CONDENSED IMIDAZO-1,2,4-AZINES.

15.* REACTION OF 1,2-DIAMINOBENZIMIDAZOLE WITH 5-PHENYL-2,3-DIHYDROFURAN-2,3-DIONE

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The reaction of 1,2-diaminobenzimidazole with 5-phenyl-2,3-dihydrofuran-2,3dione in acetic acid gave a mixture of 2-benzoylmethyl-1,2,4-triazino [2,3-a]benzimidazol-4H-3-one and 3-benzoylmethyl-1,2,4-triazino[2,3-a]benzimidazol-1H-2-one, the intramolecular cyclization of which gave isomeric 2-phenylfuro-[5,4-e]- and 2-phenylfuro[4,5-e]-1,2,4-triazino[2,3-a]benzimidazoles. Only the corresponding furo[4,5-e]-1,2,4-triazino[2,3-a]benzimidazole was isolated when the reaction was carried out in sulfuric acid.

In continuing our research on the reaction of 1,2-diaminoimidazole and its analogs with dicarbonyl reagents we studied the reaction of 1,2-diaminobenzimidazole (I) with 5-phenyl-2,3-dihydrofuran-2,3-dione (II). This reaction opens up a pathway to the synthesis of representatives of a new heterocyclic system - furo-1,2,4-triazino[2,3-a]benzimidazole derivatives.

Our investigation showed that the direction of the reaction of starting I and II depends substantially on the nature of the condensing agent. In the case of refluxing in acetic acid we isolated a mixture of two substances, which were separated under the experimental conditions (see the experimental section). One of them, which was obtained in 41% yield and had mp 302-303°C, was identical, according to data from the IR, UV, and mass spectra, to 2-benzoyl-methyl-1,2,4-triazino[2,3-a]benzimidazol-4H-3-one (III), which we previously synthesized by the reaction of diamine I with 3-benzoyl-2-propanoic acid [2]. The other product, viz., IV, with mp 286-287°C, was isolated in 21% yield; with respect to its physicochemical characteristics, it differed from III, although it corresponded to the empirical formula of the latter according to the high-resolution mass spectrum. Thus absorption bands of two carbonyl groups ($v_{C=0}$ 1670 and $v_{C=0}$ amide 1630 cm⁻¹) and a ring imino group (v_{NH} 3030 cm⁻¹) are observed in the IR spectrum. The mass spectrum of IV, like that of III [2], is characterized by a molecular-ion peak (M⁺) with maximum intensity at 304.[†] Ions at 227 ([M - C₆H₅]⁺) and 199 ($[M - C_6H_5CO]^+$, α cleavage relative to the carbonyl group) are recorded in the mass spectrum of IV; this, together with signals at 77 ($[C_6H_5]^+$) and 105 ($[C_6H_5CO]^+$), proves the presence of a benzoyl grouping. In addition to the peaks indicated, peaks of fragment ions at 160 $([M - NCCHCOPh]^+)$ and 144 ([NCCHCOPh]^+) are observed in the mass spectrum of IV; this does not contradict the proposed structure and confirms the structure of the triazine part of the molecule. Ions at 102, 103, and 131 characterize the imidazole part of the compound [2]. On the basis of these data, we proposed a 3-benzoylmethyl-1,2,4-triazino[2,3-a]benzimidazol-1H-2-one structure - isomeric with respect to III - for the second product (IV).

The formation of isomeric III and IV under the conditions of the described reaction can be explained by assuming two competitive processes. One of them involves hydration of furandione II, which leads to 3-benzoyl-2-propanoic acid, which subsequently reacts with diamine I, as described in [2]. The other process is due to initial reaction of the more reactive carbonyl group (see Fig. 1) of dione II with the electron-surplus "hydrazine" group of diamine I [2], which leads to a compound of the hydrazone A type, in which, because of the presence of water, the furan ring opens up to give B. Intramolecular dehydration of intermediate B leads to stable 3-benzoylmethyl derivative IV.

The use of strong dehydrating agents leads to different results. Thus only one product was isolated when starting reagents I and II were heated in concentrated H_2SO_4 . Absorption *See [1] for Communication 14.

 \pm Here and subsequently, the numbers that characterize the ions are the m/z values.

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Fig. 1. Molecular diagram of 5phenyl-2,3-dihydrofuran-2,3-dione.

bands of carbonyl and amino groups are absent in its IR spectrum. An M^+ peak at 286, which corresponds to the calculated molecular mass of the product of complete condensation of diamine I with dione II, is recorded in the mass spectrum of this compound (V). The M^+ ion is characterized by high resistance to electron impact ($W_M = 20\%$); this is characteristic for condensed heterosystems. (An intense peak of M^{++} ions is also observed in the spectrum.) The fragmentation of M^+ is extremely selective. Fragment ions at 105 ([PhCO]⁺), which prove the presence of a phenyl substituent in the α position of the furan fragment, and at 102 ([PCCH]⁺) are recorded, i.e., V displays all of the specific features that characterize furo-condensed azines [3].

It is known [4] that, under the influence of dehydrating agents, 2-benzoylmethylquinoxalin-4H-3-ones undergo intramolecular dehydration with the formation of the corresponding derivatives of the furan series. In this connection, it seemed of interest to realize the cyclization of isomeric benzoylmethyl derivatives III and IV. By refluxing IV in a mixture of POCl₃ with PCl, we synthesized furo[4,5-e]-1,2,4-triazine[2,3-a]benzimidazole (V), which proved to be identical to a sample obtained by direct condensation of diamine I with furandione II. By dehydration of 2-benzoylmethyl derivative III under similar conditions we were able to obtain the isomeric furo[5,4-e]-1,2,4-triazino[2,3-a]benzimidazole (VI).



A study of the fragmentation of four-ring compound VI under electron impact showed that the trend of its dissociative ionization differs little from that of isomer V. A difference in the mass spectra of isomers V and VI is displayed only when one compares the intensities of the principal fragment ions [5]. The data from the UV spectra of isomeric four-ring compounds V and VI also differ somewhat (see the experimental section).

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The electronic absorption spectra of solutions in dioxane $[(0.2-0.7)\cdot10^{-4} \text{ M}]$ were obtained with a Specord UV-vis spectrophotometer. The mass spectra of IV-VI were recorded with a Varian MAT-311a spectrometer under standard operating conditions [2]. The quantum-chemical calculations of furandione II were made by the Pariser-Parr-Pople (PPP) method with the standard parametrization [6]. The geometrical parameters of the II molecule (in view of the lack of experimental data) were selected in conformity with structures that were similarly constructed.

<u>3-Benzoylmethyl-1,2,4-triazino[2,3-a]benzimidazol-1H-2-one (IV) and 2-Benzoylmethyl-1,2,</u> <u>4-triazine[2,3-a]benzimidazol-4H-3-one (III).</u> A solution of 0.3 g (2 mmole) of diamine I and 0.35 g (2 mmole) of furandione II in 10 ml of acetic acid was refluxed for 1 h, after which 0.12 g (21%) of yellow-orange crystals of IV, with mp 286-287°C (from DMF), were removed from the hot reaction mixture by filtration. IR spectrum: 3030 (NH), 1670 (C=O), 1635 cm⁻¹ (C=O_{amide}). Mass spectrum,* m/z (%): 305 (16), 304 (M⁺, 82), 227 (23), 173 (13), 160 (24),

*Peaks of ions with intensities 10% of the maximum peak are presented.

144 (11), 131 (10), 105 (100), 103 (10), 102 (10), 85 (10), 77 (64), 73 (26). Found, %: C 67.4, H 4.2, N 8.1. C₁₇H₁₂N₄O₂. Calculated, %: C 67.1, H 4.0, N 18.4.

After the filtrate was cooled, 0.23 g (41%) of III, with mp 302-303°C (from acetic acid) [2], cyrstallized out from it.

 $\frac{2-\text{Phenylfuro}[4,5-e]-1,2,4-\text{triazino}[2,3-a]\text{benzimidazole (V).} A) A \text{ solution of 0.45 g} (3 \text{ mmole}) of diamine I and 0.53 g (3 mmole) of furandione II in 5 ml of concentrated H₂SO₄ was maintained at 70°C for 5 h, after which the mixture was cooled and poured over ice. The resulting precipitate was removed by filtration, washed successively with water, 3% NaHCO₃ solution, and water, and dried to give 0.42 g (49%) of V with mp 305-306°C (from DMF). UV spectrum, <math>\lambda_{\text{max}}$ (log ε): 262 (4.47), 314 (4.10), 390 (4.40), 406 (4.43), 470 (4.08), 502 (3.96), 542 nm (3.65). Mass spectrum, m/z (%): 287 (29), 286 (M⁺, 100), 143 (10), 105 (31), 102 (20), 77 (29). Found, %: C 71.5, H 3.6, N 19.7. C₁₇H₁₀N₄O. Calculated, %: C 71.3, H 3.5, N 19.6.

B) A mixture of 0.61 g (2 mmole) of IV, 1 g of PCl_s , and 5 ml of $POCl_3$ was refluxed for 3 h, after which it was worked up as described in experiment A to give 0.35 g (61%) of product.

 $\frac{2-\text{Phenylfuro}[5,4-e]-1,2,4-\text{triazino}[2,3-a]\text{benzimidazole (VI).}}{\text{from benzoylmethyl derivative III by a procedure similar to that used to obtain V under the conditions of experiment B. The yield of product with mp 323-324°C (from DMF) was 0.21 g (69%). UV spectrum, <math>\lambda_{\text{max}}$ (log ε): 225 (4.09), 275 (4.06), 292 (4.13), 290 nm (4.15). Mass spectrum, m/z (%): 287 (21), 286 (M⁺, 100), 143 (5), 131 (10), 128 (24), 105 (80), 104 (21), 103 (7), 102 (22), 101 (14), 90 (34), 77 (50), 76 (10), 63 (10), 51 (34). Found, %: C 71.4, H 3.4, N 19.7. C₁₇H₁₀N₄O. Calculated, %: C 71.3, H 3.5, N 19.6.

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