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THE ALKALINE AND ACIDIC DEGRADATION OF 3-AMINO-1,2,3-BENZOTRIAZIN-4-ONE AND RELATED COMPOUNDS

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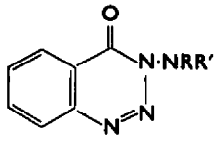
Abstract—3-Amino-1,2,3-benzotriazin-4-one hydrolysed in alkaline solution decomposes by two mechanisms: (i) by prototropic shift and loss of nitrogen to give *o*-hydrazinobenzoic acid, and (ii) by loss of amide ion (ammonia) to give *o*-azidobenzoic acid. Course (i) can be diminished in importance or excluded by appropriate modification of the 3-amino group.

In hot aqueous hydrochloric acid, 3-acetamido-1,2,3-benzotriazin-4-one undergoes ring fission, *trans*-nitrosation and loss of acetic acid to give anthranilazide, which then rearranges to benzimidazolone with loss of nitrogen.

THE present work was undertaken to clarify the modes of decomposition of substituted 3-amino-1,2,3-benzotriazin-4-ones under alkaline and acidic conditions. It has been reported that 3-amino-1,2,3-benzotriazin-4-one (Ia) decomposes in hot aqueous sodium hydroxide solution to give *o*-azidobenzoic acid;[1] under similar conditions, a number of 3-(N-acyl) derivatives (Ib)[1] and 3-(N-alkoxycarbonyl) derivatives (Ic)[2] also give *o*-azidobenzoic acid, but, unaccountably, the benzylidene derivative (Id) was said to give benzylidene *o*-carboxyphenylhydrazone.[3] No yields were indicated for any of these decomposition reactions.



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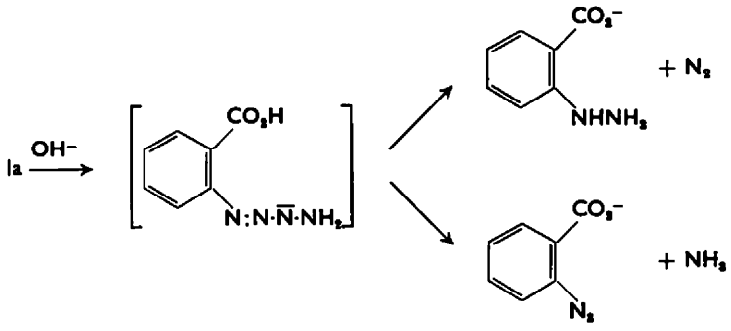
(a) R = R′ = H
(b) R = H, R′ = COMe, COPh
(c) R = H, R′ = COOMe, COOEt
(d) RR′ = PhCH:
(e) R = Me, R′ = Ph
(f) RR′ = PhCMe:

It seemed unlikely that *o*-azidobenzoic acid would be the only organic product of alkaline degradation of 3-amino-1,2,3-benzotriazin-4-one since an alternative pathway, involving prototropic shift and loss of molecular nitrogen,[4] exists for the generation of *o*-hydrazinobenzoic acid. That this pathway is actually the more important of the two was shown in the following way. The alkaline solution from decomposition of Ia was treated with benzaldehyde. After reaction, fractional acidification yielded the benzylidene derivative of *o*-hydrazinobenzoic acid (48%) followed by *o*-azidobenzoic acid (19%); the former yield represents a lower limit as

[1] G. Heller, *J. Prakt. Chem.* **111**, 36 (1925).
[2] G. Heller, *J. Prakt. Chem.* **116**, 1 (1927).
[3] G. Heller and A. Siller, *J. Prakt. Chem.* **116**, 9 (1927).
[4] This is implicit for 1,2,3-benzotriazin-4-one and related compounds. Cf. H. Finger, *J. Prakt. Chem.* **37**, 431 (1888); K. Kratz, *Ibid.* **53**, 210 (1896); M. W. Partridge and M. F. G. Stevens, *J. Chem. Soc.* 3663 (1964).

condensation with benzaldehyde is unlikely to occur quantitatively under these conditions.



This alternative can be excluded by replacing the amino-hydrogen atoms by alkyl or aryl groups as in 3-(N-methyl-N-phenyl)amino-1,2,3-benzotriazin-4-one (Ie). This compound was prepared by two routes: (a) from isatoic anhydride and *as*-methylphenylhydrazine, and (b) by reduction of *o*-nitrobenz-*as*-methylphenylhydrazide, followed in each case by treatment with nitrous acid. Decomposition of this triazine in an alkaline medium gave *o*-azidobenzoic acid in high yield (80%), together with (presumably) N-methylaniline.

The alkaline hydrolysis of 3-acetamido-1,2,3-benzotriazin-4-one (Ib, R′ = COMe) was next re-examined, and found to give *o*-azidobenzoic acid (62%) but no *o*-hydrazinobenzoic acid. This establishes that decomposition is prefaced by attack of hydroxyl ion at the ring carbonyl and not by hydrolysis of the N-acetyl group; the reaction course is then determined by departure of acetamide anion.

In the alkaline decomposition of 3-benzylideneamino-1,2,3-benzotriazin-4-one (Id), the separation of benzaldehyde was apparent before further observable decomposition occurred, suggesting that the overall process might be governed by the decomposition of 3-amino-1,2,3-benzotriazin-4-one in the presence of benzaldehyde. In fact the product distribution is benzylidene *o*-carboxyphenylhydrazine (31%) and *o*-azidobenzoic acid (36%), indicating concurrent decomposition to *o*-azidobenzoic acid and "benzaldimine", which is then hydrolysed to benzaldehyde and ammonia.

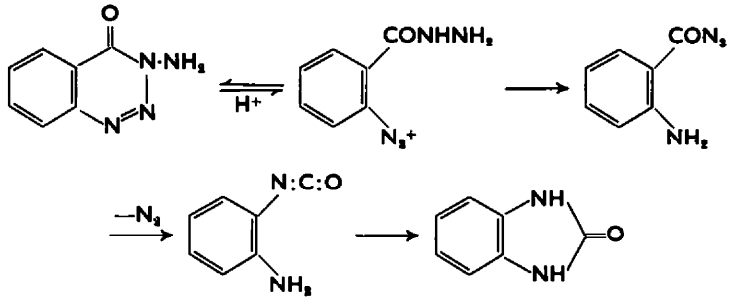
From the foregoing discussion, it seems clear that alkaline decomposition of the so-called bis-benzazimide, i.e. 4,4′dioxo-3,3′-bi(1,2,3-benzotriazinyl), is likely to yield *o*-azidobenzoic acid, anthranilic acid and nitrogen; the acid-insoluble product from this reaction was not identified[5] but its physical properties tally with those of *o*-azidobenzoic acid.

The behaviour of 3-amino-1,2,3-benzotriazin-4-one and related compounds in acidic media is determined by the concentration of acid and more particularly by temperature. Thus, Ia is sufficiently stable to be prepared by hydrolysis of its α-phenylethylidene derivative (If) with cold 18% hydrochloric acid, though at elevated temperature, acetophenone, nitrogen and benzimidazolone[6] are formed.[1] Cold 28·5% hydrochloric acid converts Ia to the isomeric anthranilazide, and, since it is known

[5] G. Heller, W. Dietrich and G. Reichardt, *J. Prakt. Chem.* **118**, 138 (1928).

[6] Through an unfortunate error in transcription, this product was subsequently reported as indiazolone: cf. J. G. Erickson, *The Chemistry of Heterocyclic Compounds* (Edited by A. Weissberger). Vol. 10; p. 25. Interscience, New York (1956).

that anthranilhydrazide can be *trans*-nitrosated by toluene-*p*-diazonium ion to anthranilazide,[3] it is possible to delineate the scheme for the acidic decomposition of Ia. Evidence for the first stage comes from interception of the diazonium ion by



β-naphthol (Bamberger-Goldberger test), and the conversion of anthranilazide to benzimidazolone in hot hydrochloric acid has now been demonstrated. Patently, acidic degradation of those triazines which yield anthranilazide under the reaction conditions will also lead to benzimidazolone. A case in point is 3-acetamido-1,2,3-benzotriazin-4-one. Ring fission in hydrochloric acid solution is demonstrable, and anthranilazide and benzimidazolone are isolable in yields dependent on reaction time, that of the former decreasing as that of the latter increases. Decomposition in hot polyphosphoric acid, however, involves fission of the amide link and leads to salicylic acid.

The structures of some triazines of type I preclude formation of anthranilazide in acid solution, and intramolecular displacement of the diazonium group as nitrogen might occur in some cases. König and Reissert's preparation of 1-phenylindiazolone[7] is probably a case in point. No 1-phenylindiazolone could, however, be isolated from Ie; this triazine develops an intense reddish-blue colouration in acid solution, probably due to intermolecular coupling, and at higher temperature charring occurs.

EXPERIMENTAL

Microanalyses were carried out by Mr. V. Manohin. 3-Amino-1,2,3-benzotriazin-4-one (Ia) and anthranilazide were prepared by the acetic acid procedure; 3-benzylideneamino-1,2,3-benzotriazin-4-one was prepared by heating equivalent amounts of (Ia) and benzaldehyde at 100° for 30 min without added solvent.[8]

Decomposition of 3-amino-1,2,3-benzotriazin-4-one in alkali

A suspension of 3-amino-1,2,3-benzotriazin-4-one (1·06 g) in 20% NaOH aq (10 ml) was heated on a steam-bath for 15 min with swirling. After ca. 5 min, an exothermic reaction occurred with vigorous evolution of N_2 and NH_3. Benzaldehyde (0·65 ml) was added to the yellow solution, and after a further 5 min the mixture was distilled in steam to remove unreacted benzaldehyde. The hot residual solution (ca. 20 ml) was then acidified with glacial acetic acid (5 ml) when benzylidene *o*-carboxyphenylhydrazone (0·75 g, 48%) separated as a pale yellow solid. Further acidification of the filtrate by addition of conc HCl (10 ml) led to the precipitation of *o*-azidobenzoic acid (0·2 g, 19%).

Benzylidene *o*-carboxyphenylhydrazone crystallized from benzene as tiny yellow needles, m.p. and mixed m.p. 222–223° (lit[8] m.p. 222–223°); the IR spectra were identical. *o*-Azidobenzoic acid crystallized from water as colourless needles, m.p. and mixed[1] m.p. 145–146° dec (lit[8] m.p. 144·5° dec); the IR spectra were identical.

[7] A. König and A. Reissert, *Ber. Dtsch. Chem. Ges.* **32**, 782 (1899).
[8] E. Bamberger and E. Demuth, *Ber. Dtsch. Chem. Ges.* **34**, 1309 (1901).

Preparation of 3-(N-*methyl*-N-*phenyl*)*amino*-1,2,3-*benzotriazin*-4-*one*

(a) Isatoic anhydride (3·0 g) and *as*-methylphenylhydrazine (2·5 ml) were heated under N_2 in an oil-bath. Vigorous gas evolution (CO_2) occurred at 100–120°; the temp was raised to 150° as reaction slackened and maintained there for 2 hr. Excess *as*-methylphenylhydrazine was then removed *in vacuo* at 100–120° for 5–6 hr. On cooling, crude anthranil-*as*-methylphenylhydrazide (4·93 g) hardened as a pale brown glass. This was powdered, and stirred into ice-cold 2 N HCl (42 ml); an ice-cold solution of $NaNO_2$ (1·7 g, 1 equiv) in water (3·5 ml) was then added with stirring during *ca.* 10 min, the temp of the mixture remaining below 10°. The sandy-coloured reaction product was collected, washed and dried. Crystallization from EtOH gave 3-(N-*methyl*-N-*phenyl*)*amino*-1,2,3-*benzotriazin*-4-*one* (2·72 g) as pale yellow plates, m.p. 110–111°, not depressed on admixture with the sample prepared by method (b) below; the IR spectra of the two samples were identical.

(b) A solution of *o*-nitrobenzoyl chloride, from the acid (5 g) and $SOCl_2$, in dioxan (10 ml) was added in portions with shaking and cooling to *as*-methylphenylhydrazine (3·2 ml) dispersed in 5% NaOH aq (90 ml), the mixture alkaline. The *o-nitrobenz*-as-*methylphenylhydrazide* (7·3 g) that separated crystallized from MeOH as pale yellow plates, m.p. 141–142°. (Found: C, 61·8; H, 4·6; N, 15·3. $C_{14}H_{12}N_4O_3$ requires: C, 62·0; H, 4·8; N, 15·5%.)

To a suspension of powdered *o*-nitrobenz-*as*-methylphenylhydrazide (4·5 g) in the two-phase system composed of hydrated $FeSO_4$ (32 g), water (80 ml) and EtOH (40 ml) at ca. 80° was added NH_3 aq (25 ml, *d* 0·88) in portions with vigorous shaking. The resulting black mass was boiled for 5 min, filtered through charcoal, the precipitate washed with boiling water (50 ml), and the filtrate and washings discarded. The black residue was extracted with boiling EtOH (50 ml, then 3 × 30 ml) and the extract then decolourized (charcoal) and evaporated leaving crude anthranil-*as*-methylphenylhydrazide (3·1 g) as a pale brown glass. This was stirred into 2 N HCl (25 ml) and treated with $NaNO_2$ aq as in (a); the addition was terminated when the mixture developed a transient green colour after ca. ¾ of the $NaNO_2$ solution had been added. A nodule of gum was removed mechanically, and the solid was collected, washed and dried. Crystallization from EtOH gave 3-(N-methyl-N-phenyl)-amino-1,2,3-benzotriazin-4-one (1·5 g) as yellow plates, m.p. 110–111°. (Found: C, 66·5; H, 4·8; N, 22·3. $C_{14}H_{12}N_4O$ requires: C, 66·7; H, 4·8; N, 22·2%.)

Decomposition of 3-(*substituted amino*)-1,2,3-*benzotriazin*-4-*ones in alkali*

(a) 3-(N-*Methyl*-N-*phenyl*)*amino*-1,2,3-*benzotriazin*-4-*one*. The triazinone (0·68 g) was heated with 20% NaOH aq (5 ml) for 10 min on a steam-bath. Dark oily drops separated, and the smell of N-methylaniline became apparent. EtOH (1·5 ml) was added as co-solvent, and heating was continued for a further 10 min. The mixture was cooled and acidified with conc HCl, when *o*-azidobenzoic acid (0·35 g, 80%) separated; identity was established by comparison (m.p. and mixed m.p. 145–146° dec, and correspondence of IR spectra) with the sample from the following experiment. No *o*-hydrazinobenzoic acid was detected in the filtrate (benzaldehyde method).

(b) 3-*Acetamido*-1,2,3-*benzotriazin*-4-*one*. A suspension of the triazinone (1·32 g) in 20% NaOH aq (10 ml) was heated on a steam-bath. The compound slowly dissolved without effervescence, though some NH_3 was evolved, to give a yellow solution which became colourless after ca. 10 min. Benzaldehyde (0·65 ml) was then added, and the mixture was worked up as described above. No benzylidene *o*-carboxyphenylhydrazone was obtained on acidification with acetic acid; further acidification with conc HCl precipitated *o*-azidobenzoic acid (0·61 g, 62%), which crystallized from water as needles, m.p. 145–146° dec.

(c) 3-*Benzylideneamino*-1,2,3-*benzotriazin*-4-*one*. The triazinone (0·6 g) was warmed with 20% NaOH aq (4 ml) on a steam-bath, the smell of benzaldehyde becoming noticeable at ca. 50°. The solid gradually dissolved and evolution of N_2 and NH_3 occurred at 80–100°. A small amount of benzaldehyde was removed by distillation in steam. Fractional acidification gave benzylidene *o*-carboxyphenylhydrazone (0·18 g, 31%) and *o*-azidobenzoic acid (0·14 g, 36%).

Anthranilic acid was not observed in these decompositions.

Decomposition of 3-*acetamido*-1,2,3-*benzotriazin*-4-*one in acid*

This triazinone and 3-amino-1,2,3-benzotriazin-4-one both give deep claret colourations with β-naphthol in warm acetic acid–conc HCl solution. (Bamberger–Goldberger test.)

(a) *In* HCl. A suspension of 3-acetamido-1,2,3-benzotriazin-4-one (2 g) in water (16 ml) and

conc HCl (4 ml) was heated on a steam-bath; the triazinone dissolved slowly with frothing to give a yellow solution which suddenly deposited a mass of faintly yellow plates. After a further 5 min, the solid A (0·78 g) was collected, washed and dried, and the combined filtrate and washings were rapidly chilled and basified with 2 N Na_2CO_3, when a solid B (0·1 g) separated.

Compound *A* crystallized from acetic acid as colourless plates, m.p. 308–309°. (Found: C, 62·9; H, 4·6; N, 21·0. Calc. for $C_7H_6N_2O$: C, 62·7; H, 4·5; N, 20·9%) and was identified as benzimidazolone by comparison (mixed m.p. and IR spectrum, which showed unusually high carbonyl absorption at 1750 cm^{-1}) with an authentic specimen.[9]

Compound *B* crystallized from benzene–light petroleum as pale yellow plates, m.p. 80–81° dec, resolidifying as plates from 95–100° and remelting at 305–308°. Compound *B* and its thermolysis product were shown to be anthranilazide and benzimidazolone respectively by comparison (mixed m.p. and IR spectra) with authentic samples; for anthranilazide, Heller and Siller[9] report m.p. 82–83° dec.[10]

The yields of benzimidazolone and anthranilazide were 60% and 6% respectively; in a similar experiment, interrupted immediately after precipitation of the benzimidazolone, the corresponding figures were 50% and 16%. In a separate experiment, a solution of anthranilazide (0·9 g) in 2 N HCl (35 m) was heated on a steam-bath. Vigorous evolution of N_2 occurred at ca. 90°; benzimidazolone (0·5 g, 67%) then separated, and was identified as in the previous case.

(b) *In polyphosphoric acid.* 3-Acetamido-1,2,3-benzotriazin-4-one (2 g) was stirred into a mixture of P_2O_5 (10 g) and syrupy phosphoric acid (15 ml) at 90°. The temp was then raised to 120–140° and the mixture stirred till gas evolution ceased (30 min). The near-colourless solution was poured onto crushed ice, and the solid (0·6 g) collected and dried; no precipitation occurred when the filtrate was basified. Crystallization from cyclohexane and then from water gave colourless needles, m.p. and mixed m.p. (with salicylic acid) 150–152°; the IR spectra of the samples were identical.

Decomposition of 3-(N-*methyl*-N-*phenyl*)*amino*-1,2,3-*benzotriazin*-4-*one in acid*

This triazinone developed intense reddish-blue colourations on warming with HCl or polyphosphoric acid; on further heating, extensive charring occurred, and only traces of salicylic acid could be isolated from these decompositions.

[9] L. S. Efros, B. A. Poraĭ-Koshits and S. G. Farbenshteĭn, *Zhur. Obshchei Khim.* **23**, 1691 (1953).
[10] Heller and Siller allude to this formation of benzimidazolone; for details of preparation of the allied mono- and di-acetyl derivatives of naphth[2,3-d]imidazolone, cf. K. Fries, R. Walter and K. Schilling, *Liebig's Annalen* **516**, 248 (1935).