666. *Triazines. Part III.*[1] *Electrophilic Substitution in 3-Phenyl-1,2,3-benzotriazin-4-one, and Decomposition of Some 3-Arylbenzotriazinones in Phosphoric Acid.*

By M. S. Gibson.

Bromination and nitration of 3-phenyl-1,2,3-benzotriazin-4-one give the *para*-substituted derivatives.

6-Phenanthridone and 2-chloro- and 2-bromo-6-phenanthridone have been isolated after decomposition of 3-phenyl-, 3-*p*-chlorophenyl-, and 3-*p*-bromophenyl-1,2,3-benzotriazin-4-one in phosphoric acid.

Apart from the experiments of Niementowski[2] on the bromination of benzimidazo-[1,2-*c*][1,2,3]benzotriazine and some homologues, there appear to have been no studies of electrophilic substitution in the 1,2,3-benzotriazine series. Our particular interest in this subject arose in connection with developing the recently reported route to phenanthridone from 3-phenyl-1,2,3-benzotriazin-4-one.[3] This triazinone (I; E = H) undergoes reversible ring scission between N-2 and N-3 in strongly acid solution, yielding a diazonium ion, *e.g.*, (II; E = H). Either species (I or II) would be expected to undergo electrophilic substitution. As a substituted anilide, an ion (II; E = H) would be substituted mainly *para* to the amide-nitrogen atom (cf. acetanilide) by an attacking electrophile (say, E^+); similar reaction of the compound (I; E = H) would, by placing a formal positive charge on N-3 in the transition state, probably also involve ring scission during the substitution process. In either event, the resulting equilibrium mixture ($I \rightleftharpoons II$) would yield the substituted triazinone on working-up. In agreement, bromine (1 mol.) in acetic acid converts compound (I; E = H) into the known bromo-compound[4] (I; E = Br); the red gum, which separates at an intermediate stage and later redissolves, probably contains the diazonium perbromide.[5] Similarly, nitration gives the nitro-compound[6] (I; $E = NO_2$).

Conditions for the decomposition of the triazinone (I; E = H) to give phenanthridone and nitrogen have been much improved, and, particularly, the production of salicylic acid minimised, by using *ca.* 100% orthophosphoric acid at 110—120° for 5—7 minutes and then at 150° for 2—3 minutes. The analogous decompositions of some substituted

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[1] Part I, *J.*, 1956, 3242; Part II, *J. Org. Chem.*, 1962, **27**, 4083.

[2] Niementowski, *Ber.*, 1898, **31**, 314; cf. Erickson, Wiley, and Wystrach, "The 1,2,3- and 1,2,4-Triazines, Tetrazines, and Pentazines," Interscience Publ., Inc., New York, 1956, Chapter 1.

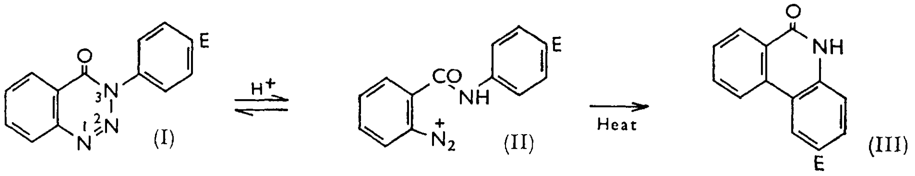
[3] Gibson, *Chem. and Ind.*, 1962, 698.

[4] Chattaway and Walker, *J.*, 1927, 329.

[5] Saunders, "The Aromatic Diazo-Compounds and Their Technical Applications," Arnold, London, 2nd edn., 1949, p. 153.

[6] Grammaticakis, *Compt. rend.*, 1956, **243**, 2094.

triazinones have also been investigated. Thus, the phenanthridones (III; E = Cl or Br) have been obtained from the triazinones (I; E = Cl or Br), though in low yield; the



triazinones (I; E = MeO and NO_2) decompose, but do not yield the corresponding phenanthridones under the above conditions. No acridones were isolated in these experiments, though the mother-liquors from crystallising 2-chlorophenanthridone (III; E = Cl) had a blue fluorescence. This is in marked contrast with the interesting thermal decompositions of the parent (I; E = H) (i) alone or (ii) in paraffin, which lead, by radical mechanisms, to (i) acridone and phenanthridone, or (ii) benzanilide, respectively.[7]

The conversion of the ion (II) into a phenanthridone (III), involving an intramolecular nucleophilic displacement of the diazonium group as nitrogen, finds a number of parallels in triazine chemistry, *e.g.*, the conversion of ethyl 4-oxo-1,2,3-benzotriazine-3-carboxylate into 1,3-benzoxazine-2,4-dione.[8]

Reversible protonation and ring scission is not a universal property of 1,2,3-triazin-4-ones, though exceptions to this behaviour are rare. Notably, the triazinones formed by allowing nitrous acid to react with 5-amino-1,3-diphenylpyrazole-4-carboxamide and the derived methylamide are insensitive to acid.[9] Last doubts (cf. Erickson *et al.* [2]) about the structures of these two compounds have now been dispelled by an examination of their infrared spectra; the former compound shows absorption bands due to N–H; the latter does not. Their ultraviolet absorption spectra are virtually identical.

EXPERIMENTAL

Microanalyses are by Mr. V. Manohin. M. p.s were determined on a Kofler block; in the cases of the phenanthridones, the block was preheated to within 10° of the m. p.

3-*Phenyl*-1,2,3-*benzotriazin*-4-*one*.—This was prepared by the Pictet–Gonset method [10] with the following modifications. *o*-Nitrobenzoic acid (5 g.) was converted (Schotten–Baumann) into the anilide (6·2 g.). The crude, powdered anilide (6 g.) was added to the two-phase system composed of ferrous sulphate (48 g.), water (130 ml.), and ethanol (60 ml.) at 80—85°. Aqueous ammonia (*d* 0·88) was then added in portions with vigorous shaking at such a rate that the mixture just boiled. When the black mass had become permanently alkaline, the mixture was boiled for 5 min., then filtered through charcoal. The solid was washed with boiling water, and the filtrate and washings were discarded. The residue was extracted with boiling ethanol (3 × 150 ml.), and the resulting solution evaporated *in vacuo* to give crude anthranilanilide. Diazotisation then gave the triazinone, which formed needles, m. p. 150—151° (lit.,[10] 151°) (3·5 g., 49% overall), from ethanol.

The following triazinones were prepared from *o*-nitrobenzoic acid and the appropriate amine under the same conditions (% overall yield of crystallised triazinone in parentheses): 3-*p*-bromo- (31%), leaflets (from ethanol), m. p. 198—199° (lit.,[4] 196°), 3-*p*-chloro- (42%), plates (from ethanol), m. p. 185—186° (lit.,[6] 186°), and 3-*p*-methoxy-phenyl-1,2,3-benzotriazin-4-one (30%), needles (from ethanol), m. p. 157° (lit.,[6] 157°).

All the above triazinones gave reddish-purple or red colours when warmed with α-naphthol in acetic acid–concentrated hydrochloric acid (Bamberger–Goldberger test) and have $\nu_{max.}$ (Nujol mull) 1685 cm.$^{-1}$ (C=O).

3-p-*Bromophenyl*-1,2,3-*benzotriazin*-4-*one*.—Bromine (0·25 ml.) was added to a solution of 3-phenyl-1,2,3-benzotriazin-4-one (1 g.) in acetic acid (10 ml.). A reddish gum slowly separated,

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[7] Hey, Rees, and Todd, *Chem. and Ind.*, 1962, 1332.

[8] Heller, *J. prakt. Chem.*, 1925, **111**, 1, 36.

[9] Justoni and Fusco, *Gazzetta*, 1938, **68**, 59.

[10] Pictet and Gonset, *Chem. Zentr.*, 1897, I, 413.

and gradually redissolved, giving a pale yellow solution. After 48 hr., the solution was poured into water, and the precipitated bromo-compound (1·1 g.) was collected. Washing and crystallisation from ethanol gave leaflets, m. p. and mixed m. p. 198—199° (Found: N, 13·8. Calc. for $C_{13}H_8BrN_3O$: N, 13·9%). The triazinone also crystallises as plates (from ethanol); these change to the leaflet form just below the m. p. (*ca.* 190°).

3-p-*Nitrophenyl*-1,2,3-*benzotriazin*-4-*one* (with J. M. BURGESS).—3-Phenyl-1,2,3-benzotriazin-4-one (1 g.) was dissolved in glacial acetic acid (0·9 ml.) and concentrated sulphuric acid (1·5 ml.). The warm golden-brown solution was cooled to 5° and stirred; (11 : 7 v/v) concentrated nitric acid–concentrated sulphuric acid (0·45 ml.) was added dropwise during 10 min. at $<15°$. The resulting brown solution was left at room temperature for 2 hr., then poured into iced water. The precipitated nitro-compound (1·1 g.) was collected, washed, and dried. Crystallisation from acetonitrile gave fine needles, m. p. 271—272° [lit.,[6] 275° (instantaneous)] (Found: C, 58·1; H, 3·1; N, 20·9. Calc. for $C_{13}H_8N_4O_3$: C, 58·2; H, 3·0; N, 20·9%). The compound developed a rapid colour in the Bamberger–Goldberger test, and showed $\nu_{max.}$ 1690 (C=O), 1530 (NO_2), and 1350 (NO_2) cm.$^{-1}$.

Decomposition of 3-*Phenyl*-1,2,3-*benzotriazin*-4-*one in Phosphoric Acid*.—The triazinone (1 g.) was added with stirring to a warm solution of phosphorus pentoxide (5 g.) in 85% orthophosphoric acid (8 ml.). The golden solution was heated at 110—120° until the vigorous nitrogen evolution had slackened (5—7 min.), and then at 150° for 2—3 min. The pale brown solution was poured into iced water (60 ml.); crude 6-phenanthridone (450 mg.) separated. Crystallisation from ethanol gave needles (220 mg.), m. p. 291—293°. A sample, sublimed at 240°/6 mm., formed needles, m. p. and mixed [11] m. p. 293—294°.

Under the same conditions, 3-*p*-chlorophenyl-1,2,3-benzotriazin-4-one (1 g.) gave a grey solid (270 mg.); two crystallisations from glacial acetic acid gave 2-chloro-6-phenanthridone (90 mg.) as needles, m. p. 324—326° (lit.,[12] 327—328°). Similarly, the bromotriazinone (1 g.) gave a grey solid (85 mg.); crystallisation from nitromethane gave 2-bromo-6-phenanthridone (35 mg.) as needles, m. p. 326—327° (lit.,[12] 325·5—326·5°). Both halogenophenanthridones showed the expected infrared absorption.[12]

Decomposition of 3-*p*-methoxyphenyl- and of 3-*p*-nitrophenyl-1,2,3-benzotriazin-4-ones as above gave mainly polymeric material. An experiment involving the decomposition of 3-phenyl-1,2,3-benzotriazin-4-one in 85% ortbophosphoric acid at 100° for 30 min. in the presence of copper powder also gave largely polymeric material.

5-*Amino*-1,3-*diphenylpyrazole*-4-*carboxamide and its* N-*methylamide and Derived Triazinones*.—*N*-α-Chlorobenzylidene-*N'*-phenylhydrazine (9·5 g.) with cyanoacetamide (3·36 g.), as described elsewhere,[9] gave a dark red tar. This was collected, dried *in vacuo*, powdered, and triturated with dry ether until the washings were pale. The crude pyrazole (2·7 g., 24%), which remained as a cream solid, formed colourless prisms (from ethanol), m. p. 184—186° (lit.,[9] 186—187°), $\lambda_{max.}$ (in EtOH) 241 mμ (4·45), $\lambda_{min.}$ 220 mμ (4·27) (these and other values in parentheses are log ε).

The crude methylamide (31%), prepared and isolated as above, crystallised from ethanol as prisms, m. p. 153—154° (lit.,[9] 153°), $\lambda_{max.}$ 240 mμ (4·58), $\lambda_{min.}$ 219 mμ (4·25).

Diazotisation of the former amide gave the triazinone, which formed prisms (from ethanol), m. p. 154—157° (decomp.) [lit.,[9] 160° (decomp.)], $\lambda_{max.}$ 240 (4·36) and 323—330 mμ (3·76), $\lambda_{min.}$ 223 (4·2) and 306—308 mμ (3·74), $\lambda_{infl.}$ 262—270 mμ (4·23), $\nu_{max.}$ 3200 (N–H), 3090 (N–H) and 1675 (C=O) cm.$^{-1}$.

The latter amide similarly gave the methyltriazinone, which formed prisms (from ethanol), m. p. 154—157° (decomp.), mixed m. p. with previous triazinone, 125—127° [lit.,[9] 155·5° (decomp.)], $\lambda_{max.}$ 242 (4·36) and 333 mμ (3·81), $\lambda_{min.}$ 223 (4·18) and 307 mμ (3·73), $\lambda_{infl.}$ 263—273 mμ (2·5), $\nu_{max.}$ 1685 (C=O) cm.$^{-1}$.

Neither triazinone reacts in the Bamberger–Goldberger colour test.

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[11] Walls, *J.*, 1935, 1405.

[12] Gilman and Eisch, *J. Amer. Chem. Soc.*, 1957, **79**, 5479.