.78
(9)	0.16	0.45	0.67
(10)	0.57	0.68	0.79
(11)		0.43	
(15)	0.75	0.86	0.88
(16)	0.68	0.88	0.90
(21)	0.37	0.43	0.46

the solutions were evaporated to dryness under reduced pressure. The residues were taken up in CH_2Cl_2 (100 ml) and the insoluble materials were filtered off. The insoluble materials were taken up in distilled water, and ammonium ions and chloride ions were detected by Nessler's reagent and silver nitrate, respectively. The organic solutions were evaporated and chromatographed on Merck PSC-ready plates (Kieselgel 60 F_{254}; 20 × 20 cm, 2 mm), with hexane–dioxane–triethylamine–ethanol (100:50:20:15) as the solvent.

(*a*) Irradiation (in ethanol, 50 h) of 3,5,6-triphenyl-2(4),5-dihydro-1,2,4-triazinium chloride (**1a**) gave (i) 3,4,5-triphenyl-1*H*-pyrazole (**5**) (80.2 mg, 24.6%), m.p. 275 °C (from EtOH) [lit.,[17] 265 °C (from EtOH)]; $\nu_{max.}$(KBr) 3 220br (NH), 1 495, 1 455, 1 440, 1 155, 975, 775, 735, and 700 cm^{-1}; δ_H [$(CD_3)_2SO$] 7.1—7.5 (15 H, m, Ph); δ_C[$(CD_3)_2SO$] 116.86 (C-4), 126.99, 127.33, 127.51, 128.24, 128.57, 130.58 (Ph Cs), 131.75 (C-1, 4-Ph), 134.01 (C-1, 3- and 5-Ph), and 144.68 (C-3 and C-5); *m/z* 296 (M^+, 100%), 295 (47.5), 190 ($C_{14}H_8N$, 5.0), 165 ($C_{13}H_9$, 30.7), and 77 (Ph, 14.8); and (ii) 2-phenyl-1*H*-phenanthro[9,10-*d*]imidazole (**9**) (70.9 mg, 21.9%), m.p. 325 °C (from acetone) [lit.,[18] 314 °C (from pyridine–water)]; $\nu_{max.}$(KBr) 3 400br (NH), 1 600, 1 460, 1 440, 1 365, 760, 735, 705, and 680 cm^{-1}; δ_H[$(CD_3)_2SO$] 7.4—7.8 (7 H, m, ArH), 8.2—8.4 (2 H, m, ArH), 8.59 (2 H, d, *J* 8 Hz, ArH), 8.86 (2 H, d, *J* 7 Hz, ArH), and 13.46 (1 H, br, NH); δ_C[$(CD_3)_2SO$] 121.95 (C-7, C-8), 122.36 and 122.54 (C-7a and C-7b) 123.65 (C-4), 124.00 (C-11), 125.17 (C-6, C-9), 126.99 (C-5, C-10), 126.17, 128.86, 129.15 (Ph Cs), 127.69 (C-3b, C-11a), 130.50 (C-1 of 2-Ph), 137.11 (C-3a, C-11b), and 149.10 (C-2).

(*b*) Irradiation of 2-methyl-3,5,6-triphenyl-2,5-dihydro-1,2,4-triazinium chloride (**2a**) (in ethanol, 35 h) furnished (i) 1-methyl-3,4,5-triphenyl-1*H*-pyrazole (**6**) (93.9 mg, 27.5%), m.p. 191—192 °C (from EtOH) [lit.,[19] 189—190 °C (from EtOH)]; $\nu_{max.}$(KBr) 1 605, 1 485, 1 455, 1 440, 1 370, 1 120, 770, 760, and 700 cm^{-1}; δ_H($CDCl_3$) 3.87 (3 H, s, Me) and 6.9—7.5 (15 H, m, ArH); δ_C($CDCl_3$) 37.38 (Me), 119.23 (C-4), 126.37, 127.30, 128.15, 128.50, 130.23, 130.49 (Ph Cs), 130.37 (C-1 of 4-Ph), 133.59 (C-1 of 3-Ph, 5-Ph), 142.31 (C-3), and 148.51 (C-5); (ii) 2-phenyl-1*H*-phenanthro[9,10-*d*]imidazole (**9**) (3.2 mg, 1.0%); and (iii) 1-methyl-2-phenyl-1*H*-phenanthro [9,10-*d*]imidazole (**10**) (142.8 mg, 42.1%).

An authentic sample of the last compound was prepared by adding simultaneously dimethyl sulphate (9.6 ml, 0.1 mol) and aqueous (12 ml) NaOH (8.7 g, 0.22 mol) to a solution of compound (**9**) (2.9 g, 10 mmol) in DMF (45 ml). The mixture was stirred for 2 h at 80 °C to complete the reaction, and was then poured into water (225 ml). The resulting crystalline product was filtered off to obtain *compound* (**10**) (2.9 g, 95.0%), m.p. 188 °C (from acetone) (Found: C, 85.5; H, 5.4; N, 9.4. $C_{22}H_{16}N_2$ requires C, 85.7; H, 5.2; N, 9.1%); $\nu_{max.}$(KBr) 1 460, 745, 725, and 700 cm^{-1}; δ_H[$(CD_3)_2SO$] 4.29 (3 H, s, Me), 7.5—7.9 (9 H, m, ArH), 8.5—8.7 (2 H, m, ArH), and 8.8—9.0 (2 H, m, ArH); δ_C[$(CD_3)_2SO$] 35.96 (Me), 121.19 (C-8), 121.84 (C-7), 123.24 (C-7a, C-7b), 123.50 (C-4), 124.38 (C-11), 125.03 (C-9), 125.38 (C-6), 126.99, 127.19, 128.62, 129.33 (Ph Cs), 127.40 (C-11a), 127.54 (C-3b), 128.27 (C-3a), 129.68 (C-5, C-10), 130.29 (C-1 of 2-Ph), 136.67 (C-11b), and 152.14 (C-2); *m/z* 308 (M^+, 100%), 293 (M − CH_3, 8.0), 204 (3.0), 190 ($C_{14}H_8N$, 14.0), and 77 (Ph, 3.0).

(*c*) 4-Methyl-3,5,6-triphenyl-4,5-dihydro-1,2,4-triazinium chloride (**3a**) was irradiated in ethanol for 100 h. Although the starting material (**3a**) had not been totally consumed, the reaction mixture was worked up and chromatographed (toluene–methanol 200:50) to give 3,4,5-triphenyl-1*H*-pyrazole (**5**) (54.4 mg, 16.7%), 1-methyl-2-phenyl-1*H*-phenanthro[9,10-*d*]imidazole (**10**) (15.6 mg, 4.6%), and unchanged starting material (**3**) (82.0 mg, 22.9% recovery).

(*d*) 4-Methyl-3,5,6-triphenyl-4,5-dihydro-1,2,4-triazine (**3**) was irradiated in the presence of aqueous HCl (5 ml; 60 mmol) for 100 h.* The solution was evaporated to dryness under reduced pressure, and the residue was triturated with excess of conc. NH_4OH (5 ml) and extracted with methylene dichloride (3 × 10 ml). The combined organic layers were dried ($MgSO_4$), and evaporated to dryness, and the residue was triturated with acetone† to give 1-(4-*methyl*-3,5,6-*triphenyl*-1,4,5,6-*tetrahydro*-1,2,4-*triazin*-6-*yl*)*ethanol* (**11**) (87.0 mg, 21.3%), m.p. 150 °C (from EtOH–hexane) (Found: C, 77.7; H, 6.7; N, 11.4. $C_{24}H_{25}N_3O$ requires C, 77.6; H, 6.8; N, 11.3%); $\nu_{max.}$(KBr) 3 375br (OH), 3 285 (NH), 1 625, 1 475, 1 455, 1 395, 1 290, 1 065, 735, and 700 cm^{-1}; δ_H[$(CD_3)_2SO$] 1.21 (3 H, d, *J* 9 Hz, *Me*CH), 2.54 (3 H, s, NMe), 4.1—4.3 (1 H, m, MeC*H*), 4.87 (1 H, s, 5-H), and 6.9—7.5 (15 H, m, ArH); δ_C[$(CD_3)_2SO$] 18.73 (*Me*CH), 38—42 (NMe + solvent), 62.22 (C-5), 63.57 (Me*C*H), 66.85 (C-6), 126.58, 127.40, 127.75, 128.19, 128.62, 128.95, 129.18, 129.71, (Ph Cs), 135.91 (C-1, of 3-Ph), 138.42 (C-1 of 5-Ph), 141.23 (C-1 of 6-Ph), and 145.53 (C-3); *m/z* 371 (M^+, 4.0%), 326 (M − 45, 100), 223 (2.8), 208 (4.1), 193 (2.3), 178 (Ph_2C_2, 3.3), 167 (6.4), 120 (6.9), 118 ($PhCNCH_3$, 26.9), 104 (PhCNH, 12.6), and 77 (Ph, 11.6); *m** 286.5 (371 → 326), 152.4 (208 → 178), 117.8 (371 → 209), and 85.5 (326 → 167).

(*e*) 2,4,5-Triphenyl-1*H*-imidazole[20] (**7**) was irradiated in ethanol in the presence of aqueous HCl (5 ml; 60 mmol) for 50 h to give the phenanthroimidazole (**9**) (290.0 mg, 98.5%), identical with the sample obtained as described in (*a*).

(*f*) 3,5,6-Triphenyl-2(4),5-dihydro-1,2,4-triazinium chloride (**1a**) was irradiated in acetonitrile for 100 h. A homogeneous solution was formed after *ca.* 20 h. Chromatographic work-up furnished the pyrazole (**5**) (88.0 mg, 27.0%); the phenanthroimidazole (**9**) (103.3 mg, 31.9%); 3,5,6-triphenyl-1,2,4-triazine (**15**) (50.4 mg, 14.8%), m.p. 144—145 °C (from benzene–hexane) [lit.,[21] 145 °C (from benzene–hexane)]; and 3-phenylphenanthro[9,10-*e*]-1,2,4-triazine (**16**) (21.3 mg, 6.3%), m.p. 187 °C (from toluene).

An authentic sample of compound (**15**) was prepared as follows. A solution of $KMnO_4$ (1.1 g, 7.0 mmol) in acetic acid (140 ml) was added dropwise to a stirred, hot solution of the dihydrotriazine (**1**) (3.1 g, 10.0 mmol) in acetic acid (140 ml). The mixture was subsequently refluxed for a further 15 min, and evaporated to dryness under reduced pressure. The residue was triturated with water (100 ml), neutralised with conc. aqueous NH_4OH, and extracted with CH_2Cl_2 (3 × 30 ml); the extract was dried ($MgSO_4$) and evaporated to give compound (**15**) (2.50 g, 80.1%), m.p. 144.5 °C; $\lambda_{max.}$(EtOH) 238 (log ε 4.10) and 328 nm infl.(3.99); $\nu_{max.}$(KBr) 1 485, 1 385, 1 360, and 695 cm^{-1}; δ_H($CDCl_3$) 7.1—7.8 (13 H, m, ArH) and 8.6—8.8 (2 H, m, ArH); δ_C($CDCl_3$) 128.35, 128.50, 128.56, 128.79, 129.47, 129.85, 130.64, 131.51 (Ph Cs), 134.82 (C-1 of 3-Ph), 135.58, 135.93 (C-1 of 5-Ph and 6-Ph), 155.50 (C-5, C-6), and 161.26 (C-3); *m/z* 309 (M^+, 10.0%), 281 (M − N_2, 6.0), 178 (Ph_2C_2, 100.0), 176 ($C_{14}H_8$, 10.0), 103 (PhCN, 6.0), and 77 (Ph, 10.0).

An authentic sample of compound (**16**) was prepared as follows. A mixture of hydrazine hydrate (3 ml, 60.0 mmol) and dry methanol (10 ml) was added dropwise to a solution of benzamidinium chloride (4.7 g, 30 mmol) in dry methanol (40 ml) under nitrogen. The mixture was stirred for a further 5 min and subsequently added dropwise to a suspension of 9,10-phenanthrenequinone (6.25 g, 30 mmol) in a mixture of dry

* Irradiation of the dihydrotriazines (1) and (**2**) in the presence of excess of aqueous HCl (5 ml; 60 mmol), gave the same products in practically the same yields as the irradiation of the dihydrotriazinium chlorides (**1a**) and (**2a**)

† The acetonic mother liquor was evaporated to dryness and the residue was chromatographed to obtain the pyrazole (**5**) (45.6 mg, 14.0%), the phenanthroimidazole (**10**) (28.0 mg, 8.3%), and starting material (**3**) (107.4 mg, 30.0% recovery).

methanol (40 ml) and dry toluene (40 ml). Triethylamine (4.2 ml, 30 mmol) was added to precipitate the crystalline product which was filtered off, and washed with methanol to give *compound* (**16**) (4.6 g, 50%), m.p. 187 °C (from toluene) (Found: C, 82.0; H, 4.5; N, 13.4. $C_{21}H_{13}N_3$ requires C, 82.1; H, 4.3; N, 13.7%); $\nu_{max.}$(KBr) 1 600, 1 500, 1 480, 1 360, 745, 715, and 680 cm^{-1}; $\delta_H(CDCl_3)$ 7.4—7.8 (7 H, m, ArH), 8.2—8.4 (2 H, m, ArH), 8.6—8.9 (2 H, m, ArH), 9.0—9.1 (1 H, m, ArH), and 9.1—9.4 (1 H, m, ArH); $\delta_C(CDCl_3)$ 123.04 (C-8, C-9), 124.97 (C-5), 126.56 (C-12), 127.56 (C-8a), 128.07 (C-8b), 128.60 (C-7, C-10), 128.89 (C-6, C-11), 127.90, 128.31, 130.59, 131.35, 132.28 (Ph Cs), 131.11 (C-12a), 134.04 (C-4b), 135.91 (C-1 of 3-Ph), 143.46 (C-4a), 144.86 (C-12b), and 161.48 (C-3); *m/z* 307 (M^+, 12.1%), 279 ($M - N_2$, 66.0). and 176 ($C_{14}H_8$, 100).

(*g*) 4-(3-Hydroxypropyl)-3,5,6-triphenyl-4,5-dihydro-1,2,4-triazinium chloride (**4a**) was irradiated in acetonitrile for 65 h. A homogeneous solution was obtained after *ca.* 30 h. After preliminary work-up as described above the mixture was chromatographed (toluene–methanol 200:50) to obtain the pyrazole (**5**) (72.7 mg, 22.3%); the triazine (**15**) (11.6 mg, 3.4%); unchanged dihydrotriazine (**4**) (11.8 mg, 2.9%); and the oily 6,9,9a-*triphenyl*-3,4-*dihydro*-2H,9aH-[1,3]*oxazino*[3,2-d][1,2,-4]*triazine* (**21**) (154.4 mg, 38.2%) (Found: C, 78.3; H, 5.95; N, 11.5. $C_{24}H_{21}N_3O$ requires C, 78.45; H, 5.8; N, 11.4%); $\nu_{max.}$(film) 1 500, 1 445, 1 435, 765, and 705 cm^{-1}; $\delta_H(CDCl_3)$ 1.84 (2 H, qui, *J* 7 Hz, 3-H_2), 3.61 (2 H, t, *J* 7 Hz, NCH_2), 3.87 (2 H, t, *J* 7 Hz, OCH_2), 7.1—7.6 (13 H, m, ArH), 7.6—7.8 (2 H, m, ArH); $\delta_H[(CD_3)_2SO]$ 1.78 (2 H, m, 3-H_2), 3.50 (2 H, m, NCH_2), 3.86 (2 H, m, OCH_2), and 7.2—7.7 (15 H, m, ArH); $\delta_C(CDCl_3)$ 25.04 (C-3), 40.07 (NCH_2), 59.47 (OCH_2), 83.78 (C-9a), 125.93, 127.68, 128.56, 128.91, 129.06, 129.17, 130.46 (Ph Cs), 132.74 (C-1 of 9a-Ph), 134.53 (C-1 of 6-Ph), 139.73 (C-1 of 9-Ph), 150.64 (C-6), and 153.16 (C-9); $\delta_C[(CD_3)_2SO]$ 24.72 (C-3), 40.81 (NCH_2), 59.91 (OCH_2), 83.31 (C-9a), 126.05, 127.89, 128.74, 129.12, 130.44 (Ph Cs), 132.78 (C-1 of 9a-Ph), 134.74 (C-1 of 6-Ph), 139.21 (C-1 of 9-Ph), 149.68 (C-6), and 152.69 (C-9); *m/z* 367 (M^+, 6.7%), 264 (43.2), 263 (54.2), 178 (Ph_2C_2, 26.2), 165 ($C_{13}H_9$, 25.6), 161 ($C_{10}H_{11}NO$, 42.7), 160 ($C_{10}H_{10}NO$, 82.0), 105 (PhCO, 100), 103 (PhCN, 48.0), and 77 (Ph, 67.6). The compositions of the fragments *m/z* 178, 165, 160, 105, 103 were confirmed by peak-matching (error ≤ 3 m*M*).

Structure Determination of Compound (**11**).—*Crystal data.* $C_{24}H_{25}N_3O$. *M* = 371.49, Monoclinic, *a* = 8.761(3), *b* = 16.312(3), *c* = 13.717(3) Å, β = 97.54(2)°, *V* = 1943.3 Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, λ = 1.541 84 Å) space group $P2_1/n$ (alt. $P2_1/c$, No. 14), *Z* = 4, D_x = 1.27 g cm^{-3}. Crystal dimensions 0.20 × 0.35 × 0.40 mm. μ(Cu-K_α) = 5.8 cm^{-1}.

Data collection and processing. CAD4 diffractometer, ω/2θ mode with scan width = 0.40 + 0.30 tan θ, ω scan rate varied from 1 to 20 deg min^{-1}, graphite-monochromated Cu-K_α radiation. Of 3 457 unique reflections collected in the range 1.5 ≤ θ ≤ 75° 2 880 with $I > 3\sigma(I)$ were taken as observed. Neither absorption nor decay correction was applied.

Structure analysis and refinement. Direct methods[22] using 288 normalised structure factors having $E \geq 1.69$. Full-matrix least-squares refinement with all non-hydrogen atoms treated anisotropically using the weighting scheme $w = 4F_o^2/\sigma^2(F_o^2)^2$ resulted in the final residuals: $R = 0.059$, $R_w = 0.079$ (R_{tot} = 0.073, *S* = 4.37). Max. and min. peak heights in final Δρ 0.30(5) e Å^{-3} while max. Δ/σ in the last cycle of refinement was 0.09. The hydrogen atoms, except those which are bound to N or O atoms, were entered in calculated positions and were only included in structure factor calculations with individual isotropic temperature factors ($B_{iH} = B_{iX} + 1$ Å^2, X = C, N, and O). H(N1) and H(069) were located in Δρ synthesis. All calculations were performed by the use of the Enraf-Nonius (Delft, 1983) *SDP* PLUS Programme Package which includes atomic scattering factors.[23] Anomalous dispersion effects were included in F_c values as suggested in the literature.[24] For $\Delta f'$ and $\Delta f''$ values see ref. 25.*

The following compounds were prepared as described in the literature.

1-*Methyl*-2,4,5-*triphenyl*-1H-*imidazole* (**8**).[26] $\delta_H(CDCl_3)$ 3.49 (3 H, s, Me), 7.1—7.3 (3 H, m, ArH), 7.3—7.6 (10 H, m, ArH), and 7.6—7.8 (2 H, m, ArH); $\delta_C(CDCl_3)$ 33.05 (Me), 126.31, 127.04, 128,03, 128.56, 128.71, 129.03, 129.14, 130.99 (Ph Cs), 130.49 (C-1 of 2-Ph), 131.25 (C-1 of 5-Ph), 131.51 (C-1 of 4-Ph), 134.88 (C-4), 137.98 (C-5), and 147.92 (C-2); *m/z* 310 (M^+, 100%), 309 (40.7), 295 (5.3), 165 ($C_{13}H_9$, 11.3), 155 (M^{2+}, 9.3), and 77 (Ph, 4.0).

Acetophenone azine (**13**).[27] $\delta_H[(CD_3)_2SO]$ 2.28 (6 H, s, 2 × Me), 7.4—7.6 (6 H, m, ArH), and 7.8—8.0 (4 H, m, ArH); $\delta_C[(CD_3)_2SO]$ 14.75 (Me), 126.66, 128.59, 129.94 (Ph Cs), 138.04 (C-1, Ph), and 157.47 (C=N).

3,6-Diphenyl-1,2(4)-dihydro-1,2,4,5-tetrazine (**14**).[28] $\delta_H[(CD_3)_2SO]$ 7.47 (6 H, m, ArH), 7.86 (4 H, m, ArH), and 9.14 (2 H, s, NH); $\delta_C[(CD_3)_2SO]$ 126.17, 128.54, 128.74, 130.32 (Ph Cs), 130.44 (C-1, Ph), and 148.22 (N–C=N).

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* *Supplementary data* (see section S.6.3 of Instructions for Authors, January issue). Tables of thermal parameters, bond lengths and angles, torsion angles, and H-atom co-ordinates have been deposited at the Cambridge Crystallographic Data Centre.

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