Ring Contraction of 1,2,4-Triazin-3-ones to Imidazolin-2-ones and 1,2,3-Triazoles [1]

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On treatment with hydroxylamine-*O*-sulphonic acid 1,2,4-triazin-3-ones undergo ring contraction to give imidazolin-2-ones in high yield. *N*-Aminotriazinones are proposed as intermediates but were not isolated. However, cinnolin-3-one undergoes an analogous ring contraction to oxindole and the intermediate *N*-aminocinnolinone was isolated and shown to rearrange to oxindole.

On treatment with ethereal chloramine at room temperature the 1,2,4-triazin-3-ones undergo a different ring contraction, *via* *N*-chloro-derivatives, to give 1,2,3-triazoles in high yield.

Mechanisms are proposed for these reactions.

OXIDATION of 3-amino-1,2,3-benzotriazin-4-one with lead tetra-acetate gave indazolone and benzocyclopropenone by fragmentation, it was suggested, of the derived amino-nitrene.[2] We wished to compare with this fragmentation that of the isomeric amino-nitrene derived from 2-amino-1,2,4-benzotriazin-3-one. Further, in the monocyclic systems, 1,2,3-triazin-4-ones are unknown whereas the 1,2,4-triazin-3-ones are readily available from the reaction of α-diketones with semicarbazide.[3] We therefore attempted to synthesise 2-amino-1,2,4-triazin-3-ones by *N*-amination of the triazinones with the standard reagents, hydroxylamine-*O*-sulphonic acid and chloramine. The *N*-amino-compounds were not isolated, however; the reaction with hydroxylamine-*O*-sulphonic acid appeared to give these derivatives which were unstable under the conditions

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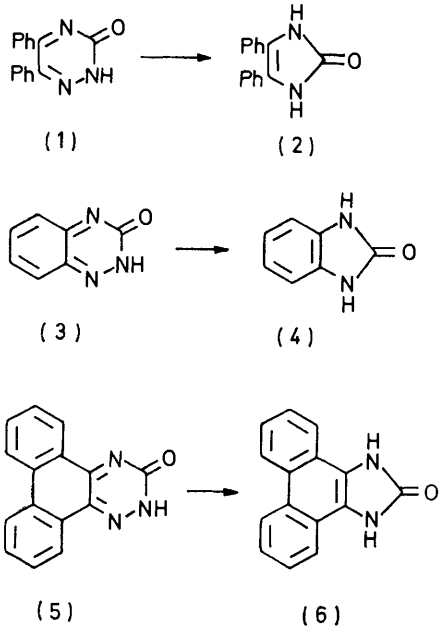
[1] Preliminary communications, C. W. Rees and A. A. Sale, *Chem. Comm.*, 1971, 531, 532.

[2] J. Adamson, D. L. Forster, T. L. Gilchrist, and C. W. Rees, *J. Chem. Soc.* (*C*), 1971, 981.

[3] J. P. Horwitz in 'Heterocyclic Compounds,' ed. R. C. Elderfield, Wiley, New York, 1961, vol. 7, p. 759.

required for their formation, and that with chloramine appeared to give *N*-chloro-derivatives which were also unstable. With both reagents, new, useful ring contractions were observed.

Reactions with Hydroxylamine-O-sulphonic Acid.—When 5,6-diphenyl-1,2,4-triazin-3-one (1) was aminated with hydroxylamine-*O*-sulphonic acid in aqueous alkali at 70°, 4,5-diphenylimidazolin-2-one (2) (68%) was produced. Similarly 1,2,4-benzotriazin-3-one (3) gave benzimidazolin-2-one (4) (87%). Phenanthro[9,10-*e*]-[1,2,4]triazin-3-one (5) was unchanged under these conditions, presumably because of its insolubility, but in aqueous ethanolic sodium hydroxide solution it gave 1,3-dihydrophenanthro[9,10-*d*]imidazol-2-one (6) (74%).



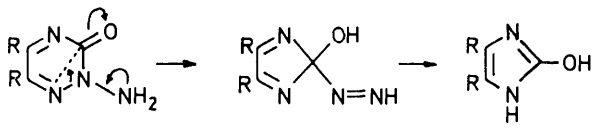
(1) (2)

(3) (4)

(5) (6)

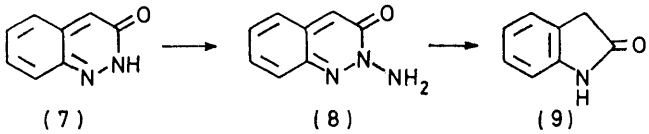
Attempts were made to isolate the *N*-amino-triazinones which we consider (see later) to be intermediates in these ring contractions. When the diphenyltriazinone (1) was treated with hydroxylamine-*O*-sulphonic acid in aqueous sodium hydroxide at 0 and at 40° it was recovered in high yield, either as the neutral species or as its sodium salt. It was also recovered almost quantitatively at higher temperatures when the alkali was omitted. Carpino [4] has shown that *N*-amino-compounds which are unstable under the basic conditions required with hydroxylamine-*O*-sulphonic acid can be prepared by using *O*-mesitoylhydroxylamine as the aminating agent. We preferred the more stable but equally effective reagent, *O*-(2,4-dinitrophenyl)hydroxylamine.[5] However, when the sodium salts of the triazinones (1), (3), and (5) were treated with this reagent in dimethylformamide at room temperature, no *N*-amino-compounds were isolated, and again ring contraction occurred to give the imidazolinones (2) (83%), (4) (15%), and (6) (55%). With methylene chloride as solvent the diphenyltriazinone (1) again gave only the imidazolinone (2) and unchanged aminating agent.

Nevertheless, the 2-amino-compounds are considered to be intermediates in these reactions; the smooth ring contraction, involving the breaking of the ring N–N bond, and loss of nitrogen, then follows logically (Scheme 1).



SCHEME 1

This mechanism does not require the presence of the 4-nitrogen atom; hence we considered that cinnolin-3-one (7) should undergo an analogous ring contraction to give oxindole (9), and that the intermediate *N*-amino-derivative (8) might well be more stable than the *N*-aminotriazinones. Cinnolin-3-one was therefore treated with hydroxylamine-*O*-sulphonic acid in aqueous alkali at 60°; oxindole was indeed formed (32%) and the *N*-amino-compound (8) was isolated, in low yield (7%). This yield was increased to 22% at lower temperatures;



(7) (8) (9)

compound (8) could also be prepared by the amination of cinnolinone (7) with *O*-(2,4-dinitrophenyl)hydroxylamine. The 2-amino-structure of (8) was proved by its quantitative deamination to (7) with nitrous acid and its formation with methanolic copper(II) chloride of a green copper chelate, in which the carbonyl absorption frequency had shifted characteristically from 1665 to 1620 cm^{-1}. 1-Amino-2-pyridones have been shown to form highly crystalline copper chelates with copper(II) chloride.[6]

Under the amination conditions the *N*-aminocinnoline (8) gave oxindole (9), supporting the mechanism of Scheme 1 for the formation of imidazolinones. Furthermore, compound (8) decomposed vigorously at its m.p. (130°) to give oxindole (64%), and more smoothly in boiling toluene (90%), presumably by a mechanism entirely analogous to that of Scheme 1. Cinnolin-3-one and 2-methylcinnolin-3-one gave no such ring contraction, even in boiling 1,2,4-trichlorobenzene (210°). A mechanism involving initial Cope-type opening of the heterocyclic ring to a ketone is thus less likely. The alternative ring expansion of (8) to give a seven-membered α-carbonyl azo-ring which could lose nitrogen to give oxindole was rendered unlikely by the failure to intercept this intermediate in a Diels–Alder reaction with tetraphenylcyclopentadienone.

Reactions with Chloramine.—Since reaction of the 1,2,4-triazin-3-ones with hydroxylamine-*O*-sulphonic

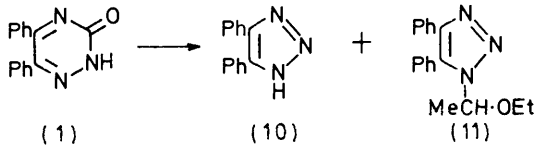
[4] L. A. Carpino, *J. Org. Chem.*, 1965, **30**, 321.

[5] T. Sheradsky, *J. Heterocyclic Chem.*, 1967, **4**, 413; *Tetrahedron Letters*, 1968, 1909.

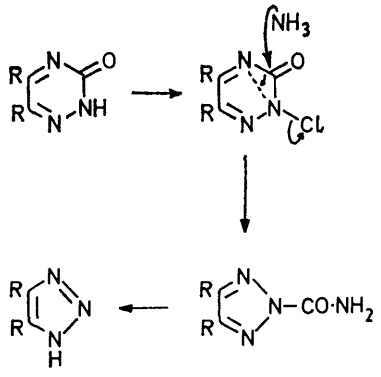
[6] I. E. El-Kholy and F. K. Rafla, *J. Chem. Soc.* (*C*), 1969, 974.

acid did not give the desired *N*-amino-compounds, we turned to chloramine as aminating reagent. Chloramine is often effective in aminating lactam anions under milder conditions, *i.e.* in ether at room temperature. However treatment of the sodium salts of the triazinones (1), (3), and (5) with ethereal chloramine gave none of the *N*-amino-derivatives but caused another, unexpected, ring contraction to give 1,2,3-triazoles, formally derived from the triazinones by extrusion of carbon monoxide.

Since neither *N*-amino-compounds nor their decomposition products were observed, the reactions were



repeated on the neutral triazinones and again 1,2,3-triazoles were formed, in higher yield. Thus (1) gave 4,5-diphenyltriazole (10) (94%), (3) gave benzotriazole (12) (65%), and (5) gave phenanthro[9,10-*d*]triazole (92%). In each case ammonium chloride separated from the ethereal solution almost quantitatively. Chloramine was thus acting as an oxidising rather than aminating agent, probably by initial conversion of the triazinones into their *N*-chloro-derivatives. This is supported by the similar conversion of the triazinone (1) into the triazole (10) by other *N*-chlorinating agents; aqueous sodium hypochlorite and acetic acid gave 52% and *N*-chlorobenzotriazole in benzene gave 100% conversion. *N*-Chlorination could lead to a Favorskii-type rearrangement (Scheme 2; shown for the chloramine reaction) to give the 2-substituted triazole which would presumably be readily hydrolysed to the parent triazole during isolation.

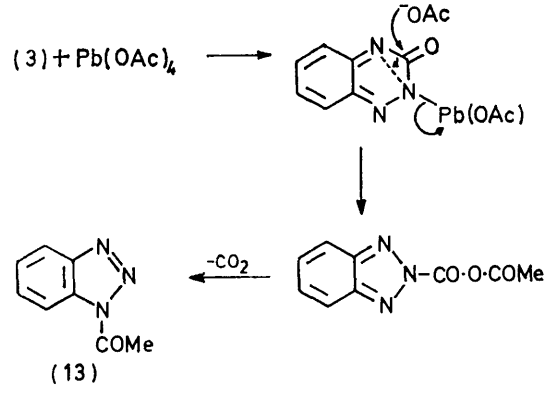


SCHEME 2

Ethereal chloramine, readily prepared and standardised, probably has considerable potential as an oxidant under very mild conditions. There seem to be few examples of its use as a simple oxidising agent,[7] in contrast to its widespread use in aminations. Its reactivity is probably similar to that of the more convenient reagent, 1-chlorobenzotriazole.[8]

This oxidation of triazinones provides a new, simple route to 1,2,3-triazoles, particularly useful for 4,5-diaryltriazoles which are otherwise not readily accessible.

It was of interest to see if other oxidants would cause a similar triazinone-to-triazole ring contraction. When the benzotriazinone (3) was oxidised with lead tetra-acetate in boiling benzene, 1-acetylbenzotriazole (13) (86%) and benzotriazole (3%) were formed. Benzotriazole gave only traces of 1-acetylbenzotriazole under these conditions and so the acetyl derivative must be the primary product, giving a small amount of benzotriazole on chromatographic work-up. 1-Acetylbenzotriazole is slowly hydrolysed to benzotriazole on keeping. A mechanism basically the same as that for the chloramine oxidation is proposed in Scheme 3; the final step, loss of carbon dioxide from the mixed anhydride with transfer of the acetyl group to N-1, could be intramolecular.



SCHEME 3

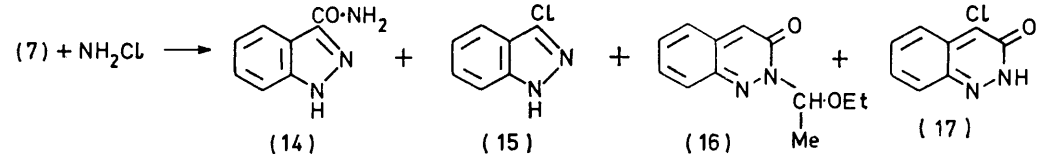
A minor product (4%) of the reaction of the diphenyltriazinone (1) with chloramine was 1-(1-ethoxyethyl)-4,5-diphenyltriazole (11). The structure of (11) followed from its n.m.r. spectrum and its ready hydrolysis with cold dilute sodium hydroxide to give 4,5-diphenyl-1,2,3-triazole quantitatively. It had previously been found[8] that treatment of benzotriazole (12) with ethereal chloramine gave 1-(1-ethoxyethyl)benzotriazole and that this resulted from the formation and spontaneous radical reaction of 1-chlorobenzotriazole with ether. Presumably the ether (11) arose in the same way by the conversion of some of the primary product, the diphenyltriazole (10), into its *N*-chloro-derivative. This reaction, and an analogous one described later, provide further evidence for the formation of *N*-chloro-derivatives under these reaction conditions.

By direct analogy with the foregoing triazinone reactions, cinnolin-3-one (7) would be expected to react with chloramine to give indazole-2-carboxamide or, after hydrolysis, indazole. However this reaction proved to

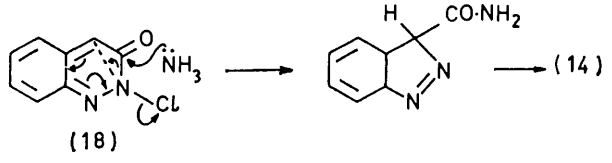
[7] G. A. Jaffari and A. J. Nunn, *J. Chem. Soc.* (*C*), 1971, 823.
[8] C. W. Rees and R. C. Storr, *J. Chem. Soc.* (*C*), 1969, 1474.

be more complex. Cinnolin-3-one was oxidised by chloramine, and ammonium chloride was formed almost quantitatively; the organic products were indazole-3-carboxamide (14) (18%), 4-chlorocinnolin-3-one (17) (18%), 2-(1-ethoxyethyl)cinnolin-3-one (16) (1·7%), and 3-chloroindazole (15) (1·8%); 7% of the cinnolinone (7) was recovered.

The substituted ether (16) was presumably formed from the *N*-chloro-derivative, as described before. The 4-chlorocinnolinone (17) could also be formed from this *N*-chloro-compound by rearrangement, or possibly by



direct chlorination of cinnolinone (7). 3-Chloroindazole (15) would be the product of ring contraction of (17) in exact analogy with the triazinone-to-triazole conversion. However, formation of indazole-3-carboxamide from cinnolinone requires the triazinone-to-triazole mechanism (Scheme 2) to be amended slightly to the extended rearrangement shown [arrows in (18)] where additional



driving force is provided by aromatisation of the *o*-quinonoid system.

EXPERIMENTAL

M.p.s were determined on a Kofler micro heating stage with corrected thermometers. ^{1}H N.m.r. spectra were recorded on a Varian T60 60 MHz spectrometer, and i.r. spectra for KBr discs or Nujol mulls on a Perkin-Elmer 257 spectrometer. Mixtures to be chromatographed were adsorbed on the support from a suitable solvent by evaporation in a rotatory evaporator. Petroleum refers to the fraction of b.p. 40—60°. Lead tetra-acetate was freed from acetic acid by filtration and stored over concentrated sulphuric acid. Hydroxylamine-*O*-sulphonic acid [9] was stored over concentrated sulphuric acid. Chloramine was prepared from ammonia and sodium hypochlorite [7] to give an approximately 0·17M-solution in ether (iodometric assay).

Reaction of 1,2,4-*Triazin*-3(2H)-*ones with Hydroxylamine*-O-*sulphonic Acid* (*HOS*).—(a) 5,6-*Diphenyl*-1,2,4-*triazin*-3(2H)-*one* (1). The triazinone [10] (5 g) was dissolved in a solution of sodium carbonate (13 g) and sodium hydroxide (5 ml; 2N) in water (200 ml) at 70°. HOS (11 g, 0·1 mol) was added over 5 min during which the mixture frothed and pale yellow crystals separated. The suspension was stirred at 60° for 15 min; the solid was collected, washed with hot dilute sodium carbonate solution and then with water, and crystallised from ethylcellosolve to give 4,5-diphenylimidazolin-2-one (3·2 g, 68%), m.p. 310—311° (lit.,[11] 320°), identical (i.r. spectrum and mixed m.p.) with an authentic specimen prepared from benzoin and urea.[11] After treatment of the diphenyltriazinone with HOS in aqueous alkali at 40°, followed by neutralisation, the triazinone was recovered (97%). After similar treatment at 0° the *sodium salt* of the triazinone separated (15%) and was crystallised from ethanol, m.p. >340° (Found: C, 66·3; H, 3·9; N, 15·6. $C_{15}H_{10}N_3NaO$ requires C, 66·4; H, 3·7; N, 15·5%), $\nu_{max.}$ 1530, 1221, 1080, 1050, 1028, 824, 756, and 748 cm^{-1}; the filtrate, on neutralisation, gave diphenyltriazinone (55%).

(b) 1,2,4-*Benzotriazin*-3(2H)-*one* (3). The benzotriazinone [12] (441 mg, 3 mmole) was dissolved in water (25 ml) containing sodium hydroxide (720 mg, 18 mmol). HOS (2·0 g, 18 mmol) was added over 30 min to the stirred solution at 60—70° and more sodium hydroxide was added as required to maintain an alkaline pH. The mixture was cooled and extracted with chloroform. Evaporation and crystallisation from water gave benzimidazolin-2-one (354 mg, 87%), m.p. and mixed m.p. 310—311° (decomp.), identical (i.r. spectrum) with an authentic specimen.

(c) *Phenanthro*[9,10-e][1,2,4]*triazin*-3(2H)-*one* (5). The phenanthrotriazinone [13] (2·47 g, 0·01 mol) was dissolved in water (500 ml) containing ethanol (50 ml) and sodium hydroxide (4 g, 0·1 mol) at 85°. HOS (8 g, 0·07 mol) was added in portions to the stirred solution at 85°. The solution was allowed to cool and the precipitate was collected, washed with water, and crystallised from acetic acid to give 1,3-*dihydrophenanthro*[9,10-d]*imidazol*-2-*one* (6) (1·73 g, 74%), m.p. >350° (Found: C, 76·7; H, 4·3; N, 12·2. $C_{15}H_{10}N_2O$ requires C, 76·9; H, 4·3; N, 12·0%), *m/e* 234 (M^+), 206, 205, 180, and 117, $\nu_{max.}$ 3150br, 1700, 1685, 1644, 1014, 825, 748, and 721 cm^{-1}. The filtrate was acidified with 2N-hydrochloric acid to yield the starting triazinone (0·5 g, 20%). In the absence of ethanol, the reaction mixture was heterogeneous and starting triazinone (97%) was recovered.

Reaction of 1,2,4-*Triazin*-3(2H)-*ones with* O-(2,4-*Dinitrophenyl*)*hydroxylamine*.—(a) 5,6-*Diphenyl*-1,2,4-*triazin*-3(2H)-*one* (1). The triazinone (1 mmol) was dissolved in dry dimethylformamide (5 ml), sodium hydride (50 mg of a 50% dispersion, 1 mmol) was added, and the solution was stirred until gas evolution ceased (10 min). The hydroxylamine [5] (199 mg, 1 mmol) was then added; the mixture was stirred for 1·5 h and poured into water, and the precipitate was collected, washed thoroughly with water, and crystallised from acetic acid to give 4,5-diphenylimidazolin-2-one (195 mg, 83%), m.p. and mixed m.p. 310—312°, identical (i.r. spectrum) with an authentic specimen.[11] When the reaction was repeated in the absence of sodium hydride no reaction had occurred after 8 h. When the reaction was

[7] R. Gösl and A. Meuwsen, *Chem. Ber.*, 1959, **92**, 2521.
[9] H. Biltz, *Ber.*, 1905, **38**, 1418.
[10] H. Biltz, *Annalen*, 1905, **339**, 243.
[11] H. Biltz, *Annalen*, 1905, **339**, 243.
[12] F. Arndt and B. Rosenau, *Ber.*, 1917, **50**, 1248.
[13] P. V. Laakso, R. Robinson, and H. P. Vandrewala, *Tetrahedron*, 1957, **1**, 103.

repeated with methylene chloride in place of dimethylformamide, after 6 h the imidazolinone (27%) was isolated and the hydroxylamine (31%) was recovered.

(b) 1,2,4-*Benzotriazin*-3(2H)-*one* (2). The foregoing reaction was repeated with the benzotriazinone (1 mmol). The reaction mixture was poured into water and extracted with ether, the extracts were evaporated, and the residue was crystallised from water to give benzimidazolin-2-one (20 mg, 15%), m.p. and mixed m.p. 309—311°.

(c) *Phenanthro*[9,10-e][1,2,4]*triazin*-3(2H)-*one* (5). The foregoing method gave, on pouring the reaction mixture into water, a brown precipitate which was crystallised from acetic acid (charcoal) to give the phenanthroimidazolinone (6) (130 mg, 55%).

Reaction of Cinnolin-3(2H)-*one* (7) *with Hydroxylamine*-O-*sulphonic acid* (*HOS*).—(i) Cinnolinone [14] (3·92 g, 0·027 mol) was dissolved in water (200 ml) containing potassium hydroxide (8·4 g, 0·15 mol) at 40°. HOS (11·3 g, 0·1 mol) was added in one portion and the temperature maintained between 40 and 45° by addition of ice. The mixture became deep red and on cooling a brown solid (2·45 g) separated; this was collected, washed with water, dried, and crystallised from a large volume of chloroform (charcoal) to give bright yellow crystals of 2-*aminocinnolin*-3(2H)-*one* (8) (0·75 g, 17%), m.p. 128—130° (decomp.). Further recrystallisations from chloroform gave material of m.p. 130—131° (decomp.) (Found: C, 59·4; H, 4·4; N, 25·8. $C_8H_7N_3O$ requires C, 59·6; H, 4·4; N, 26·0%), *m/e* 161 (M^+), 146, 133, 105, and 104, $\nu_{max.}$ 3280, 3160, 3105, 1664, 1656, 1385, 1188, 872, 760, and 745 cm^{-1}, τ 2·6—3·3 (5H, m), and 0·00br (2H, s, disappears on addition of D_2O). Concentration of the remaining chloroform solution gave the starting cinnolinone (1·55 g, 40%).

(ii) The foregoing reaction was repeated with sodium hydroxide in place of potassium hydroxide and with a reaction temperature of 55—60°. The resulting solution was cooled and filtered to give a brown solid. Crystallisation of this from chloroform gave 2-aminocinnolin-3-one (0·95 g, 22%), m.p. 129—131°. The aqueous solution was extracted with chloroform to give a viscous red oil. This was combined with the mother liquors from the crystallisation and chromatographed on silica to give oxindole (9) (1·06 g, 30%), m.p. and mixed m.p. 125—127° (from water), identical (i.r. spectrum) with an authentic specimen.

(iii) Reaction (ii) was repeated with a reaction temperature of 60—70° to give 2-aminocinnolin-3-one (7%), oxindole (32%), and starting cinnolinone (7%).

(iv) Reaction (ii) was repeated with 50% aqueous ethanol as solvent; similar results were obtained.

Deamination of 2-*Aminocinnolin*-3(2H)-*one* (8).—The *N*-amino-compound (80 mg, 0·5 mmol) was dissolved in acetic acid (5 ml), and sodium nitrite (35 mg, 0·5 mmol) in water (5 ml) was added dropwise at room temperature. The mixture was neutralised with sodium hydrogen carbonate and extracted with chloroform to give cinnolinone (70 mg, 96%).

Copper Chelate of 2-*Aminocinnolin*-3(2H)-*one* (8).—The *N*-amino-compound (161 mg, 1 mmol) in hot methanol (20 ml) was added to a solution of copper(II) chloride dihydrate (340 mg, 2 mmol) in hot methanol (20 ml). On cooling, dark green crystals of the *copper chelate* of (8) (146 mg, 49%) separated; m.p. 184—186° (decomp.) (Found: C, 32·9; H, 2·5; Cl, 25·0; N, 13·9. $C_8H_7Cl_2CuN_3O$ requires C, 32·5; H, 2·4; Cl, 24·0; N, 14·2%), $\nu_{max.}$ 3058, 3017, 1618, 1610, 1500, 905, and 785 cm^{-1}.

Thermolysis of 2-*Aminocinnolin*-3(2H)-*one* (8).—(i) *Alone*. The *N*-amino-compound (36 mg) was cautiously heated to 135° and after its explosive decomposition the residue was sublimed to give oxindole (19 mg, 64%), m.p. and mixed m.p. 124—127°, identical (i.r. spectrum) with authentic material.

(ii) *In toluene*. The *N*-amino-compound (54 mg) was heated under reflux in dry toluene (20 ml) for 6 h. The toluene was then evaporated off and the residue was chromatographed on silica to give oxindole (40 mg, 90%). When this experiment was repeated in the presence of tetraphenylcyclopentadienone, the latter (88%) and oxindole (47%) were the only products isolated by chromatography.

Cinnolin-3-one and 2-methylcinnolin-3-one were recovered (71 and 100%, respectively) after being heated under reflux in 1,2,4-trichlorobenzene for 5 h.

Reaction of 1,2,4-*Triazin*-3(2H)-*ones with Chloramine*.—(a) 5,6-*Diphenyl*-1,2,4-*triazin*-3(2H)-*one* (1). The triazinone (1·0 g, 4 mmol) was dissolved in dry methylene chloride (100 ml) and ethereal chloramine (17 mmol) was added. After 24 h the mixture was filtered to give ammonium chloride (210 mg, 100%). The filtrate was chromatographed on silica to give, with 10% ether–petroleum, 1-(1-*ethoxyethyl*)-4,5-*diphenyltriazole* (11) (44 mg, 4%), as an oil, n_D^{23} 1·6632, b.p. *ca.* 100° at 0·1 mmHg (Found: C, 72·8; H, 6·6; N, 14·1. $C_{18}H_{19}N_3O$ requires C, 73·7; H, 6·5; N, 14·3%), $\nu_{max.}$ 3055, 1600, 1575, 1435, 1370, 1330, 1305, 1280, 1260, 1240, 1160—1100 (C–O–C stretch), 1060, 1040, 1000, 940, 850, and 780—690 cm^{-1}, τ 8·88 (t, CH_3), 8·23 (d, CH_3), 6·51 (q, CH_2), 4·29 (q, CH), and 2·63 (10 aromatic protons), *m/e* 293 (M^+), 264, 221, 193, 165, 104, and 103. Trituration of the oil with cold dilute aqueous sodium hydroxide gave 4,5-diphenyl-1,2,3-triazole quantitatively. Elution with 50% ether–petroleum gave 4,5-diphenyltriazole (837 mg, 94%), recrystallised from nitromethane, m.p. and mixed m.p. 136—138°, identical (i.r. spectrum) with an authentic specimen. When the triazinone (1) was first converted into its sodium salt with sodium hydride, treatment with chloramine gave the substituted ether (11) (28%) and 4,5-diphenyltriazole (40%).

(b) 1,2,4-*Benzotriazin*-3(2H)-*one* (3). The benzotriazinone (0·5 g, 3·4 mmol) was dissolved in dry methylene chloride (100 ml) and dimethylformamide (50 ml). Ethereal chloramine (8·5 mmol) was added and the mixture stirred overnight. Ammonium chloride (185 mg, 100%) slowly separated. The filtrate was washed with water, dried, and chromatographed on silica to give, with ether, benzotriazole (12) (264 mg, 65%), m.p. and mixed m.p. 96—99°, [from petroleum (b.p. 60—80°)]. The sodium salt of (3) gave benzotriazole (7%) and benzotriazinone (3) (56%).

(c) *Phenanthro*[9,10-e][1,2,4]*triazin*-3(2H)-*one* (5). The phenanthrotriazinone (0·5 g, 2 mmol) was dissolved in dimethylformamide (80 ml) and treated with ethereal chloramine (5 mmol). The mixture was set aside for 48 h and then filtered to give ammonium chloride (86 mg, 80%). The ether and dimethylformamide were evaporated off under reduced pressure and the residue crystallised from acetic acid to give phenanthro[9,10-*d*]triazole (400 mg, 91%), m.p. and mixed m.p. 322—325° (decomp.) (lit.,[15] 306°), identical (i.r. spectrum) with an authentic specimen.

Oxidation of the Triazinone (1) *with* 1-*Chlorobenzotriazole*.—

[14] H. E. Baumgarten, W. F. Murdock, and J. E. Dirks, *J. Org. Chem.*, 1961, **26**, 803; H. E. Baumgarten, P. L. Creger, and R. L. Zey, *J. Amer. Chem. Soc.*, 1960, **82**, 3977.

[15] R. Epsztein, *Bull. Soc. chim. belges*, 1957, **66**, 438.

The triazinone (249 mg, 1 mmol) was dissolved in dry benzene (50 ml) and 1-chlorobenzotriazole [8] (153 mg, 1 mmol) was added to the stirred solution. After an induction period of 2 min the mixture became cloudy and then cleared (30 min); it was stirred overnight and then chromatographed on silica to give, with 30% ether–petroleum, 4,5-diphenyltriazole (220 mg, 100%), and with 60% ether–petroleum and 10% ethanol–ether, benzotriazole (75 mg, 63%).

Oxidation of the Triazinone (1) *with Sodium Hypochlorite.*—The triazinone (498 mg, 2 mmol) was dissolved in acetic acid (5 ml) and treated with M-sodium hypochlorite dropwise until no more gum separated. The aqueous solution was decanted and the gum dissolved in chloroform, dried, and chromatographed on silica to give, with 20% ether–petroleum, a complex mixture of oils (t.l.c.), and with 40% ether–petroleum, 4,5-diphenyltriazole (230 mg, 52%).

Oxidation of 1,2,4-*Benzotriazin*-3(2H)-*one* (3) *with Lead Tetra-acetate.*—The triazinone (147 mg, 1 mmol) was dissolved in benzene (50 ml) and lead tetra-acetate was added in portions to the solution heated under reflux. The mixture was boiled for a further 2 h and then cooled and filtered, and the precipitate was washed with methylene chloride. The filtrate and washings were evaporated and the residue chromatographed on silica to give, with 30% ether–petroleum, 1-acetylbenzotriazole (139 mg, 86%), m.p. and mixed m.p. 50—51°, identical (i.r. spectrum) with an authentic specimen prepared from benzotriazole and acetic anhydride. Further elution with 10% ethanol–ether gave benzotriazole (4 mg, 3·3%), m.p. and mixed m.p. 93—97°.

Oxidation of Cinnolin-3(2H)-*one* (7) *with Chloramine.*—Cinnolinone (0·73 g, 5 mmol) was dissolved in dry methylene chloride (150 mg) and ethereal chloramine (8·5 mmol) was added. The mixture was stirred overnight and then filtered to give ammonium chloride (260 mg, 95%). The filtrate was chromatographed on silica. 60% Ether–petroleum gave a yellow fluorescent oil that slowly crystallised; recrystallisation from petroleum (b.p. 60—80°) gave 2-(1-*ethoxyethyl*)*cinnolin*-3(2H)-*one* (30 mg, 1·5%), m.p. 94—97° (decomp.) (Found: C, 65·3; H, 6·6; N, 12·4. $C_{12}H_{14}N_2O_2$ requires C, 66·0; H, 6·3; N, 12·8%), $\nu_{max.}$ 1660, 1644, 1625, 1252, 1125, 950, and 755 cm^{-1}; τ 2·35—3·0 (5H, m), 3·4 (1H, q), *ca.* 6·5 (2H, m), 8·4 (3H, d), and 8·85 (t, 3H). 70% Ether–petroleum gave an oil which on sublimation gave 3-chlorindazole (22 mg, 1·8%), m.p. and mixed m.p. 148—148·5° (lit.,[16] 148°) [from petroleum (b.p. 60—80°)], identical (i.r. spectrum) with an authentic specimen.[16] 5% Ethanol–ether gave a red oil which on sublimation gave yellow needles of 4-chlorocinnolin-3(2*H*)-one (156 mg, 17·5%), m.p. and mixed m.p. 220—223° (decomp.) (from ethanol) (lit.,[17] 220°) (Found: C, 53·3; H, 2·8; N, 15·6. Calc. for $C_8H_5ClN_2O$: C, 53·2; H, 2·8; N, 15·5%), *m/e* 180 (M^+), 152, and 117; i.r. spectrum identical with that of an authentic specimen prepared by reaction of cinnoline with t-butyl hypochlorite. 10% Ethanol–ether gave a mixture which on sublimation gave prisms of indazole-3-carboxamide (143 mg, 18%), m.p. 279—284°; recrystallisation from ethanol gave material of m.p. 286—288° (lit.,[18] 285—286°) (Found: C, 59·8; H, 4·5; N, 25·9. Calc. for $C_8H_7N_3O$: C, 59·6; H, 4·3; N, 26·0%), *m/e* 161 (M^+), 145, and 118; $\nu_{max.}$ 3330—2780, 1670, 1635, 1620, 1605, 1590, 1080, 900, 770, and 748 cm^{-1}. 50% Ethanol–ether gave a mixture which on sublimation gave cinnolinone (50 mg, 7%).

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