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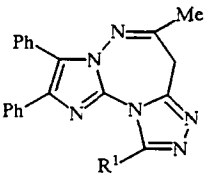
SYNTHESIS OF SUBSTITUTED IMIDAZO[1,2-*b*]-1,2,4-TRIAZOLO[4,3-*d*]-1,2,4-TRIAZEPINE AND 4H-IMIDAZO[1,2-*b*]-1,2,4-TRIAZINO[4,3-*d*]-1,2,4-TRIAZEPIN-7-ONE

V. P. Kruglenko, M. V. Povstyanoi, N. A. Klyuev, and V. A. Idzikovskii

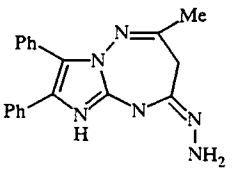
According to our results [1], 5H-2-methyl-4-hydrazino-7,8-diphenylimidazo[1,2-*b*]-1,2,4-triazepine (I) exists predominantly in the hydrazone form. A compound with such a structure has the possibility of reacting with nucleophiles at the amino group and $N_{(5)}$ with annelation to the triazepine unit of the bicycle I.

We first established that when the hydrazine I was boiled in formic acid (2 h) or in triethoxymethane, 2-methyl-9,10-diphenylimidazo[1,2-*b*]-1,2,4-triazolo-[4,3-*d*]-1,2,4-triazepine (II) was formed, while when equimolar amounts of I and cyanogen bromide were boiled in methanol (II), its 6-amino derivative III was formed.

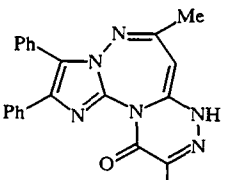
The previously unknown 4H-2,6-dimethyl-(IV) and 4H-2-methyl-6-(β-carboxyethyl)-9,10-diphenylimidazo-[1,2-*b*] 1,2,4-triazino[4,3-*d*]triazepin-7-ones (V) were produced by reaction of the hydrazine I with pyruvic or α-ketoglutaric acid (mole ratio 1:1.5) in boiling isopropanol (5 h).



II, III



I



IV, V

R^1 = H, NH_2, R^2 = Me, $(CH_2)_2COOH$

2-Methyl-9,10-diphenylimidazo[1,2-*b*]-1,2,4-triazolo[4,3-*d*]-1,2,4-triazepine (II). M.p. 179-180°C (propanol-2). ^1H NMR spectrum (DMSO-D_6): 2.57 (3H, s, 2-CH_3), 3.63 (2H, s, 3-CH_2), 7.5 ppm (11H, m H_{arom}). Mass spectrum, *m/z* (I_{rel}, %): 341 (25); M^+ 340 (100); $[M-HCN]^+$ 313 (8); $[(M-HCN)-HCN]^+$ 286 (6); $[(M-HCN)-N_2]^+$ 285 (3); $[(M-HCN)-N_2-CH_3CN]^+$ 244 (5); $[PhCCNPh]^+$ 195 (50); $[PhCCPh]^+$ 178 (5); $[PhCN]^+$ 103 (25). Yield 55-70%.

2-Methyl-6-amino-9,10-diphenylimidazo[1,2-*b*]-1,2,4-triazolo[4,3-*d*]-1,2,4-triazepine(III). M.p.271-272°C(DMF). ^1H NMR spectrum (DMSO-D_6): 2.22 (3H, s, 2-CH_3), 3.33 (2H, s, 3-CH_2), 7.4 (10H, m, H_{arom}), 8.68 ppm (2H, s, 6-NH_2). Mass spectrum, *m/z* (I_{rel}, %): M^+ 355 (100), $[M-NH_2]^+$ 339 (47), $[(M-NH_2)-CH_3CN]^+$ 298 (20), $[PhCCPh]^+$ 178 (14); $[PhCN]^+$ 103 (13). Yield 67%.

4H-2,6-Dimethyl-10,11-diphenylimidazo[1,2-*b*]-1,2,4-triazino[4,3-*d*]-1,2,4-triazepin-7-one(IV). M.p.315°C(DMF-H_2O). ^1H NMR spectrum (DMSO-D_6): 2.27 (3H, s, 6-CH_3), 2.33 (3H, s, 2-CH_3), 6.02 (1H, s, 3-CH_2), 7.35 (10H, m, H_{arom}), 7.82 ppm (1H, s, 4-NH). Mass spectrum, *m/z* (I_{rel}, %): M^+ 382 (100), $[M-NCCH_3]^+$ 341 (14), $[M-CO(CH_3)CN]^+$ 313 (13), $[(M-CH_3CN)-CH_3CNNH]^+$ 285 (28), $[PhCCPh]^+$ 178 (44); $[PhCN]^+$ 103 (50). Yield 74%.

4H-2-Methyl-6-(β-carboxyethyl)-10,11-diphenylimidazo[1,2-*b*]-1,2,4-triazino[4,3-*d*]-1,2,4-triazpin-7-one(V). M.p. 284-285°C (DMF-H_2O). Yield 68%.

Kherson Industrial Institute, Kherson 325008 and A. N. Severtsov Institute for the Problems of Ecology and Evolution, Russian Academy of Sciences, Moscow 117071. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1420-1421, October, 1997. Original article submitted May 30, 1997.

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Results of elemental analyses for compounds II-V corresponded with calculated values.

REFERENCE

1. V. P. Kruglenko, V. A. Idzikovskii, N. A. Klyuev, and M. V. Povstyanoi, Khim. Geterotsikl. Soedin., No. 3, 386 (1988).