# 1,2,3-Benzotriazin-4-ones and Related Systems. Part II.[1] Thermolytic Decomposition of Substituted 1,2,3-Benzotriazin-4-ones and Isatoic Anhydrides

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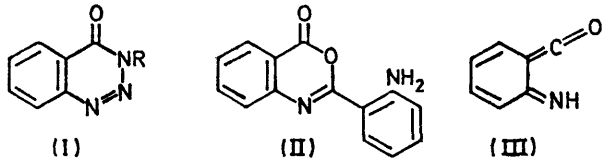
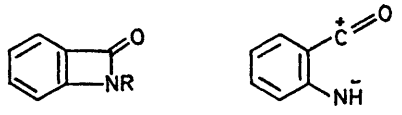
Several nuclear-substituted 1,2,3-benzotriazin-4-ones have been thermolysed in an inert solvent. In each case the major identifiable product proved to be a 2-(*o*-aminophenyl)-3,1-benzoxazin-4-one. Nuclear-substituted isatoic anhydrides on thermolysis behaved similarly.

We have recently shown [1] that 1,2,3-benzotriazin-4-one (I; R = H) on heating in an inert solvent yields 2-(*o*-aminophenyl)-3,1-benzoxazin-4-one (II) as the major product. The benzoxazinone is considered to arise *via* a Diels–Alder-type cycloaddition of the iminoketen (III), formed by loss of nitrogen from the triazinone (I),



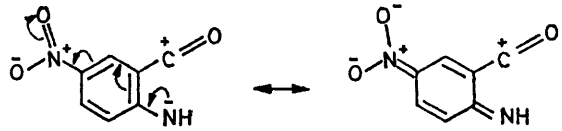
(I) (II) (III)



(IV) (V)

across the carbonyl bond of a second molecule of (III). The intermediate iminoketen may be regarded as a valence tautomer of the hitherto unknown benzazetone (IV; R = H). *N*-Substituted benzazetones have been proposed as intermediates in the decomposition of 3-substituted 1,2,3-benzotriazin-4-ones by various workers.[2-4] However, no work has been reported on the thermal decomposition of nuclear-substituted benzotriazinones. Such decompositions are of interest since a polar form (V) of the benzazetone (IV) could

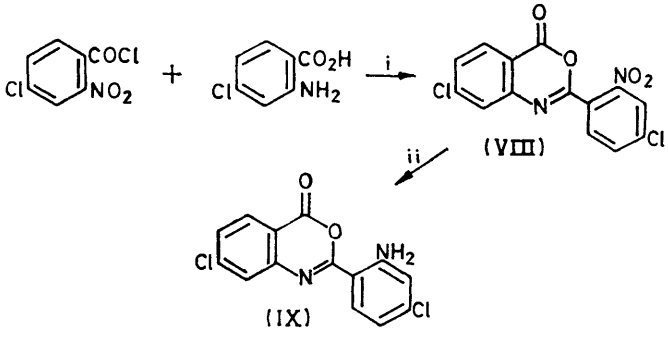
(VI) (VIa)



(VII) (VIIa)

well be stabilised by mesomeric interaction of a suitably placed substituent with either the carbonyl or the imine function of (V) [*e.g.* (VI) ⟷ (VIa) and (VII) ⟷ (VIIa)]. It was hoped that stabilisation of this type would cause a lowering of the decomposition temperature of the benzotriazinone and hence not only increase the possibility of isolating the intermediary benzazetone, but also render the synthetically useful iminoketen (III) more readily available.

Accordingly 6-chloro-, 7-chloro-, 6-methoxy-, 7-methoxy-, and 6-nitro-1,2,3-benzotriazin-4-one were prepared and made to decompose in boiling 1-methylnaphthalene. In each case, however, the decomposition temperature of the benzotriazinone was little changed from that of the unsubstituted triazinone (I; R = H), and in no instance was there any indication of a benzazetone in the products. In fact heating the benzotriazinones in solution at *ca.* 250° gave in each case (except when the substituent was nitro) the appropriately substituted 2-(*o*-aminophenyl)-3,1-benzoxazin-4-one as the sole identifiable product, in 40—50% yield.



Scheme 1

Reagents: i, PhCOCl, pyridine; ii, Ni–$H_2$

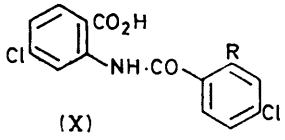
In the case of 6-nitro-1,2,3-benzotriazin-4-one, t.l.c. of the reaction mixture indicated the formation of a multitude of products, none of which corresponded to the expected benzoxazinone.

The benzoxazinones were characterised by their i.r. spectra (carbonyl stretching at *ca.* 1760 $cm^{-1}$) and by elemental analysis. In the case of the dichloro-compound (IX), the structure was confirmed by unambiguous synthesis as indicated in Scheme 1. The anthranilamide (X; R = $NO_2$) was not isolated but was cyclised directly to give the chloronitrobenzoxazinone (VIII) with benzoyl chloride.[5] The nitro-compound

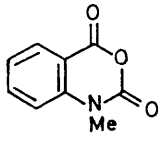
[1] H. E. Crabtree, R. K. Smalley, and H. Suschitzky, *J. Chem. Soc.* (*C*), 1968, 2730, is considered to be Part I.
[2] E. M. Burgess and G. Milne, *Tetrahedron Letters*, 1966, 93.
[3] G. Ege and F. Pasedach, *Chem. Ber.*, 1968, **101**, 3089.
[4] G. Ege, *Chem. Ber.*, 1968, **101**, 3079.
[5] D. I. Bain and R. K. Smalley, *J. Chem. Soc.* (*C*), 1968, 1593.

was reduced to the required amine (IX) by Raney nickel and hydrogen at atmospheric pressure. A trace of alkali in the nickel catalyst resulted in isolation of the hydrolysis product of the benzoxazinone (IX), *i.e.* the *N*-acyl anthranilic acid (X; R = $NH_2$) rather than the benzoxazinone itself. The susceptibility of 3,1-benzoxazin-4-ones towards alkaline hydrolysis is well known,[6] and the kinetics of the hydrolytic ring opening have recently been investigated.[7]

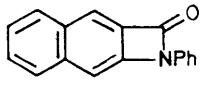
The *N*-phenylnaphthazetone (XI) has been isolated [8] and characterised as a stable crystalline solid from the photolytic decomposition of the 3-phenyl-1,2,3-naphthotriazin-4-one (XII), and several workers [2,4,9] have shown that benzazetones are involved as intermediates in the photolytically induced breakdown of benzotriazinones. However, Ege [4] has pointed out that benzotriazinone itself (I; R = H) and benzotriazinones possessing a saturated substituent (*e.g.* Me) at the 3-position are photostable. Our observations are in



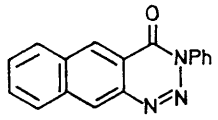
(X)



(XIV)



(XI)

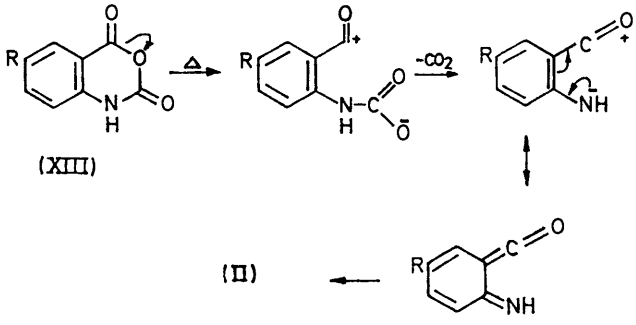


(XII)

accord with this: solutions of the nuclear-substituted benzotriazinones in either tetrahydrofuran or acetone are unaffected after u.v. irradiation for 3 days.

It has also been shown [1] that isatoic anhydride (XIII; R = H) will decompose in solution at temperatures above its m.p. (242°) to yield as major product the aminobenzoxazinone (II). Formation of the product (II) is readily explained in terms of loss of carbon dioxide from the isatoic anhydride, probably in a stepwise manner (Scheme 2), to give the iminoketen intermediate (III), identical with that formed by loss of nitrogen from the benzotriazinone (I; R = H). In order to compare the merit of isatoic anhydride decompositions with those of benzotriazinones as a source of intermediate (III), several substituted isatoic anhydrides were prepared and their thermal decomposition in an inert solvent investigated.

Each of the isatoic anhydrides studied had a higher temperature of decomposition than the corresponding benzotriazinone. Thermolysis of 6-nitroisatoic anhydride (XIII; R = $NO_2$) in 1-methylnaphthalene at 250° gave only a complicated mixture of unidentified products. In this reaction, and in the case of the nitro-substituted benzotriazinone, the by-products may be



(XIII)

(II)

SCHEME 2

the result of oxidation by the nitro-group. In the case of 6-bromo- and 6-chloro-isatoic anhydride (XIII; R = Br or Cl) only the appropriately substituted aminobenzoxazinones were isolated, albeit in lower yields (10—15%) than those obtained by decomposition of the corresponding benzotriazinone.

The mass spectra of the prepared benzotriazinones and isatoic anhydrides have been measured. The benzotriazinones exhibit fragmentation patterns in accord with the recently reported [10,11] spectra of 1,2,3-benzotriazin-4-one and several of its 3-substituted derivatives; *i.e.* the initial fragmentation involves loss of nitrogen to give the species (*M* — 28), which is thought to be the 1,2-dihydro-2-oxobenzazetium ion, and which suffers further losses of 28 and 27 mass units corresponding to carbon monoxide and hydrogen cyanide, respectively.

As expected, in all the isatoic anhydrides studied the base peak is formed by loss of 44 mass units (carbon dioxide). Isatoic anhydride itself (XIII; R = H), after initial loss of carbon dioxide, yields a spectrum virtually identical with that exhibited by 1,2,3-benzotriazin-4-one (I; R = H). Comparison of the mass spectra of 6-chloro-1,2,3-benzotriazin-4-one and 6-chloroisatoic anhydride (XIII; R = Cl) revealed after initial loss of 28 ($N_2$) and 44 ($CO_2$) mass units, respectively, the same fragmentation pattern.

The mass spectrum of *N*-methylisatoic anhydride (XIV) also exhibits ready loss of carbon dioxide (*M* — 44; base peak). However, the compound proved to be stable at its m.p. (174°) and was recovered unchanged from boiling 1-methylnaphthalene, whereas at 300° slow decomposition to give a mixture of traces of unidentified products was observed.

*Synthesis of Benzotriazinones.*—Diazotisation of *o*-aminobenzamides proved to be the most effective method.[12a] 7-Chloro-1,2,3-benzotriazin-4-one was also prepared, but in much lower yield, by treatment of

[6] 'The Chemistry of Heterocyclic Compounds,' ed. R. H. Wiley, Interscience, New York, 1962, vol. 17, p. 359.
[7] A. Williams and G. Salvadori, *J. Chem. Soc.* (*B*), 1971, 1105.
[8] G. Ege and E. Beisiegel, *Angew. Chem. Internat. Edn.*, 1968, **7**, 303.
[9] G. Ege, *Angew. Chem. Internat. Edn.*, 1965, **4**, 699.
[10] J. C. Tou, L. A. Shadoff, and R. H. Rigterink, *Org. Mass Spectrometry*, 1969, **2**, 355.
[11] C. Wünsche, G. Ege, E. Beisiegel, and F. Pasedach, *Tetrahedron*, 1969, **25**, 5869.
[12] 'The Chemistry of Heterocyclic Compounds,' ed. A. Weissberger, Interscience, New York, 1956, vol. 10, (*a*) p. 14; (*b*) p. 16.

diazotised methyl 2-amino-4-chlorobenzoate with ammonium hydroxide.[12b]

*Synthesis of Isatoic Anhydrides.*—The required isatoic anhydrides were prepared by oxidation of the corresponding isatins with chromium trioxide in acetic acid solution.[13] The isatins were obtained by cyclisation of isonitrosoacetanilides with concentrated sulphuric acid.[14,15] By this method 5-methoxyisatin was obtained only in low yield, and the use of 90% sulphuric acid as recommended in the literature [16,17] again gave only poor yields,* as did the use of polyphosphoric acid.[18]

## EXPERIMENTAL

$^1$H N.m.r. spectra were measured for solutions in deuteriochloroform unless otherwise stated, with a Varian A60A instrument (tetramethylsilane as internal reference). I.r. spectra were measured for Nujol mulls with a Perkin-Elmer 227 spectrophotometer.

6-*Nitro*-1,2,3-*benzotriazin*-4-*one*.—To a suspension of finely ground 2-amino-5-nitrobenzamide (4·5 g), prepared by treating 5-nitroisatoic anhydride with ammonium hydroxide,[19] in a mixture of concentrated hydrochloric acid (14 ml) and water (45 ml) maintained at 0—5° was added dropwise with stirring a solution of sodium nitrite (2·8 g) in water (16 ml). The mixture was stirred for 30 min at 0—5° and then filtered to yield 6-nitro-1,2,3-benzotriazin-4-one (4·15 g, 86·5%), which crystallised from ethanol as pale yellow needles, m.p. 194° (decomp.). [lit.,[20] 195° (decomp.)].

6-*Chloro*-1,2,3-*benzotriazin*-4-*one*.—(a) 5-*Chloro*-2-*nitrobenzoic acid*. To a boiling solution of 5-chloro-2-nitrotoluene (21·5 g) in pyridine (110 ml) and water (83·5 ml), potassium permanganate (6 × 9·2 g) was added at hourly intervals. The mixture was then heated under reflux for a further 1 h and filtered hot. The residue was washed with hot 50% aqueous pyridine (2 × 50 ml) and the combined washings and filtrate were evaporated to dryness. The residue was dissolved in ether (250 ml) and then extracted with 2M-sodium hydroxide (2 × 50 ml). Acidification of the alkaline extracts gave 5-chloro-2-nitrobenzoic acid (8·6 g, 49·4%) as a white granular solid, m.p. 139° (lit.,[21] 138—140°).

From the ether layer, 5-chloro-2-nitrotoluene (6·6 g) was recovered.

(b) 5-*Chloro*-2-*nitrobenzamide*. A solution of 5-chloro-2-nitrobenzoic acid (7·7 g) in dry benzene (90 ml) and thionyl chloride (3 ml) was heated under reflux for 90 min. The solution was cooled and then cautiously neutralised with concentrated ammonium hydroxide to give 5-chloro-2-nitrobenzamide (6·5 g, 83·5%), which crystallised from ethanol as needles, m.p. 156·5° (lit.,[22] 154°).

(c) 2-*Amino*-5-*chlorobenzamide*. 5-Chloro-2-nitrobenzamide (6·52 g) was hydrogenated in 1 : 1 benzene–ethanol (150 ml) over Raney nickel at atmospheric pressure. After filtration and distillation, 2-amino-5-chlorobenzamide (4·32 g, 87%) was obtained as a white solid, m.p. 170° (lit.,[22] 172°).

(d) 2-Amino-5-chlorobenzamide (3·13 g) was treated with sodium nitrite as described in the preparation of 6-nitro-1,2,3-benzotriazin-4-one. 6-Chloro-1,2,3-benzotriazin-4-one (2·58 g, 82%) crystallised from ethanol as pale yellow needles, m.p. 205—206° (decomp) [lit.,[23] 210—211° (decomp.)].

7-*Chloro*-1,2,3-*benzotriazin*-4-*one*.—*Method A*. To a suspension of methyl 2-amino-4-chlorobenzoate [24] (2·32 g) in water (35 ml) and hydrochloric acid (15 ml) maintained at 0—5°, a solution of sodium nitrate (3 g) in water (17 ml) was added dropwise with stirring. The resulting solution was stirred at 0—5° for 1 h and then rapidly filtered. The clear diazonium chloride solution was made alkaline with concentrated ammonium hydroxide solution while the temperature of the mixture was kept below 5°. The basified solution was filtered to remove starting material and acidified with concentrated hydrochloric acid. 7-Chloro-1,2,3-benzotriazin-4-one (0·12 g, 5·3%) was obtained as a buff solid, m.p. 213° (decomp.) [lit.,[23] 215—216° (decomp.)].

*Method B*. (a) 4-*Chloro*-2-*nitrobenzamide*. 4-Chloro-2-nitrobenzoic acid (27 g; m.p. 138—140°), prepared (51%) by alkaline permanganate oxidation [25] of 4-chloro-2-nitrotoluene, was converted into the amide, as described for the preparation of 5-chloro-2-nitrobenzamide, and crystallised from ethanol as needles (21·6 g, 80%), m.p. 172° (lit.,[26] 172°).

(b) 2-*Amino*-4-*chlorobenzamide*. Catalytic reduction (Ni–$H_2$) of 4-chloro-2-nitrobenzamide (7·3 g) as for the preparation of 2-amino-5-chlorobenzamide, gave 2-amino-4-chlorobenzamide (5·9 g, 95%), m.p. 181° (lit.,[24] 181·5°).

(c) The triazinone was prepared by diazotisation of 2-amino-4-chlorobenzamide (3·1 g) as already described for the preparation of 6-nitro-1,2,3-benzotriazin-4-one. The product was obtained as a brown solid (2·89 g, 87%) which crystallised from ethanol as needles, m.p. 215° (decomp.).

6-*Methoxy*-1,2,3-*benzotriazin*-4-*one*.—(a) 5-*Methoxy*-2-*nitrobenzoic acid*. 5-Methoxy-2-nitrobenzoic acid [m.p. 134° (lit.,[27] 133°)] was prepared (8·42 g, 26%) by oxidation with alkaline potassium permanganate of 3-methyl-4 nitroanisole (26·05 g), obtained [28] from 3-methyl-4-nitrophenol.

(b) 5-*Methoxy*-2-*nitrobenzamide*. 5-Methoxy-2-nitrobenzoic acid (6·17 g) was converted *via* the acid chloride into 5-methoxy-2-nitrobenzamide (4·9 g, 80%) as previously described. The amide crystallised from ethanol as white prisms, m.p. 158° (lit.,[29] 158°).

* We thank a referee for details concerning the preparation of 5-methoxyisatin in good yield.

[13] ' The Chemistry of Heterocyclic Compounds,' ed. A. Weissberger, Interscience, 1954, vol. 17, p. 364.
[14] T. Sandmeyer, *Helv. Chim. Acta*, 1919, **2** 234.
[15] C. S. Marvel and G. S. Miers, *Org. Synth.*, 1951, Coll. Vol. I (2nd edn.), p. 327.
[16] B. R. Baker, R. E. Schaub, J. P. Joseph, F. J. McEvoy, and J. H. Williams, *J. Org. Chem.*, 1952, **17**, 164.
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[18] E. B. Mullock and H. Suschitzky, unpublished results; but see ' Practical Heterocyclic Chemistry,' A. O. Fitton and R. K. Smalley, Academic Press, London, 1968, p. 11.
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[21] K. Brand and H. Zöller, *Ber.*, 1907, **40**, 3324.
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[24] E. B. Hunn, *J. Amer. Chem. Soc.*, 1923, **45**, 1024.
[25] N. J. Leonard and S. N. Boyd, jun., *J. Org. Chem.*, 1946, **11**, 405.
[26] G. Heller, *Ber.*, 1916, **49**, 523.
[27] S. Sanoh and Y. Hayashi, *J. Chem. Soc. Japan*, 1954, **75**, 927.
[28] C. F. Koelsch, *J. Amer. Chem. Soc.*, 1944, **66**, 2019.
[29] H. J. Zeitler, *Z. physiol. Chem.*, 1965, **340**, 73.

(c) A suspension of 2-amino-5-methoxybenzamide (1·66 g) obtained by catalytic reduction (Ni–$H_2$) of 5-methoxy-2-nitrobenzamide as described previously, was diazotised as in the earlier examples. 6-*Methoxy*-1,2,3-*benzotriazin*-4-*one* (1·1 g, 62%) crystallised from 2-ethoxyethanol as pale yellow needles, m.p. 232—233° (decomp.) (Found: C, 54·0; H, 3·9; N, 23·9. $C_8H_7N_3O_2$ requires C, 54·2; H, 4·0; N, 23·7%), $\nu_{max.}$ 3220 and 3095 (NH), and 1673 $cm^{-1}$ (C=O).

7-*Methoxy*-1,2,3-*benzotriazin*-4-*one*.—(a) 4-*Methoxy*-2-*nitrobenzamide*. 4-Methoxy-2-nitrobenzoic acid (m.p. 193°; 33·5%) was prepared [30] by acidic hydrolysis of 4-cyano-3-nitroanisole [31] (lit.,[30] m.p. 195°), and was converted into the *amide* (10 g, 83%) as described previously. The product formed white *prisms*, m.p. 156° (from ethanol) (Found: C, 48·9; H, 3·9; N, 14·3. $C_8H_{10}N_2O_3$ requires C, 49·0; H, 4·1; N, 14·3%).

(b) A suspension of 2-amino-4-methoxybenzamide (3·04 g), prepared by catalytic reduction (Ni–$H_2$) of 4-methoxy-2-nitrobenzamide as previously described, was diazotised as for the preparation of 6-nitro-1,2,3-benzotriazin-4-one. 7-Methoxy-1,2,3-benzotriazin-4-one (2·78 g, 86%) was obtained as a white solid, which crystallised from 2-ethoxyethanol as needles, m.p. 218—219° (decomp.) (Found: C, 53·95; H, 4·0; N, 24·0. Calc. for $C_8H_7N_3O_2$: C, 54·2; H, 4·0; N, 23·7%) (lit.,[32] m.p. 220—221°), $\nu_{max.}$ 3210 and 3095 (NH), and 1680 $cm^{-1}$ (C=O), *m/e* 177 ($M^+$).

*Thermolysis of Substituted* 1,2,3-*Benzotriazin*-4-*ones*.—*General method*. A suspension of the benzotriazinone (1 g) in 1-methylnaphthalene (15 ml) was added dropwise during 5 min to boiling 1-methylnaphthalene (85 ml). Refluxing was continued for *ca.* 10 min, and then the mixture was evaporated to *ca.* 5 ml under reduced pressure. Trituration of the gummy residue with light petroleum yielded, in all cases except that of the nitro-substituted benzotriazinone, a yellow solid. The product was purified by either column or preparative thin-layer chromatography.

(a) 6-*Nitro*-1,2,3-*benzotriazin*-4-*one*. Treatment as outlined in the general method gave mainly charred material which was extracted with chloroform. T.l.c. of the extract revealed a multitude of products, none of which was isolated in quantity.

(b) 6-*Chloro*-1,2,3-*benzotriazin*-4-*one*. Chromatographic separation of the residue from the thermolysis, on a silica column ($CHCl_3$ as eluant), gave 2-(2-*amino*-5-*chlorophenyl*)-6-*chloro*-3,1-*benzoxazin*-4-*one* (0·36 g, 41%), which crystallised from 2-ethoxyethanol as pale yellow needles, m.p. 222° (Found: C, 54·9; H, 2·5; N, 9·15: $C_{14}H_8Cl_2N_2O_2$ requires C, 54·75; H, 2·6; N, 9·1%), $\nu_{max.}$ 3485 and 3310 ($NH_2$), and 1746 $cm^{-1}$ (C=O), *m/e* 307.

(c) 7-*Chloro*-1,2,3-*benzotriazin*-4-*one*. The solid obtained by trituration of the thermolysis residue with light petroleum was extracted with hot light petroleum (b.p. 100—120°) to yield a yellow crystalline solid, which was recrystallised from ethanol. 2-(2-*Amino*-4-*chlorophenyl*)-7-*chloro*-3,1-*benzoxazin*-4-*one* (0·35 g, 40%) formed pale yellow needles, m.p. 246° (Found: C, 54·9; H, 2·7; N, 9·1. $C_{14}H_8Cl_2N_2O_2$ requires C, 54·75; H, 2·6; N, 9·1%), $\nu_{max.}$ 3487 and 3312 ($NH_2$), and 1745 $cm^{-1}$ (C=O), *m/e* 306 and 310.

(d) 6-*Methoxy*-1,2,3-*benzotriazin*-4-*one*.—The solid obtained by trituration of the thermolysis residue with light petroleum was extracted with hot light petroleum (b.p. 100—120°). The extracts were evaporated to yield a yellow solid, which was purified by preparative t.l.c. ($SiO_2$–$CHCl_3$). 2-(2-*Amino*-4-*methoxyphenyl*)-7-*methoxy*-3,1-*benzoxazin*-4-*one* (0·32 g, 38%) was obtained as a solid which crystallised from 1 : 1 chloroform–light petroleum (b.p. 100—120°) as pale yellow needles, m.p. 182° (Found: C, 64·6; H, 4·85; N, 9·6. $C_{16}H_{14}N_2O_4$ requires C, 64·4; H, 4·7; N, 9·4%), $\nu_{max.}$ 3440 and 3290 ($NH_2$), and 1740 $cm^{-1}$ (C=O), *m/e* 298.

(e) 6-*Methoxy*-1,2,3-*benzotriazin*-4-*one*.—The solid obtained after trituration of the thermolysis residue with light petroleum was purified as in the previous example. 2-(2-*Amino*-5-*methoxyphenyl*)-6-*methoxy*-3,1-*benzoxazin*-4-*one* (0·39 g, 46%) crystallised from chloroform as pale yellow needles, m.p. 175° (Found: C, 64·7; H, 4·6; N, 9·4. $C_{16}H_{14}N_2O_4$ requires C, 64·4; H, 4·7; N, 9·4%), $\nu_{max.}$ 3455 and 3305 ($NH_2$), and 1743 $cm^{-1}$ (C=O), *m/e* 298.

2-(2-*Amino*-4-*chlorophenyl*)-7-*chloro*-3,1-*benzoxazin*-4-*one*.—(a) 7-*Chloro*-2-(4-*chloro*-2-*nitrophenyl*)-3,1-*benzoxazin*-4-*one*. To a solution of 2-amino-4-chlorobenzoic acid (0·85 g, 0·005 mol) in pyridine (10 ml) was added 4-chloro-2-nitrobenzoyl chloride (1·09 g, 0·005 mol). The mixture was shaken for 5 min at room temperature and then benzoyl chloride (0·7 g, 0·005 mol) was added. The pyridine solution was shaken for a further 5 min, then set aside for 25 min, and poured into cold water (50 ml). The precipitate (1·1 g, 66%) crystallised from ethanol as yellow *needles*, m.p. 150° (Found: C, 50·0; H, 1·75; N, 8·2. $C_{14}H_6Cl_2N_2O_4$ requires C, 49·9; H, 1·8; N, 8·3%), $\nu_{max.}$ 1755 $cm^{-1}$ (C=O).

(b) Hydrogenation of the nitro-compound (0·65 g) in ethanol–benzene over a carefully washed, alkali-free Raney nickel catalyst gave 7-chloro-2-(2-amino-4-chlorophenyl)-3,1-benzoxazin-4-one (0·36 g), identical (mixed m.p. and i.r. spectrum) with the product obtained from the thermolysis of 7-chloro-1,2,3-benzotriazin-4-one.

Reduction of the nitro-compound over Raney nickel containing small amounts of alkali yielded a solid product, the i.r. spectrum of which indicated it to be the sodium salt of 2-(2-amino-4-chlorobenzamido)-4-chlorobenzoic acid, m.p. 360°, $\nu_{max.}$ 3487 and 3320 (NH), and 1672 and 1550 $cm^{-1}$ (C=O), rather than the expected benzoxazinone.

Attempted reduction of the nitrobenzoxazinone with hydrogen over 5% palladium–charcoal failed.

*Preparation of Isonitrosoacetanilides and Isatins*.—5-Chloro-, 5-bromo-, and 5-methoxy-isatin were prepared [15] from the corresponding 4-substituted isonitrosoacetanilides.

*Cyclisation of* p-*Methoxyacetanilide Oxime with Polyphosphoric Acid*.—*p*-Methoxyacetanilide oxime (10 g) was added to polyphosphoric acid (200 g) and the mixture was stirred at 60° for 6 h, then poured on crushed ice (1000 g), and stirred until all the polyphosphoric acid had been destroyed. The dark solution was extracted with chloroform to yield 5-methoxyisatin (0·1 g), m.p. 198—199°.

*Preparation of Isatoic Anhydrides*.—6-Chloro- and 6-bromo-isatoic anhydride were prepared by oxidation [16] of the corresponding 5-substituted isatins. Isatoic anhydride, 6-nitroisatoic anhydride, and *N*-methylisatoic anhydride are commercially available.

*Thermolysis of Isatoic Anhydrides*.—*General method*. The isatoic anhydrides (1—4 g) were heated under reflux

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in 1-methylnaphthalene (15—50 ml) for 24 h. The bulk of the solvent was removed by vacuum distillation and the remaining mixture (*ca.* 5 ml) was transferred to a chromatography column ($Al_2O_3$) and eluted with light petroleum (b.p. 40—60°) in order to remove the remaining 1-methylnaphthalene. Further elution with chloroform yielded, in each case, the appropriately substituted benzoxazin-4-one (10—15%).

2-(2-*Amino*-5-*bromophenyl*)-6-*bromo*-3,1-*benzoxazin*-4-*one* (0·25 g), obtained from the decomposition of 6-bromoisatoic anhydride, crystallised from 2-ethoxyethanol as prisms, m.p. 231° (Found: C, 42·4; H, 2·3; N, 6·8. $C_{14}H_8Br_2N_2O_2$ requires C, 42·2; H, 2·0; N, 7·0%), $\nu_{max.}$ 3505 and 3340 ($NH_2$), and 1770 $cm^{-1}$ (C=O).

*Thermolysis of* 6-*Nitroisatoic Anhydride*.—T.l.c. of the reaction mixture obtained from the thermolysis of 6-nitroisatoic anhydride revealed the presence of some fifteen components. Attempts to separate this mixture on an alumina gave only small amounts of unidentified products. In all other cases the 3,1-benzoxazin-4-one obtained exhibited a characteristic i.r. spectrum, and the products obtained from thermolysis of 6-chloro-1,2,3-benzotriazin-4-one and 6-chloroisatoic anhydride were identical (mixed m.p. and i.r. spectra).

*Thermolysis of* N-*Methylisatoic Anhydride*.—*N*-Methylisatoic anhydride (1 g) was recovered unchanged after being heated under reflux in 1-methylnaphthalene for 1 h. The anhydride showed signs of slow decomposition when heated in an oil-bath at 300° for 2 h.

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