RECYCLIZATION REACTIONS OF HETEROCYCLES.

XXI.* RECYCLIZATION OF AZOLIDONES TO BENZIMIDAZOLE DERIVATIVES

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2-Thioxo-4-oxazolidone and thiazolidines containing heteroatom substituents (0, S, and NH) in the 2 and 4 positions are converted to benzimidazole derivatives on reaction with o-phenylenediamine. The direction of these recyclizations depends on the nature of the heteroatom substituents in the 2 and 4 positions of the heteroring.

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When azolidones react with hydrazines, they undergo recyclization to triazolones or triazolethiones [2]. It seemed of interest to ascertain whether, in analogy with hydrazines, azolidones would undergo recyclization with o-phenylenediamine, which could lead to the formation of triazepine systems.

Reactions of lactones (for example, [3-5]) with o-phenylenediamine, in which benzimidazole derivatives are obtained, have been described. Although azolidones I-V have more extensive structural possibilities for cyclotransformations, it was found that they also undergo recyclization exclusively to benzimidazole derivatives VI-IX with o-phenylenediamine. These transformations proceed via different pathways, depending on the nature of the heteroatoms in the 2 and 4 positions, which determine the site of nucleophilic attack. With azolidine I (X = Y = S, Y = 0) primary attack takes place in the 4 position, and recyclization is accompanied by cleavage of the heteroring C-N bond. Imine X, which is converted to benzimidazole VI when it is heated in alcohol, was isolated as an intermediate. At the same time, the reaction begins with the 2 position in rhodanine II (X = Y = S, Z = 0), pseudothiohydantoin III (X = S, Y = NH, and Z = 0), and oxazolidine V (X = Z = 0, Y = S), and recyclization to benzimidazole VII is due to cleavage of the ring C-S(0) bond.

Isorhodanine I undergoes recyclization with o-phenylenediamine somewhat more readily than II and III. The reaction of I takes place in alcohol, whereas the reaction with II and III proceeds in boiling water (only in the presence of acid in the case of pseudothiohydantoin III). Thiazolidinedione IV undergoes recyclization to benzimidazole IX only when it is fused with o-phenylenediamine.

When VII is heated in aqueous alkali solution, it undergoes hydrolysis to 2-aminobenzimidthazole XI; this confirms its structure. The structure of VI was proved by alternative syn-



*See [1] for communication XX.

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thesis by the method in [6]. Compound X was characterized by means of dibenzylidene derivative XII. The structures of the compounds obtained are in agreement with their IR and PMR spectra (see the experimental section).

EXPERIMENTAL

The IR spectra of KBr pellets and mineral oil suspensions of the compounds were recorded with a UR-20 spectrometer. The PMR spectra of solutions of the compounds in dimethyl sulfoxide (DMSO) were recorded with a BS-487C spectrometer (80 MHz); the chemical shifts are presented relative to DMSO. The individuality of the compounds was monitored by thin-layer chromatography (TLC) on activity IV Al₂O₃. The molecular weights of VI and VII were determined by the Rast method in cyclohexanol and camphir, respectively.

<u>2-Mercaptomethylbenzimidazole (VI).</u> A) A mixture of 1.33 g (10 mmole) of isorhodanine I and 1.08 g (10 mmole) of o-phenylenediamine in 20 ml of ethanol was refluxed for 1 h, after which it was cooled and treated with 70 ml of water, and the mixture was allowed to stand. The resulting precipitate was removed by filtration, washed with water, and dried to give 1 g (60%) of product. Recrystallization from 50% ethanol gave white needles with mp 120-124°C (at the bulk of the thermometer); after melting, the compound solidified and remelted at 184-187°C (dec.). When the melting point was determined in a capillary by the standard method, the compound turned yellow and did not melt above 320°C. The product had Rf 0.9 (elution with methanol) and was identical to a sample synthesized by the method in [6]. IR spectrum (cm⁻¹): 3380 m (NH) and 2575 w (SH).

B) A suspension of 0.2 g of azolidone X in 15 ml of ethanol was refluxed for 1 h, after which it was cooled and diluted with water, and the precipitate was separated and dried. The yield was 0.1 g (62%).

 $\frac{2-(\alpha-\text{Mercaptoacetamido})\text{ benzimidazole (VII). A)}{A \text{ mixture of } 4.56 \text{ g (30 mmole) of the hydrochloride of pseudothiohydantoin III and 3.2 g (30 mmole) of o-phenylenediamine in 60 ml of water was refluxed for 2 h, after which it was cooled, and the resulting precipitate was removed by filtration, washed with water and alcohol, and dried to give 3.45 g (55%) of a product with mp 229-230°C (dec., from acetic acid) and Rf 0.47 (elution with dioxane). IR spectrum (cm⁻¹): 3325 s, 3215 m, 3170 m (associated NH), 2570 w (SH), 1680 s (CO, amide I), 1575 s and 1525 m (amide II, Ar), and 1310 w and 1270 m (amide III). PMR spectrum, <math display="inline">\delta$ (ppm): 6.7-7.3 m (4Har) and 3.6 s (CH₂). Found, %: C 52.5; H 4.4; N 20.3; S 15.3. M 205. C9H9N₃OS. Calculated, %: C 52.2; H 4.3; N 20.3; S 15.4. M 207.

B) A mixture of 0.7 g (5 mmole) of rhodanine II and 1 g (10 mmole) of o-phenylenediamine in 10 ml of water was refluxed for 40 min, after which it was cooled, and the precipitate was removed by filtration, washed with water and alcohol, and dried. The yield was 0.5 g (50%).

Hydrolysis of 2-(α -Mercaptoacetamido)benzimidazole (VII). A 1-g (5 mmole) sample of benzimidazole VII was refluxed in 10 ml of 10% KOH solution for 1.5 h, after which it was cooled and filtered to give 0.1 g of colorless crystals of XI with mp 226-227°C (from water). Evaporation of the mother liquor gave another 0.3 g of the same substance for an overall yield of 0.4 g (66%). IR spectrum (cm⁻¹): 3390 s and 3330 m (NH₂), 3140 m (NH), 1670 s (C=N), 1575 s, and 1315 w and 1270 s (imidazole ring). No melting-point depression was observed for a mixture of this product with a sample obtained by the method in [7].

 $\frac{2-(\alpha-Hydroxyacetamido) \text{ benzimidazole (VIII).}}{2-(\alpha-Hydroxyacetamido) \text{ benzimidazole (VIII).}} A mixture of 1.17 g (10 mmole) of oxazolid$ ine V and 1.08 g (10 mmole) of o-phenylenediamine in 15 ml of water was refluxed for 30 min,after which it was cooled, and the resulting precipitate was removed by filtration, washedwith water and alcohol, and dried to give 1.15 g (60%) of a product with mp 210-211°C (fromacetic acid) and Rf 0.34 (elution with methanol). IR spectrum (cm⁻¹): 3360 m (OH), 3340 mand 3300 s (NH), 1700 s (CO, amide I), 1580 and 1530 m (amide II, Ar), and 1310 w and 1280 $m (amide III). PMR spectrum, <math>\delta$ (ppm): 7.1-7.6 m (4H_{ar}), 6.5 broad s (NH), and 4.2 s (CH₂). Found, %: C 57.0; H 5.0; N 21.9. C₉H₉N₃O₂. Calculated, %: C 56.5; H 4.7; N 21.9.

<u>2-Benzimidazolone (IX)</u>. A 4.68-g (40 mmole) sample of thiazolidinedione IV was fused with 4.36 g (40 mmole) of o-phenylenediamine on an oil bath at 170-180°C for 15 min, after which the mixture was cooled and treated with ether. The mixture was filtered, and the solid material was washed with water and dried to give 3.4 g (63%) of IX with mp 304-305°C (from propanol). No melting-point depression was observed for a mixture of this product with a genuine sample of 2-benzimidazolone.

4-(o-Anilinimino)-2-thiazolidone (X). A mixture of 1.33 g (10 mmole) of isorhodanine I and 1.08 g (10 mmole) of o-phenylenediamine in 30 ml of methanol was stirred at room temperature for 30 min, after which the precipitated was removed by filtration, washed with methanol, and dried to give 1.4 g (68%) of a product with mp 145-146°C (dec., from propanol) and Rf 0.4 (elution with methanol). IR spectrum (cm^{-1}) : 3395 m and 3300 s (NH_2) , 3230 m (NH), 1690 s (CO, amide I), 1565 and 1530 m (amide II, Ar), and 1300 m and 1275 m (amide III). PMR spectrum, δ (ppm): 10.4 s (NH), 6.5-7.2 m (4H_{ar}), 5.2 broad s (NH₂), and 4.5 s (CH₂). Found, %: C 52.4; H 4.4; N 20.3; S 15.6. C₉H₉N₃OS. Calculated, %: C 52.1; H 4.3; N 20.2; S 15.4.

4-(o-Benzylideneanilinimino)-5-benzylidene-2-thiazolidone (XII). A mixture of 0.5 g (2.4 mmole) of 4-(o-anilinimino)-2-thiazolidone and 0.53 ml (5 mmole) of benzaldehyde in 5 ml of glacial acetic acid was heated until the starting components dissolved completely, after which the solution was allowed to stand at room temperature for 10 min. It was then diluted with water and filtered, and the solid was dried to give 0.8 g (87%) of a product with mp 197-198°C (from benzene) and $R_f 0.78$ (elution with chloroform). IR spectrum (cm⁻¹): 3290 m (NH), 1735 s (CO, amide I), 1570 s and 1540 m (amide II, Ar), 1310 w and 1270 m (amide III). Found, %: C 72.1; H 4.2; N 11.1; S 8.1. C₂₃H₁₇N₃OS. Calculated, %: C 72.1; H 4.4; N 11.0; S 8.3.

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EFFECT OF PERFLUOROPHENYL GROUPS ON THE NATURE OF THE ELECTRONIC ABSORPTION SPECTRA OF 1, 3, 5-TRIARYL- Δ^2 -PYRAZOLINES

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The results of calculations by the self-consistent field (SCF) MO Pariser-Parr-Pople (PPP) method explain the nature of the electron transitions responsible for the electronic absorption spectra of 1,3,5-triphenylpyrazoline and its perfluorophenyl derivatives. The perfluorophenyl group behaves like a strong electron donor in the excited states. According to the results of the calculation, a perfluorophenyl group in the l position of the pyrazoline ring deviates markedly from the planar conformation.

Like their long-wave absorption, the luminescence of 1,3,5-triarylpyrazolines (I) is due to the electron transitions in the chromophore system (II), which includes 1- and 3-aryl groups [1-3]. The long-wave band is an intramolecular charge-transfer band in system II [3-5].



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