ISOINDOLO[1',2':2,3]PYRIDO[3",2":4',5']THIENO[3',2':4,5]-PYRIMIDO[1,6-*a*]BENZIMIDAZOL-8(12bH)-ONE. A NOVEL POLYCONDENSED HETEROCYCLIC SYSTEM

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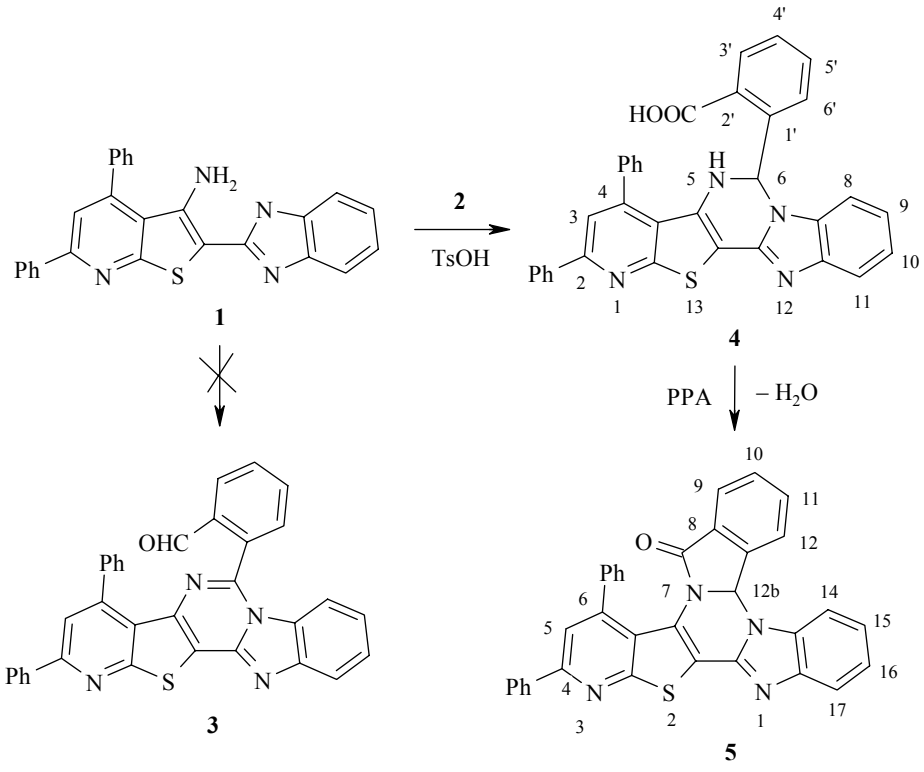
Keywords: 2-(2,4-diphenyl-5,6-dihydrobenzo[4,5]imidazo[1,2-*c*]pyrido[3',2':4,5]thieno[2,3-*e*]pyrimidin-6-yl)benzoic acid, 4,6-diphenylisoindolo[1',2':2,3]pyrido[3",2":4',5']thieno[3',2':4,5]pyrimido[1,6-*a*]-benzimidazol-8(12bH)-one, intramolecular cyclization.

Previous studies by us [1-3] and others [4-6] have described 3-amino-2-(benzimidazol-2-yl)thieno[2,3-*b*]pyridines. It was shown that carboxylic acid anhydrides or orthoesters react readily with 3-amino-2-(benzimidazol-2-yl)thieno[2,3-*b*]pyridines to give the pentacyclic heteroaromatic systems benzo[4,5]-imidazo[1,2-*c*]pyrido[3',2':4,5]thieno[2,3-*e*]pyrimidines and with aldehydes to give 5,6-dihydrobenzo-[4,5]imidazo[1,2-*c*]pyrido[3',2':4,5]thieno[2,3-*e*]pyrimidines.



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It was of interest to study the reaction of 3-amino-2-(benzimidazol-2-yl)thieno[2,3-*b*]pyridines with compounds containing aldehyde and carboxyl groups in the same molecule. In particular, in the case of 3-amino-(benzimidazol-2-yl)-4,6-diphenylthieno[2,3-*b*]pyridine (**1**) we have investigated the route of the reaction with *ortho*-formylbenzoic acid (**2**). It was found that, when the reaction was carried out in toluene in the presence of a catalytic amount of *p*-toluenesulfonic acid it gave not the 22π-electron heteroaromatic system **3** but rather the pentacyclic heterocycle **4** which contains conjugated thienopyridine and benzimidazole systems. Compound **4** is readily dehydrated in polyphosphoric acid to give the novel heterocyclic system **5**.

As shown by an AM1 quantum chemical-calculation of the geometry of compound **5** its pentacyclic framework consists of two planes intersecting at the $N_{(7)} - C_{(12B)}$ at an angle of 120° and this uniquely controls the optimal configuration of the sp^3-hybridized $C_{(12b)}$ atom in the molecule.

The remarkable simplicity of the mass spectra of compounds **4** and **5** was noted. The molecular ion (I = 5%) of compound **4** sequentially loses a molecule of H_2 (aromatization of the pyrimidine ring) and of CO_2 (decarboxylation)to give the stable cation radical [M-46] (I = 100%). Compound **5**, on the other hand, appears stable to electron impact and its mass spectrum has only two significant strong peaks for the molecule ion (I = 84%) and [M-28] ([M-CO]) (I = 100%).

IR spectra were taken on a Specord-M80 instrument as a suspension in vaseline oil and ^{1}H NMR spectra of a Bruker AM-300 instrument (300 MHz) using DMSO and with TMS as internal standard. Mass spectra were taken on a Varian CH-6 instrument (EI, 70 eV).

2-(2,4-Diphenyl-5,6-dihydrobenzo[4,5]imidazo[1,2-*c*]pyrido[3',2':4,5]thieno[2,3-*e*]pyrimidin-6-yl)-benzoic acid (4). Yield 78% with mp 220°C (decomp.) (from DMF). IR spectrum, ν, cm^{-1}: 1710 (COOH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 6.19 (1H, d, J_{CHNH} = 7.5, H-6); 7.02-7.23 (6H, m, 4 *meta*-H and 2 *para*-H phenyl substituents); 7.28-7.35 (4H, m, H-8,9,10,11); 7.37 (1H, d, J_{CHNH} = 7.5, H-5); 7.42-7.62 (4H, m, 4 *ortho*-H phenyl substituents); 7.68 (1H, m, H-4'); 7.77 (1H, s, H-3); 8.08 (1H, d, *J* = 8, H-3'); 8.22 (2H, m, H-5',6'): the protons of the COOH group exchange with solvent water protons and give a broad singlet signal at 3.3 ppm (in contrast to all of the other spectra in which this signal is very sharp). Mass spectrum, *m/z* (I_{rel}, %): 550 (5), 548 (15), 504 (100). Found, %: C 74.25; H 3.96; N 10.25. $C_{34}H_{22}N_4O_2S$. Calculated, %: C 74.16; H 4.08; N 10.17.

4,6-Diphenylisoindolo[1',2':2,3]pyrido[3'',2'':4',5']thieno[3',2':4,5]pyrimido[1,6-a]benzimidazol-8(12bH)-one (5). Yield 67% with mp 345 C (decomp.) (from DMF). IR spectrum, ν, cm^{-1}: 1670 (amide). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.15-7.25 (3H, m) and 7.40-7.50 (2H, m) – 4-C_6H_5 protons: 7.52-7.62 (3H, m) and 7.65-7.68 (2H, m) – 6-C_6H_5 protons; 7.28 (2H, m, H-14, H-16); 7.70 (1H, m, H-15); 7.75 (1H, m, H-17); 7.95 (1H, dd, *J* = 7.7, *J*' = 7.6, H-10); 8.22 (2H, m, H-11, H-12); 8.63 (1H, d, *J*' = 7.6, H-9). Mass spectrum, *m/z* (I_{rel}, %): 532 (84), 504 (100), 266 (12), 43 (12). Found, %: C 76.58; H 3.85; N 10.48. $C_{34}H_{20}N_4OS$. Calculated, %: C 76.67; H 3.78; N 10.52.

REFERENCES

1. E. A. Kaigorodova, L. D. Konyushkin, E. Yu. Kambulov, and G. D. Krapivin, *Khim. Geterotsikl. Soedin.*, 856 (1997). [*Chem. Heterocycl. Comp.*, **33**, 752 (1997)].
2. E. Yu. Kambulov, V. K. Vasilin, E. A. Kaigorodova, L. D. Konyushkin, and G. D. Krapivin, *Khim. Geterotsikl. Soedin.*, 287 (2003). [*Chem. Heterocycl. Comp.*, **39**, 255 (2003)].
3. E. A. Kaigorodova, A. A. Osipova, V. K Vasilin, L. D. Konyushkin, and G. D. Krapivin, *Izv. Vuz. Khim. i Khim. Tekhnol*, **47**, No. 2, 107 (2004).
4. E. A.–G. Bakhite, *J. Chin. Chem. Soc.*, **48**, 1175 (2001).
5. E. A. Bakhite, A. G. Al-Sehemi, and Y. Yamada, *J. Heterocycl. Chem.*, **42**, 1069 (2005).
6. Sh. M. Radwan, A. M. Kamal El-Dean, and E. A. Bakhite, *J. Chin. Chem. Soc.*, **52**, 303 (2005).