# 1,2,3-Benzotriazin-4(3H)-ones and Related Systems. Part 5.[1] Thermolysis of 3-Aryl- and 3-Alkenyl-1,2,3-benzotriazin-4(3H)-ones

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3-Aryl-1,2,3-benzotriazin-4(3H)-ones in boiling 1-methylnaphthalene or as solids undergo thermal decomposition and rearrangement to 9-acridones, whereas in paraffin oil at 300 °C only benzanilides are formed. In contrast, thermolysis of 3-(α-naphthyl)-1,2,3-benzotriazin-4(3H)-one and the isomeric 3-phenylnaphtho[2,3-d]-v-triazin-4(3H)-one in hot paraffin oil yield benzo[c]acridone and benzo[c]phenanthridone, and benzo[b]acridone, respectively. Photolysis of the 3-arylbenzotriazinones in tetrahydrofuran also gives 9-acridones but in poor yields.
Some 3-alkenyl-1,2,3-benzotriazin-4(3H)-ones have been prepared. The 3-(prop-1-enyl) and 3-(β-styryl) derivatives undergo thermal decomposition to give 3-methyl- and 3-phenyl-quinolin-4(1H)-one, respectively, the latter in practicable yield.

THE thermolysis of 3-phenyl-1,2,3-benzotriazin-4(3H)-one (1; R = Ph) has been investigated by Hey, Rees, and Todd.[2] They found that the benzotriazinone in paraffin oil at 250 °C decomposes, probably via a radical pathway, to give benzanilide as the major product (41%).

(1)   (2)

path b   path a

(4)   (3)   (5)
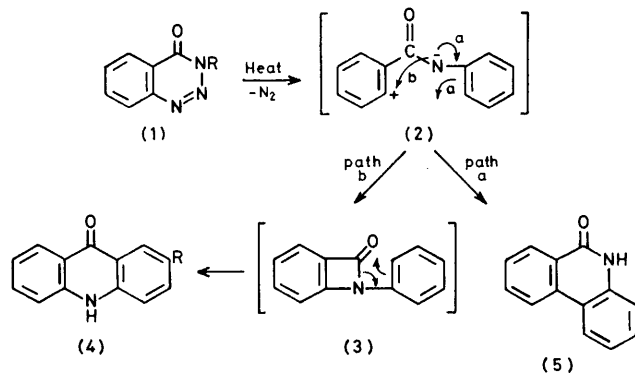
SCHEME 1

In contrast, 9-acridone (4; R = H) (55%) and phenanthridin-6-one (5) (12.5%) are formed when 3-phenyl-1,2,3-benzotriazin-4(3H)-one is pyrolysed at 320 °C in the absence of solvent. Acridone and phenanthridinone formation has been rationalised[3] on the basis of the reaction sequence outlined in Scheme 1. Loss of nitrogen from the triazinone ring yields the zwitterion † (2), which can either ring-close directly to phenanthridinone (path a) or yield acridone by way of an electrocyclic ring-opening of the benzazetinone intermediate (3) (path b).

These observations prompted us to investigate for synthetic reasons the thermal decomposition and rearrangement under various conditions of 3-aryl-1,2,3-benzotriazin-4(3H)-ones and naphtho[2,3-d]-v-triazin-4(3H)-ones. Also, some structurally related and novel 3-alkenyl-1,2,3-benzotriazin-4(3H)-ones have been synthesised and their thermal decompositions examined.

The 3-arylbenzotriazinones (7; Ar = α-naphthyl and p-XC₆H₄; X = NO₂, Me, OMe, Br, or Cl) were prepared by the route outlined in Scheme 2, and thermolysed in

† Homolytic loss of nitrogen and a corresponding radical pathway has also been considered.[2]

boiling 1-methylnaphthalene (b.p. 242 °C), in hot paraffin at 300 °C, and as solids at 250—300 °C. Results are given in the Table in the Experimental section.

In accord with previous observations [2] thermolysis in paraffin oil gave, in all but one instance, the corresponding benzanilides, albeit in poor yields. However, in boiling 1-methylnaphthalene and in the absence of solvent, the anticipated 2-substituted-9-acridones were obtained in poor to moderate yields. The one exception was again the 3-(p-nitrophenyl) derivative (7; Ar = p-NO₂C₆H₄), which decomposed violently, especially in the solid state to give tarry intractable material. Decomposition times in 1-methylnaphthalene (15—20 min at 240—245 °C) are much less than those reported [2] for thermolysis in paraffin oil (91% recovery of starting material after 48 h at 250 °C) and in the absence of solvent (82% recovery of benzotriazinone after 5 h at 250 °C). Also noteworthy is the absence of phenanthridinones in these decompositions.

In marked contrast, the thermolysis of 3-(α-naphthyl)-1,2,3-benzotriazin-4(3H)-one (7; Ar = α-naphthyl) in hot (300 °C) paraffin oil gave none of the expected anilide but instead a mixture of benzo[c]acridone (8) and benzo[c]phenanthridinone (9) in 17 and 45% yield, respectively. Presumably, these benzo-derivatives are formed in a series of reactions analogous to those outlined in Scheme 1. However, unlike in Scheme 1, the product arising from pathway (a), i.e. the benzophenanthridinone, is now the major product. The isomeric 3-phenylnaphtho[2,3-d]-v-triazin-4(3H)-one (11b), pre-


(6)   (7)
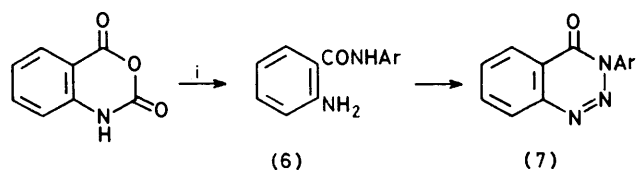
SCHEME 2   Reagents: i, ArNH₂; ii, NaNO₂–HCl

pared as indicated in Scheme 3, on thermolysis in paraffin oil, again gave no anilide but benzo[b]acridone (10) in 20% yield. Presumably, this product results by loss of nitrogen from the naphthotriazinone followed by rearrangement of the naphthoazetinone (12) as in the

formation of 9-acridone (Scheme 1, path b). The naphthoazetinone (12), along with benzo[b]acridone (5%), has been isolated in excellent yield (92%) as a stable, yellow crystalline solid from the photolysis of naphthotriazinone (11b) in tetrahydrofuran (THF).[4] On further irradiation the naphthoazetinone rearranges to benzo[b]acridone.

The absence of 'anilide-type' products from the decomposition of benzotriazinones in paraffin oil has been noted previously,[5] during the thermolysis of 1,2,3-benzotriazin-4(3H)-one (1; R = H), which at 240 or 300 °C gave not benzamide, but 2-(o-aminophenyl)-3,1-benzoxazin-4(3H)-one (15) in surprisingly high yield (75%).* The formation of the benzoxazinone (15) is

(8)   (9)

(10)

(a), R = H; (b) R = C₆H₅
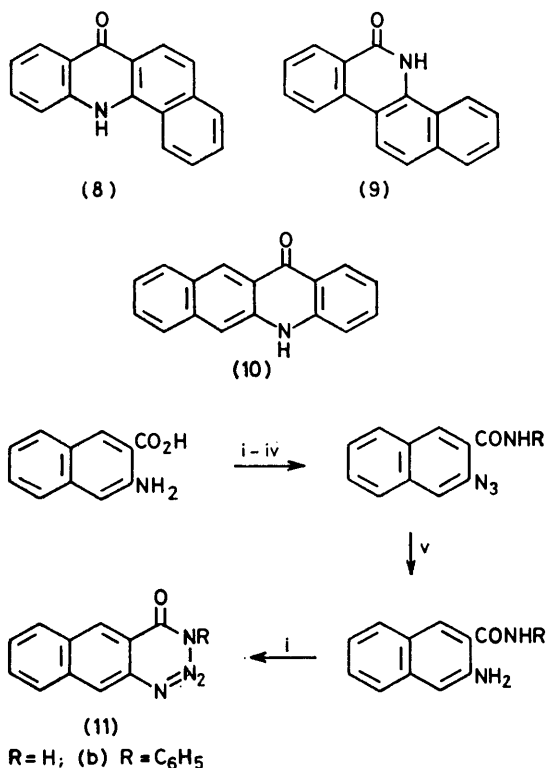
SCHEME 3 *Reagents:* i, NaNO₂–HCl; ii, NaN₃; iii, SOCl₂; iv, NH₃ or PhNH₂; v, Raney Ni–H₂

explained on the basis of a (4 + 2) cyclodimerisation of the imino-keten intermediate (14) as outlined in Scheme 4.[3] Attempts to bring about a comparable reaction using the unsubstituted naphthotriazinone (11a) (prepared as shown in Scheme 3) failed. Thermolysis in either paraffin oil or in 1-methylnaphthalene gave only tarry products. The absence of a cycloadduct corresponding to the benzoxazinone (15) is probably due to loss in benzenoid character of the whole naphthalene system on forming the imino-keten (13; R = H) necessary for cyclodimerisation. As expected on the basis of Ege's work [6] on the photolysis of 3-alkyl-

* In boiling 1-methylnaphthalene, the yield of (15) was 44%.[3a]
† 1,2,3-Benzotriazin-4(3H)-ones are known to suffer ring-fission under both acidic and basic conditions.[8]

1,2,3-benzotriazin-4(3H)-ones, the parent naphthotriazinone (11a) is photostable and remains unchanged even after prolonged irradiation (48 h) in THF solution. The 3-arylbenzotriazinones (7) under similar conditions
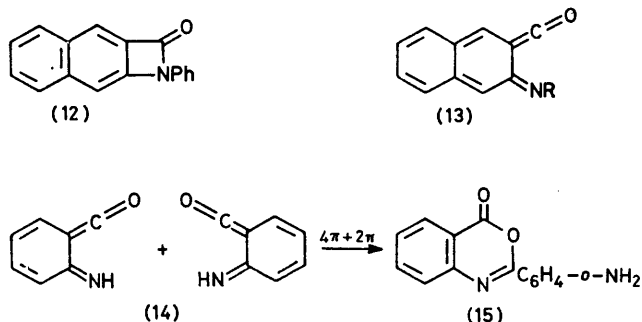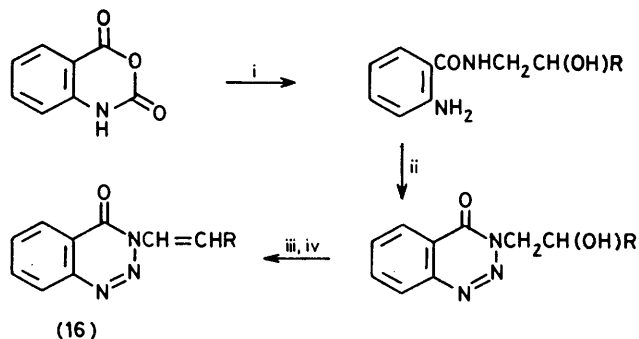

SCHEME 4

gave acridones but in very poor yields (see Table). The photo-decomposition and -rearrangement of 3-phenyl-1,2,3-benzotriazin-4(3H)-ones to 9-acridones has been reported previously.[6,7]

In view of the above results it became of interest to study the thermolysis of the structurally related 3-alkenyl-1,2,3-benzotriazin-4(3H)-ones (16), which by analogy to the reactions illustrated in Scheme 1, should yield 3-substituted quinolin-4(1H)-ones, or a mixture of quinolinone and 4-substituted isoquinolin-1(2H)-one. The required 3-alkenylbenzotriazinones (16; R = H, Me, and Ph) were prepared as outlined in Scheme 5. Introduction of the vinyl side-chain was achieved in each case in high yield and without cleavage of the benzotriazinone ring † by treating the O-(p-tosyl) derivative of the appropriate 3-(hydroxyalkyl)benzotriazinone with potassium t-butoxide in t-butyl alcohol at room temperature.[9]

Thermolysis of the 3-vinyl derivative (16; R = H) in hot paraffin oil and in boiling 1-methylnaphthalene was disappointing in that only polymeric material was obtained. Possibly, rapid polymerisation of the vinyl


(16)

SCHEME 5 *Reagents:* i, RCH(OH)CH₂NH₂,H₂O; ii, NaNO₂, HCl; iii, p-TsCl–C₅H₅N; iv, BuᵗO⁻K⁺, BuᵗOH

side-chain is the dominant reaction. Similarly, the propenyl derivative (16; R = Me) gave only polymer when decomposed in paraffin oil at 220—240 °C. However, in boiling 1-methylnaphthalene it decomposed to

give a mixture of products from which the known 3-methylquinolin-4(1*H*)-one (17; R = Me) was isolated (12%) as the sole identifiable product. Likewise, the β-styryl derivative (16; R = Ph) decomposed in boiling 1-methylnaphthalene to give 3-phenylquinolin-4(1*H*)-one (17; R = Ph) (35%) along with much tar. Inexplicably, decomposition of the 3-(β-styryl)benzotriazinone in paraffin oil at 300 °C proceeded smoothly and cleanly to 3-phenylquinolin-4(1*H*)-one in much greater yield (70%). The formation of 3-substituted quinolinones is
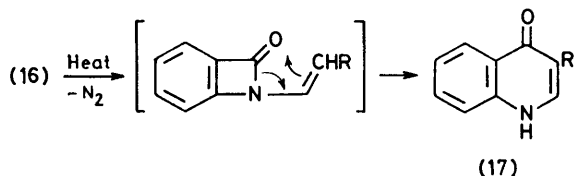
Scheme 6

compatible with the process outlined in Scheme 6. No isoquinolinones were isolated.

Photolysis of the 3-alkenylbenzotriazinones proved to be unrewarding. The vinyl and propenyl derivatives gave in addition to unchanged material only polymers,

hot benzene, which on evaporation gave the *o*-aminobenzanilide sufficiently pure for direct use in the next stage of the reaction. The crude anilides were stirred rapidly in a mixture of concentrated hydrochloric acid (100 ml) and water (200 ml) at room temperature. The resulting solution was cooled to 0—5 °C and then diazotised using an excess (20%) of sodium nitrite in water. The reaction mixture was stirred for 2—3 h at 0—5 °C and filtered to give the 3-aryl-1,2,3-benzotriazin-4(3*H*)-one which was recrystallised from ethanol.

The following derivatives of 1,2,3-benzotriazin-4(3*H*)-one were prepared: 3-phenyl-, m.p. 150 °C (lit.,[10] 151 °C); 3-(*p*-nitrophenyl)- (36%), m.p. 252 °C (decomp.) (lit.,[10] 254 °C); 3-(*p*-tolyl)- (41%), m.p. 141 °C (decomp.) (lit.,[10] 143 °C); 3-(*p*-bromophenyl)- (32%), m.p. 197 °C (lit.,[11] 196 °C); 3-(*p-chlorophenyl*)- (60%), m.p. 186—187 °C (Found: C, 60.4; H, 3.3; N, 16.2. $C_{13}H_8ClN_3O$ requires C, 60.55; H, 3.1; N, 16.3%), *m/e* 257 and 259 (M^+); 3-(*p-methoxyphenyl*)- (64%), m.p. 156 °C (Found: C, 66.6; H, 4.1; N, 16.7. $C_{14}H_{11}N_3O_2$ requires C, 66.4; H, 4.4; N, 16.6%), *m/e* 253 (M^+); 3-(α-*naphthyl*)- (39%), m.p. 145 °C (Found: C, 74.5; H, 4.02; N, 15.6. $C_{17}H_{11}N_3O$ requires C, 74.7; H, 4.03; N, 15.4%), *m/e* 273 (M^+). The 3-(α-naphthyl)-derivative was also prepared by *o*-nitrobenzoylation (using *o*-nitrobenzoyl chloride) of α-naphthylamine in pyridine solution. The *N*-(*o*-nitrobenzoyl)-α-

Products from decomposition of 3-aryl-1,2,3-benzotriazin-4(3*H*)-ones (7)

(7) Ar	% Yield (g) of 9-acridone (4) from decomposition of (7)				% Yield of PhCONHAr from heating of (7) in paraffin oil *
	(a) Heat as solid	(b) Heat in 1-methylnaphthalene	(c) *hv* in THF	(4) R	
Ph	27 (0.24)	42 (0.36)	2	H [a]	2
p-NO₂C₆H₄					
p-MeC₆H₄	21 (0.18)	35 (0.31)	1	Me [b]	2
p-MeOC₆H₄	5 (0.05)	15 (0.13)		MeO [c]	
p-BrC₆H₄	15 (0.14)	33 (0.3)	1	Br [d]	1
p-ClC₆H₄	18 (0.16)	27 (0.24)	1	Cl [e]	1

* In each case large amounts (>90%) of starting material were recovered.

[a] M.p. 352 °C (lit.,[12] 354 °C). [b] M.p. 334—337 °C (lit.,[13] 338 °C); [c] M.p. 280—283 °C (lit.,[14] 282—284 °C). [d] M.p. >360 °C (lit.,[15] >360 °C); 9-(4-dimethylaminophenyl) derivative, m.p. 240 °C (lit.,[16] 239 °C). [e] M.p. >360 °C (lit.,[15] >360 °C); 9-(4-dimethylaminophenyl) derivative, m.p. 227 °C (lit.,[17] 230 °C).

whereas the styryl derivative (16; R = Ph) furnished a low yield (10%) of a yellow crystalline material of high molecular weight (M^+ >350) which has not yet been identified.

EXPERIMENTAL

[1]H N.m.r. spectra were measured unless otherwise stated for CDCl₃ solutions (SiMe₄ as internal standard) on a Varian EM-360 or a Perkin-Elmer R32 n.m.r. spectrometer. Mass spectra were obtained on an A.E.I. MS12 mass spectrometer. I.r. spectra were recorded as Nujol mulls or liquid films on either a Perkin-Elmer 297 or 257 grating i.r. spectrophotometer.

Preparation of 3-Aryl-1,2,3-benzotriazin-4(3H)-ones.—General method. A finely ground mixture of arylamine (0.012 mol) and isatoic anhydride (16.3 g, 0.01 mol) was heated on an oil-bath until reaction commenced and carbon dioxide was evolved. The reaction mixture was maintained at this temperature until gas evolution ceased. After cooling, the glassy solid residue was extracted with

naphthylamine, m.p. 203 °C, was reduced in ethanol solution at atmospheric pressure using hydrogen and 5% Pd–C. Diazotisation of *N*-(*o*-aminobenzoyl)-α-naphthylamine (m.p. 155 °C) as in the general method gave the 3-(α-naphthyl)-benzotriazinone, m.p. 145 °C (95%).

Thermolysis of 3-Aryl-1,2,3-benzotriazin-4(3H)-ones.— (a) *In the solid state.* The 3-arylbenzotriazinone (1 g) contained in a 25-ml flask fitted with a long air-condenser containing a loose cotton-wool plug, was gently heated until decomposition commenced. The reactions were exothermic, particularly in the case of the 3-(*p*-nitrophenyl) derivative. The charred residue was finely ground and separated by preparative t.l.c. (SiO₂–CHCl₃). Yields of acridones so obtained are given in the Table.

(b) *In 1-methylnaphthalene.* A suspension of the 3-arylbenzotriazinone (1 g) in 1-methylnaphthalene (25 ml) was heated under reflux for 15—30 min. The excess of solvent was then removed under reduced pressure, and the semisolid residue triturated with light petroleum (b.p. 100—120 °C) to give the crude 9-acridone (see Table). The acridones were purified by column chromatography (SiO₂).

(c) *In paraffin oil*. A suspension of the benzotriazinone (1 g) in paraffin oil (50 ml) was heated at 300 $\pm$ 10 °C for 2 h. After the reaction mixture had been cooled, light petroleum was added to it until all the product had precipitated. Chromatographic separation of the crude solid on silica gave mainly starting material (see Table) together with a small quantity of anilide, which was identified by comparison with the anilide obtained from the reaction of isatoic anhydride with the appropriate arylamine. The 3-(*p*-nitrophenyl)benzotriazinone gave only tars.

Photolysis of 3-Aryl-1,2,3-benzotriazin-4(3H)-ones.—Irradiations were carried out during 24 h on a solution of the benzotriazinone (0.5 g) in dry THF (225 ml) using a medium-pressure Hg lamp and a Pyrex filter. Removal of the solvent followed by separation of the residue by preparative t.l.c. (SiO_2–$CHCl_3$) gave mainly starting material together with a small amount of acridone (see Table).

Thermolysis of 3-(α-Naphthyl)-1,2,3-benzotriazin-4(3H)-one.—A slurry of 3-(α-naphthyl)-1,2,3-benzotriazinone (1 g) in liquid paraffin (10 ml) was added to liquid paraffin (10 ml) at 300 °C. When effervescence ceased, the mixture was cooled and the products precipitated by the addition of light petroleum. The solid (0.65 g) so obtained was dissolved in hot glacial acid. On cooling the acid solution, benzo[*c*]acridone (0.15 g, 17%), m.p. 365—367 °C (lit.,[15] >360 °C), was obtained as pale yellow prisms. The mother-liquor on evaporation to dryness gave benzo[*c*]phenanthridinone (0.4 g, 45%), as a buff residue, which could be recrystallised from a small volume of glacial acetic acid, m.p. 330 °C (lit.,[18] 332 °C).

Preparation of Naphtho[2,3-d]-v-triazin-4(3H)-one and Its 3-Phenyl Derivative.—A solution of 3-amino-2-naphthoic acid [19] (4.7 g) and sodium nitrite (1.8 g) in 2M-sodium hydroxide (100 ml) and water (50 ml) was added, with constant stirring, to 4M-hydrochloric acid (90 ml) at 0—5 °C. The resulting diazonium chloride solution was filtered off and the filtrate added dropwise to a stirred solution of sodium acetate (30 g) and sodium azide (2 g) in water (100 ml). The reaction mixture was stirred until nitrogen evolution ceased and was then acidified and filtered. The residue of 2-azido-3-naphthoic acid was dried and recrystallised from ethanol and had m.p. 180—185 °C (decomp.) (4.4 g, 81%) (Found: C, 61.6; H, 3.51; N, 19.7. $C_{11}H_7N_3O_2$ requires C, 61.9; H, 3.3; N, 19.7%), *m/e* 213 (M^+); $\nu(N_3)$ 2 130 and $\nu(CO)$ 1 710 cm^{-1}.

A mixture of the azido-acid (1.7 g) and thionyl chloride (1 ml) in dry benzene (10 ml) was heated under reflux for 45 min. Removal of the solvent under reduced pressure gave 2-azido-3-naphthoyl chloride as a pale yellow crystalline solid which was dissolved without further purification in pyridine (10 ml). To the pyridine solution was added concentrated ammonia solution (5 ml) and the reaction mixture was set aside at room temperature overnight. Removal of the solvent under reduced pressure afforded crude 3-*azido-2-naphthamide* (0.6 g, 35%), which crystallised from ethanol as white prisms, m.p. 150—155 °C (decomp.) (Found: C, 62.5; H, 3.50; N, 26.2. $C_{11}H_8N_4O$ requires C, 62.6; H, 3.8; N, 26.4%); *m/e* 212 (M^+).

Similarly prepared from 2-azido-3-naphthoyl chloride (6 g) and aniline (2.5 g) was 3-*azido-2-naphthanilide* (6.1 g, 75%), which crystallised from ethanol as yellow crystals, m.p. 175—180 °C (decomp.) (Found: C, 70.5; H, 4.1; N, 19.2. $C_{17}H_{12}N_4O$ requires C, 70.8; H, 4.2; N, 19.4%), *m/e* 288 (M^+). A solution of 3-azido-2-naphthamide (0.6 g)

in ethanol (50 ml) containing a catalytic quantity of 10% Pd–C was stirred under a H_2 atmosphere for 8 h. The solution was filtered, and the filtrate evaporated to dryness to yield 3-amino-2-naphthamide (0.4 g, 75%), m.p. 232—234 °C (lit.,[20] 234—236 °C).

3-Azido-2-naphthanilide (5 g) was reduced similarly using a Raney Ni catalyst to yield 3-*amino-2-naphthanilide* (3.8 g, 83%), which crystallised from ethanol as yellow prisms, m.p. 235—237 °C (Found: C, 77.8; H, 5.4; N, 10.8. $C_{17}H_{14}N_2O$ requires C, 77.8; H, 5.4; N, 10.7%), *m/e* 262 (M^+).

To a stirred suspension of 3-amino-2-naphthamide (1.6 g) in concentrated hydrochloric acid (25 ml) and water (40 ml) at 0—5 °C was added dropwise a solution of sodium nitrite (1 g) in water (15 ml). The resulting mixture was stirred at 0 °C for 1 h and then filtered to give naphtho-[2,3-*d*]-*v*-triazin-4(3*H*)-one (1 g, 59%), which crystallised from glacial acetic acid as pale pink needles, m.p. 252—254 °C (decomp.) (lit.,[21] 250 °C).

Prepared similarly was 3-phenylnaphtho[2,3-*d*]-*v*-triazin-4(3*H*)-one (72%) as white crystals from glacial acetic acid, m.p. 221—223 °C (lit.,[4] 226 °C).

Thermolysis of Naphtho[2,3-d]-v-triazin-4(3H)-one.—Decomposition (1 g) in liquid paraffin at 300 °C was carried out as for 3-(α-naphthyl)benzotriazinone. Addition of light petroleum (b.p. 60—80 °C) to the reaction mixture precipitated a mass of carbonaceous material which was insoluble in chloroform and in ethanol and from which no products could be isolated.

Photolysis of the unsubstituted naphthotriazinone (1 g) in dry THF (200 ml) for 12 h resulted in quantitative recovery of starting material.

Thermolysis of 3-Phenylnaphtho[2,3-d]-v-triazin-4(3H)-one.—The thermolysis was carried out as in the previous example. Addition of light petroleum (b.p. 60—80 °C) to the cold reaction mixture brought about precipitation of a brown solid, which on chromatographic separation on alumina ($CHCl_3$ as eluant) gave benzo[*b*]acridone (0.06 g, 20%), m.p. 300—306 °C (lit.,[21] 304—305 °C) as the sole identifiable product.

3-(2-Hydroxyethyl)-1,2,3-benzotriazin-4(3H)-one.—To a solution of ethanolamine (6.7 g) in water (30 ml) at room temperature was added portionwise isatoic anhydride (16.3 g). After the initial effervescence had ceased the dark brown solution was heated on a water-bath at 100 °C for 15 min. The mixture was then acidified by addition of concentrated hydrochloric acid, cooled, and diazotised by addition of a solution of sodium nitrite (7 g) in water (20 ml). The mixture was stirred at 0—5 °C for 0.5 h and then neutralised using ammonia solution. The reaction mixture was filtered to yield 3-(2-*hydroxyethyl*)-1,2,3-*benzo-triazin*-4(3*H*)-*one* as a buff residue (15.1 g, 66%) which crystallised from ethyl acetate as off-white prisms, m.p. 117 °C; $\nu(C=O)$ 1 650 cm^{-1} and $\nu(OH)$ 3 450 cm^{-1} (Found: C, 56.4; H, 4.75; N, 22.2. $C_9H_9N_3O_2$ requires C, 56.6; H, 4.75; N, 22.0%), *m/e* 191 (M^+).

The 3-(2-hydroxypropyl)- and 3-(2-hydroxy-2-phenethyl)-derivatives were prepared similarly using 2-hydroxy-propylamine and 2-amino-1-phenylethanol, respectively. 3-(2-*Hydroxypropyl*)-1,2,3-*benzotriazin*-4(3*H*)-*one* (58%) crystallised from benzene–light petroleum (b.p. 80—100 °C) had m.p. 68 °C; $\nu(C=O)$ 1 660 and $\nu(OH)$ 3 480 cm^{-1} (Found: C, 58.35; H, 5.4; N, 20.85. $C_{10}H_{11}N_3O_2$ requires C, 58.5; H, 5.4; N, 20.5%), *m/e* 205 (M^+). 3-(2-*Hydroxy-2-phen-ethyl*)-1,2,3-*benzotriazin*-4(3*H*)-*one* (62%) crystallised from

ethyl acetate–light petroleum (b.p. 80—100 °C), m.p. 148 °C; ν(C=O) 1 660 and ν(OH) 3 420 cm⁻¹ (Found: C, 67.3; H, 4.9; N, 15.8. $C_{15}H_{13}N_3O_2$ requires C, 67.4; H, 4.9; N, 15.7%), m/e 267 (M⁺).

Tosylation.[22]—To a solution of 3-(2-hydroxyethyl)-1,2,3-benzotriazin-4(3H)-one (10 g) in pyridine (250 ml) at 0 °C was added portionwise toluene-p-sulphonyl chloride (20 g). The mixture was stirred at 0 °C for 7 h, poured into ice–water (2 l) and filtered to yield 3-(2-p-*tosyloxyethyl*)-1,2,3-*benzotriazin*-4(3H)-*one* (17.5 g, 97%), which crystallised from chloroform–light petroleum (b.p. 80—100 °C), m.p. 161 °C; ν(C=O) 1 680 cm⁻¹ (Found: C, 55.6; H, 4.44; N, 12.3. $C_{16}H_{15}N_3O_4S$ requires C, 55.6; H, 4.4; N, 12.3%), m/e 345 (M⁺).

Similarly prepared were 3-(2-p-*tosyloxypropyl*)-1,2,3-*benzotriazin*-4(3H)-*one* (97%) which crystallised from ethyl acetate–light petroleum (b.p. 80—100 °C), m.p. 181 °C; ν(C=O) 1 700 cm⁻¹ (Found: C, 56.75; H, 4.8; N, 11.8. $C_{17}H_{17}N_3O_4S$ requires C, 56.8; H, 4.9; N, 11.7%), m/e 359 (M⁺), and 3-[2-(p-*tosyloxy*)-2-*phenethyl*]-1,2,3-*benzotriazin*-4(3H)-*one* (85%), m.p. 150 °C (decomp.) [EtOAc–light petroleum (b.p. 80—100 °C)]; ν(C=O) 1 700 cm⁻¹ (Found: C, 62.5; H, 4.7; N, 10.05. $C_{22}H_{19}N_3O_4S$ requires C, 62.7; H, 4.5; N, 9.7%), m/e 421 (M⁺).

3-Vinyl-1,2,3-benzotriazin-4(3H)-one.—To a solution of potassium (1.25 g) in dry t-butyl alcohol (65 ml) was added 3-(2-p-tosyloxyethyl)-1,2,3-benzotriazin-4(3H)-one (10 g) and the mixture was stirred at room temperature for 75 min. Removal of the solvent under reduced pressure and trituration of the residue with water (50 ml), gave 3-*vinyl*-1,2,3-*benzotriazin*-4(3H)-*one* (3.2 g, 64%), which crystallised from ethyl acetate–light petroleum (b.p. 80—100 °C) as white needles, m.p. 109 °C; ν(C=O) 1 695 cm⁻¹ (Found: C, 61.8; H, 4.05; N, 23.9. $C_9H_7N_3O$ requires C, 62.4; H, 4.07; N, 24.3%), m/e 173 (M⁺). ¹H N.m.r. δ 5.2 (d, 1 H, =CH₂ cis-H, J 9 Hz), 6.07 (d, 1 H, =CH₂, trans-H, J 17 Hz), 7.55—8.32br (m, 5 H, aromatics and N–CH=).

Prepared similarly were 3-(*prop*-1-*enyl*)-1,2,3-*benzotriazin*-4(3H)-*one* (84%) as white needles from EtOAc–light petroleum (b.p. 80—100 °C), m.p. 164 °C; ν(C=O) 1 665 cm⁻¹ (Found: C, 63.9; H, 4.9; N, 22.6. $C_{10}H_9N_3O$ requires C, 64.2; H, 4.6; N, 22.45%), m/e 187 (M⁺). ¹H N.m.r. δ 1.94 (d, 3 H, CH₃, J 7 Hz), 6.42—6.77br (m, 1 H, =CHMe), 7.34—8.4br (m, 5 H, aromatics and –N–CH=), m/e 187 (M⁺); and 3-(β-*styryl*)-1,2,3-*benzotriazin*-4(3H)-*one* (95%) as bright yellow prisms from EtOAc–light petroleum (b.p 80—100 °C), m.p. 166 °C; ν(C=O) 1 695 cm⁻¹ (Found: C, 72.0; H, 4.6; N, 16.8. $C_{15}H_{11}N_3O$ requires C, 72.3; H, 4.45; N, 16.9%). ¹H N.m.r. δ 7.1—8.36br (m, aromatic and vinyl protons), m/e 249 (M⁺).

Thermolysis of 3-Vinyl-1,2,3-benzotriazin-4(3H)-one.— (a) *In liquid paraffin at* 220—240 °C. Decomposition (2.5 g) of material was carried out as for the 3-(α-naphthyl)-benzotriazinone. Addition of light petroleum (b.p. 60—80 °C) to the reaction mixture yielded a dark brown tar; t.l.c. (Al₂O₃–CHCl₃) investigation of which indicated a complex mixture of products.

(b) *In* 1-*methylnaphthalene.* A solution of 3-vinyl-1,2,3-benzotriazin-4(3H)-one (2 g) in 1-methylnaphthalene (30 ml) was boiled for 15 min. Removal of solvent gave a black semisolid, which t.l.c. again showed to be a complex mixture of products.

Thermolysis of 3-(Prop-1-enyl)-1,2,3-benzotriazin-4(3H)-one.—(a) *In liquid paraffin.* 3-(Prop-1-enyl)-1,2,3-benzo-triazin-4(3H)-one (2.5 g) was decomposed in a similar

manner to the 3-vinyl derivative. Only intractable tarry products were obtained.

(b) *In* 1-*methylnaphthalene.* A solution of 3-(prop-1-enyl)-1,2,3-benzotriazin-4(3H)-one (3 g) in 1-methyl-naphthalene (25 ml) was boiled for 2 h. Removal of solvent under reduced pressure gave a brown oily residue, the t.l.c. (Al₂O₃–EtOAc) of which showed starting material and a complex mixture of products. Column chromato-graphy (Al₂O₃–EtOAc) gave as a first fraction starting material (1.1 g, 37%). Elution with methanol gave 3-methylquinolin-4(1H)-one (0.3 g, 12%) as pale yellow needles, from ethanol–ethyl acetate, m.p. 233 °C (lit.,[23] 229 °C), m/e 159 (M⁺). Further elution with methanol gave only tarry products.

Thermolysis of 3-(β-Styryl)-1,2,3-benzotriazin-4(3H)-one. —(a) *In liquid paraffin.* 3-(β-Styryl)-1,2,3-benzotriazin-4(3H)-one (2.5 g) was decomposed in a similar manner to the 3-vinyl derivative. Dilution of the reaction mixture with light petroleum (b.p. 60—80 °C) yielded an orange solid, which on crystallisation from ethanol gave 3-phenyl-quinolin-4(1H)-one (1.5 g, 70%) as white needles, m.p. 260 °C (lit.,[24] 257 °C). Mixed m.p. with an authentic sample was undepressed.

(b) *In* 1-*methylnaphthalene.* A solution of the β-styryl-benzotriazinone (2.5 g) was heated under reflux in 1-methylnaphthalene (25 ml) for 1.25 h. The mixture on cooling deposited 3-phenylquinolin-4(1H)-one (0.8 g, 35%) as white needles, m.p. 260 °C. The filtrate on evaporation yielded a dark tarry intractable residue.

Photolysis of 3-Alkenyl-1,2,3-benzotriazin-4(3H)-ones.—A solution of the benzotriazinone (2 g) in dry THF (250 ml) was photolysed (medium-pressure lamp–Pyrex filter) for several hours [12 h for 3-vinyl-, 24 h for 3-propenyl-, and 5 h for 3-(β-styryl)-derivative]. In the case of the vinyl and propenyl derivatives evaporation of the solvent gave a semisolid residue which on chromatographic separation (Al₂O₃–CHCl₃) yielded starting material (0.9 and 0.7 g) respectively and tars.

The 3-(β-styryl)-derivative gave an orange solution, which on t.l.c. (SiO₂–benzene) displayed a predominant yellow spot, R_F 0.9, along with several minor components. Separation of the residue from the reaction mixture on a silica column, benzene as eluant, gave a yellow solid (0.2 g), m.p. 135—150 °C (decomp.) (Found: C, 77.3; H, 5.3; N, 6.0), m/e 120, 205, 256, 296, 306, and 341 (no obvious M⁺).

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