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# THERMAL REARRANGEMENT OF SOME 3-SUBSTITUTED-2,1-BENZISOXAZOLES

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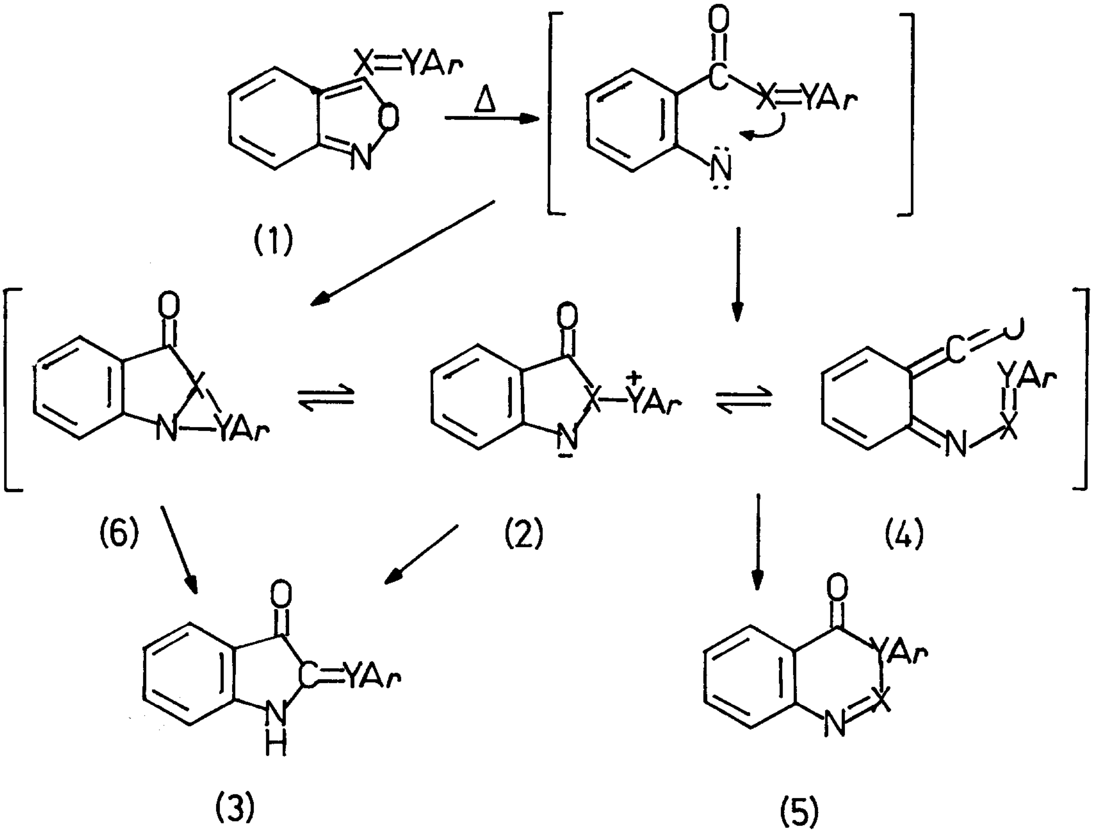
Summary 3-(Phenyliminomethyl)- and 3-arylazo-2,1-benzisoxazoles undergo thermal rearrangement to 3-phenylquinazolin-4-one and 3-aryl-1,2,3-benzotriazin-4-ones, respectively.

In a recent letter[1] the thermal rearrangements of some 3-(β-styryl)-2,1-benzisoxazoles (1; X=Y=CH) to 3-aryl-4-quinolones and 2-arylideneindoxyls (3; Y=CH) were discussed. As outlined in Scheme 1 loss of a proton from the dipolar structure (2; X=Y=CH) is a likely reaction path to 2-arylideneindoxyls (3), whereas quinolone formation is understandable on



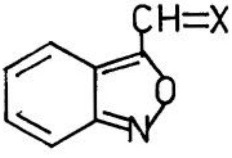
Scheme 1

the basis of an electrocyclisation of the iminoketen (4; X=Y=CH). An alternative to the dipolar structure (2) is the tricyclic intermediate (6) which by appropriate bond fission of the three-membered ring can yield (3) directly.

The relative ease of these rearrangements suggested that other 2,1-benzisoxazoles (anthranils) bearing unsaturated 3-substituents might undergo analogous transformations. We now report on the synthesis and thermal rearrangement of the anil (1; X=CH, Y=N, Ar=Ph) and the azoanthranils (1; X=Y=N, Ar=Ph and *p*-$\mathrm{ClC_6H_4}$) to 3-phenylquinazolin-4-one and 3-aryl-1,2,3-benzotriazin-4-ones, respectively.

3-Formylanthranil (7; X=O) has been prepared only once before[2] and then by a lengthy procedure. An alternative route utilising a Kröhnke aldehyde synthesis on 3-(bromomethyl)-2,1-benzisoxazole (prepared by the action of NBS on 3-methylanthranil) has been developed which gives the aldehyde (7; X=O) in 40-50% overall yield. Condensation with aniline furnished the anil (7; X=NPh), m.p. 72°C[3] (lit.[2] *ca.* 40°C).

In boiling anisole (b.p. 155°C) the anil undergoes slow decomposition (24 h) to a mixture of the rearranged product, 3-phenylquinazolin-4-one[4] (5; X=CH, Y=N, Ar=Ph) (25%), starting material (25%) and much tar. At higher temperatures (e.g. in 1-methylnaphthalene, b.p. 245°C) decomposition is rapid (10 min) and more complex. In addition to the phenylquinazolinone (30%) other as yet unidentified products are obtained.[5]



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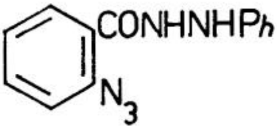

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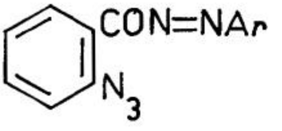
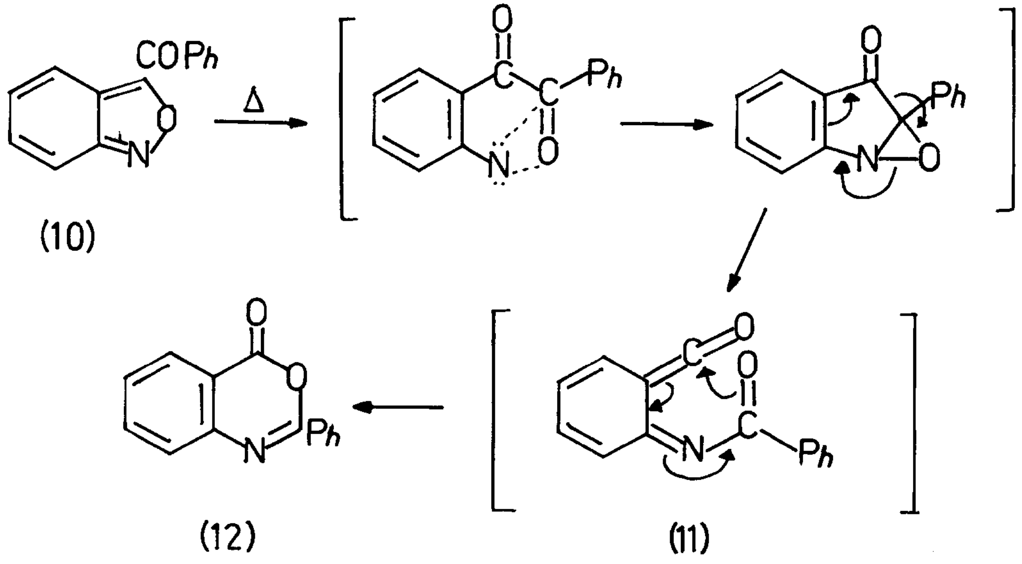


(9)

3-Arylazo-2,1-benzisoxazoles have not been prepared previously. Significantly, however, their *N*-oxides have been suggested as transient intermediates in the photo-decomposition of *N*-aryl-2-nitrobenzhydrazonyl bromides to 3-aryl-1,2,3-benzotriazin-4-ones,[6] i.e. the products expected on the basis of the reaction sequence (1 → 5) outlined in the Scheme (X=Y=N). By analogy with known procedures[7] for the preparation of 2,1-benzisoxazoles a likely synthetic route to the required azo-anthranils is by decomposition of *o*-azidobenzoylazo compounds (9). The benzoylazo compound (9; Ar=Ph) was obtained as a moderately stable red-oil by oxidising *N*-(*o*-azidobenzoyl)phenyl hydrazine (8) with lead tetra-acetate in $\mathrm{CH_3CN}$,[8] and which on thermolysis in boiling xylene gave the azo-anthranil (1; X=Y=N, Ar=Ph), red crystals, m.p. 89°C. Thermal rearrangement of the azo-anthranil was accomplished in boiling o-dichlorobenzene (b.p. 178°C), and was easily monitored by observing the disappearance of the characteristic red-azo-compound colour, which was complete after ca. 15 min. Removal of solvent, followed by crystallisation (EtOH) of the residue gave 3-phenyl-1,2,3-benzotriazin-4-one (5; X=Y=N, Ar=Ph) (50%), m.p. 150°C, identical in all respects with a genuine sample prepared[9] by diazotisation of N-(o-aminobenzoyl)aniline.

Oxidation of (8) to its benzoylazo derivative was also successful using N-chlorobenzotriazole in $CH_2Cl_2$.[10] However, decomposition of the crude semi-solid (m.p. ca. 40°C) azo-compound in boiling xylene gave as major product[11] a different azo-anthranil (m.p. 140°C) to the one described above; the mass spectrum (m/e 259, 261, $M^+$), and elemental analysis indicated the presence of a chloro substituent.[12] Thermal rearrangement of the chloroazo-compound gave a crystalline solid, m.p. 184°C (60%) which was identical (mixed m.p., superimposable i.r.) with a genuine sample[13] of 3-(p-chlorophenyl)-1,2,3-benzotriazin-4-one (5; X=Y=N, Ar=p-$ClC_6H_4$). Hence, the benzoylazo-compound must be the p-chlorophenyl derivative (9; Ar=p-$ClC_6H_4$).

Related to the above rearrangements is the thermal rearrangement of 3-benzoyl-2,1-benzisoxazole (10) to 2-phenyl-3,1-benzoxazin-4-one (12).[14] A mechanistic rationale for rearrangement under basic conditions has been proposed which culminates in electrocyclisation of the acyliminoketene (11). However, for rearrangement under neutral



Scheme 2

conditions (e.g. in n-butyl vinyl ether at 160°C) a reaction sequence (Scheme 2) analogous to that outlined in Scheme 1 could well be operating.

Further work is in progress to extend the scope of this, apparently, general rearrangement [(1) → (5)] of 3-substituted anthranils.

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11. Decomposition of the p-chlorobenzoylazo derivative is accompanied by formation of 3-(p-chlorophenyl)-1,2,3-benzotriazin-4-one (6%). This product corresponds to the 3-aryl-4(1H)-quinolones formed in the rearrangement of o-azidochalcones to 3-(β-styryl)anthranils - see reference 1.
12. Oxidation of (5) with NBS in $CH_2Cl_2$ yields a dibromo-azo-compound, and hence a dibromo-azo-anthranil, the structures of which are under investigation.
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