

A Novel Synthesis of a Benzimidazo[1,2-c]benzopyrimidine by Photolysis of 4-(Benzotriazol-1-yl-2-phenylquinazoline (1)

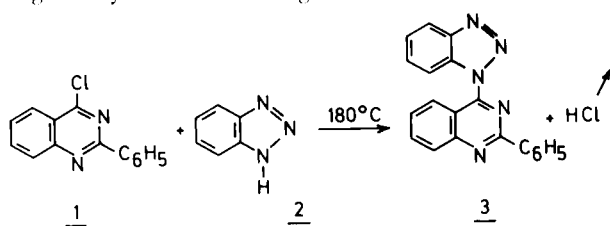
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Received April 4, 1974

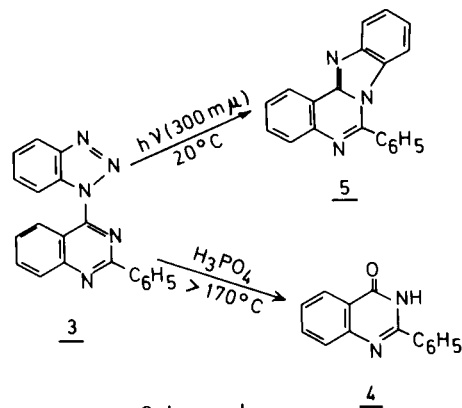
A novel synthesis of 6-phenylbenzimidazo[1,2-c]benzopyrimidine (**5**) by photolysis of 4-(benzotriazol-1-yl-2-phenylquinazoline (**3**) is described. The acid-catalysed thermolysis of **3** leads to an extensive degradation yielding 2-phenyl-4-quinazolinone (**4**).

The photolysis and the thermal decomposition of benzotriazoles and triazole derivatives have been extensively investigated recently (2-5). In particular, we have shown (6,7) that the photolysis of substituted benzotriazoles follows in some cases, a path completely different from the classical acid-catalysed decomposition of the substituted benzotriazoles. We wish now to report on a novel example of the selectivity of this process while using readily available starting material.



Scheme a.

4-(Benzotriazol-1-yl-2-phenylquinazoline (**3**) which is readily prepared from 4-chloro-2-phenylquinazoline (**1**) and benzotriazole (**2**) (Scheme a), reacts with phosphoric



Scheme b.

acid at 170° to give a small yield of 2-phenyl-4-quinazolinone (**4**) (Scheme b) besides some tars and water soluble unidentified material.

In opposition, the photolysis of **3** led exclusively to 6-phenylbenzimidazo[1,2-c]benzopyrimidine (**5**) which was identified by analysis and mass spectrometry. The formation of this polycyclic derivative (**5**) in the photolytic process may be explained as reported by the cyclization of the diradical (**6**) or possibly the corresponding mesomeric 1,5-dipole (**8**) obtained after elimination of nitrogen from the benzotriazole moiety of **3**.

Compound **4** was identified by its melting point (9), analysis and ir spectroscopy: this compound shows the typical absorption of an amido group at $6.0\ \mu$.

As far as the polycyclic compound (**5**) is concerned, the ir spectrum was very different from **4**: characteristic bands for an unsaturated nitrogen-containing heterocycle are observed at $6.16\text{-}6.29\ \mu$.

The uv spectrum of **5** shows a pattern which is compatible with a condensed polycyclic system. The starting material **3** absorbs at a longer wavelength than **5** (see Fig. 1) and the absorption at $340\text{-}354\ \text{nm}$ is obviously responsible for the photodecomposition of the benzotriazolyl group of **3**. In fact, this result is another example of the selectivity of the photolysis of benzotriazole derivatives for the preparation of condensed heterocyclic systems. In contrast to the classical acid-catalysed decomposition, the photolytic process is very general for the preparation of polycondensed cyclic systems as our results show that the acid-catalysed decomposition can follow three different paths, in cases which all afford exclusively condensed heterocyclic compounds by photolysis:

a) Cyclization of a cationic intermediate on a position different from the nitrogen atom which is involved in the photolytic process (6).

b) Cyclization of a cationic intermediate on the *same* position as in the photolytic process when the other position is blocked by a substituent or a condensed cyclic group (7). The yield is however better in the photolytic process than in the acid-catalysed decomposition.

c) Cleavage or destruction of the molecule as reported in this article.

In conclusion, it is therefore very useful to compare both methods of decomposition of benzotriazole derivatives as the classical acid catalysed decomposition is often unsuitable for the preparation of condensed polycyclic heterocycles or follows a very different route (6,7).

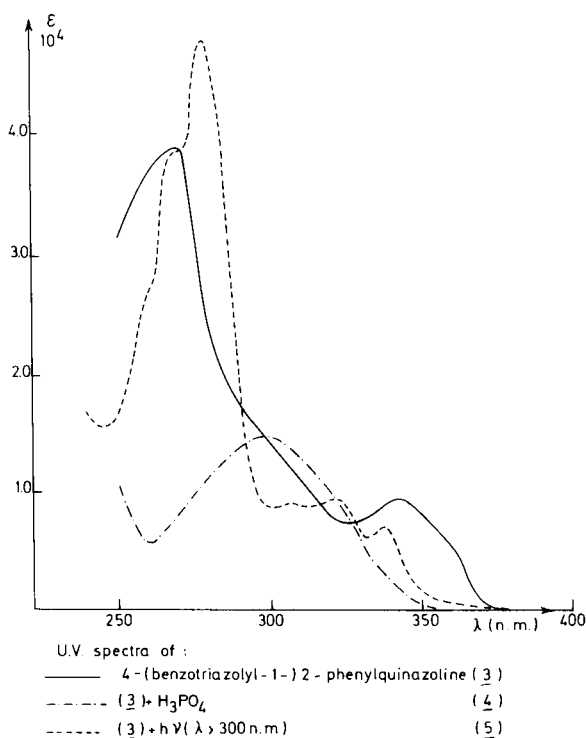


FIGURE 1

EXPERIMENTAL

Starting Material.

Benzotriazole (2) and 4-chloro-2-phenylquinazoline (1) are commercial products which are available from Merck and Aldrich.

Preparation of 4-(Benzotriazol-1-yl)-2-phenylquinazoline (3).

Benzotriazole (2) (0.04 mole) was heated progressively to 180° in an oil bath until evolution of hydrogen chloride was complete. The mixture remained solid through the whole process. The solid was recrystallized from ethanol in which it was slightly soluble. (The compound was much more readily soluble in THF, pyridine and benzene), m.p. (from ethanol) 200°. The yield was practically quantitative. The ir spectrum (in potassium

bromide) showed bands at 6.2, 6.27, 6.39, 6.46, 6.9, 7.05, 7.26, 7.43, 9.64, 10.24, 12.02, 12.74, 13.10, 13.40, 14.34 and 14.59 μ. Uv absorption (in dioxane) took place at 354 (s) (ε = 8,200), 340 (ε = 9,200), 293 (s) (ε = 17,000) and 268 (ε = 38,500) nm (see Figure).

Anal. Calcd. for C₂₀H₁₃N₅: C, 74.3; H, 4.0; N, 21.7. Found: C, 74.6; H, 4.1; N, 21.4.

Photolysis of 3.

A solution of 3 (0.7 g.) in benzene (50 ml.) was irradiated overnight through Pyrex (λ > 290 nm) under Argon at 30-40° with a uv lamp (Philips HPK 125 W.) cooled with a water-jacket. Evaporation of the solvent gave 5 in 80% yield. The raw material was washed with acetone and purified by crystallization from benzene-heptane; m.p. 240° (slightly yellow crystals). The ir spectrum (in potassium bromide) showed bands at 6.16, 6.29, 6.52, 6.94, 12.99, 13.20 and 13.52 μ. The uv spectrum of 5 showed maxima at 338 (ε = 6,750), 323 (ε = 9,200), 308 (ε = 8,800), 278 (ε = 47,000) and 269 (s) (ε = 38,000) nm in dioxane (see Figure). MW (mass spectrometry): Calcd: M/e = 295; Found: 295.

Anal. Calcd. for C₂₀H₁₃N₃: C, 81.3; H, 4.4; N, 14.2. Found: C, 81.5; H, 4.5; N, 14.1.

Acid-Catalysed Decomposition of 3.

A suspension of 3 (2 g.) in phosphoric acid (10 ml.) was heated at 185° during 15 minutes until nitrogen evolution was complete. The mixture was poured into water and the precipitate was filtered. Compound 4 was obtained in 12% yield. Recrystallization from benzene gave pure 4 as white needles, m.p. 240-241° (reported for 2-phenyl-4-quinazolinone (3), 240-241°). The ir spectrum (in potassium bromide) showed bands at 6.0 (very strong), 6.25, 6.42, 6.75, 7.73, 10.63, 13.04 (strong) and 14.45 (strong) μ. The band at 6.0 μ is typical for an amido group. The uv spectrum showed a maximum at 300 nm (ε = 14,200) in dioxane (see Figure).

Anal. Calcd. for C₁₄H₁₀N₂O: C, 75.6; H, 4.5; N, 12.6. Found: C, 75.6; H, 4.5; N, 12.6.

Acknowledgments.

We are indebted to Professor Martin, Université Libre de Bruxelles, for having generously authorized the mass spectrum measurements in his Department and to Dr. Kaisin for having kindly made these spectra.

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