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2-(1-ADAMANTYL)-7-METHYLIMIDAZO-[1,2-*a*]PYRIDINE AND ITS REACTIONS WITH N-BROMOSUCCINIMIDE

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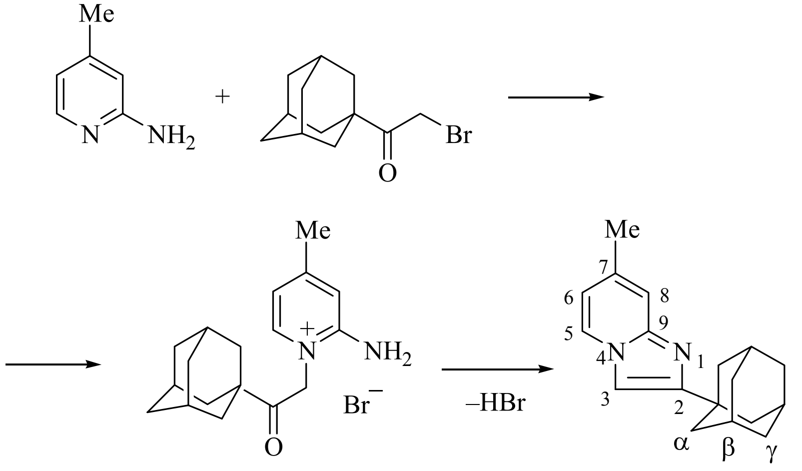
In reaction with equimolar amount or twice the amount of N-bromosuccinimide 2-(1-adamantyl)-7-methylimidazo[1,2-a]pyridine, obtained from 2-amino-4-methylpyridine and bromomethyl 1-adamantyl ketone, is converted into 2-(1-adamantyl)-3-bromo-7-methylimidazo[1,2-a]pyridine. With three times the amount of N-bromosuccinimide it gives 2-(1-adamantyl)-3-bromo-7-formylimidazo[1,2-a]pyridine.

Keywords: 2-(1-adamantyl)-7-methylimidazo[1,2-*a*]pyridine, N-bromosuccinimide, bromination.

Investigations of the reaction of 2-(1-adamantyl)-7-methylimidazo[1,2-*a*]pyridine (**1**), which we obtained in [1], with N-bromosuccinimide (NBS) showed that its reaction with one or two moles of N-bromosuccinimide led, without affecting the methyl group, to the introduction of a bromine atom only at position 3 of the imidazole ring, i.e., to compound **2**. In reaction with three times the amount of N-bromosuccinimide in the presence of trace quantities of water 2-(1-adamantyl)-3-bromo-7-formylimidazo-[1,2-*a*]pyridine (**3**) is formed. We suppose that compound **3** is the product from hydrolysis of 2-(1-adamantyl)-3-bromo-7-dibromomethylimidazo[1,2-*a*]pyridine (**a**) formed during the reaction.



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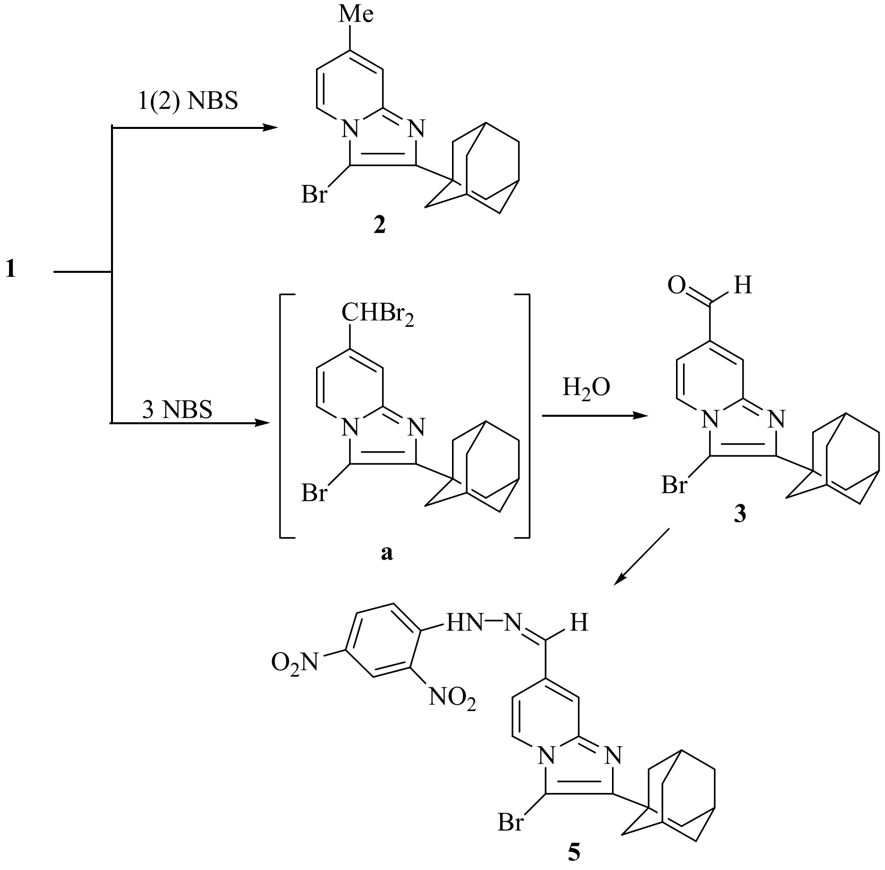

Compound **3** exhibits typical chemical properties of carbonyl compounds. Thus, it forms hydrazone **5** with 2,4-dinitrophenylhydrazine.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a JNM-FX900 instrument (90 MHz) with TMS as internal standard.

2-(1-Adamantyl)-7-methylimidazo[1,2-*a*]pyridine (1). Solution of pyridinium bromide **4** (10 mmol) in glacial acetic acid was boiled for 1 h. The reaction mixture was then treated with water, the precipitate was separated, then kept in 40% solution of sodium hydroxide for 1 h. ^{1}H NMR spectrum (deuterochloroform), δ, ppm (*J*, Hz): 1.80 (6H, s, α-H); 2.02 (6H, s, β-H); 2.08 (3H, s, γ-H); 2.35 (3H, s, CH_3); 6.54 (1H, d, J_{65} = 7.2, H-6); 7.20 (1H, s, H-8); 7.32 (1H, s, H-3); 7.90 (1H, d, J_{56} = 7.2, H-5). Found, %: N 10.41. $C_{18}H_{22}N_2$. Calculated, %: N 10.52.

2-(1-Adamantyl)-3-bromo-7-methylimidazo[1,2-*a*]pyridine (2). Mixture of equimolar amounts (3.8 mmol) of compound **1** and N-bromosuccinimide, catalytic amounts of benzoyl peroxide, and carbon tetrachloride (30 ml) was boiled until N-bromosuccinimide precipitate had completely disappeared. Succinimide was separated, and the filtrate was evaporated under vacuum. The residue was treated with hexane, and the precipitate was separated. Yield 51%; mp 161-163°C (aqueous ethanol). ^{1}H NMR spectrum (DMSO-d$_6$), δ, ppm (*J*, Hz): 1.80 (6H, s, α-H); 2.12 (3H, s, γ-H); 2.20 (6H, s, β-H); 2.44 (3H, s, CH_3); 6.90 (1H, d, J_{65} = 7.2, H-6); 7.33 (1H, s, H-8); 8.18 (1H, d, J_{56} = 7.2, H-5). Found, %: Br 22.95. $C_{18}H_{21}BrN_2$. Calculated, %: Br 23.14.

2-(1-Adamantyl)-3-bromo-7-formylimidazo[1,2-*a*]pyridine (3). This compound was obtained similarly to compound **2** from compound **1** (3 mmol) and N-bromosuccinimide (9 mmol) with the addition of one drop of water. Yield 57%; mp 129-131°C (aqueous ethanol). ^{1}H NMR spectrum (DMSO-d$_6$), δ, ppm (J, Hz): 1.80 (6H, s, α-H); 2.10 (3H, γ-H); 2.17 (6H, s, β-H); 7.40 (1H, d, J_{65} = 7.2, J_{68} = 1.5, H-6); 8.24 (1H, s, H-8); 8.40 (1H, d, J_{56} = 7.2, H-5); 10.01 (1H, s, CHO). Found, %: Br 22.00. $C_{18}H_{19}BrN_2O$. Calculated, %: Br 22.24.

N-[2-(1-Adamantyl)-3-bromoimidazo[1,2-*a*]-7-pyridylmethylene]-N-(2,4-dinitrophenyl)hydrazine (5). Mixture of solutions of equimolar amounts (3 mmol) of compound **3** and 2,4-dinitrophenylhydrazine in dioxane was boiled for 1 h and treated with a small amount of water. The precipitate that separated after cooling was separated. Yield 40%; mp 273-275°C. ^{1}H NMR spectrum (DMSO-d$_6$), δ, ppm (J, Hz): 1.78 (6H, s, α-H); 2.10 (3H, s, γ-H); 2.18 (6H, s, β-H); 7.68-8.85 (7H, m, ArH, CH=N); 11.70 (1H, s, NH). Found, %: Br 14.70. $C_{24}H_{23}BrN_6O_4$. Calculated, %: Br 14.81.

1-[3-(1-Adamantyl)-2-oxoethyl]-2-amino-3-methylpyridinium Bromide (4). To boiling solution of 2-amino-4-methylpyridine (3.2 mmol) in ethyl acetate (10 ml) we added with stirring a solution of bromomethyl 1-adamantyl ketone (3.2 mmol) in ethyl acetate (3 ml). The reaction mass was boiled for 1 h, and the precipitate was separated. Yield 75%; mp 248-250°C (ethanol–ether). Found, %: Br 22.54. $C_{17}H_{23}BrN_2O$. Calculated, %: Br 22.75.

REFERENCES

1. R. I. Yurchenko, N. N. Svarovskaya, A. D. Ponomarenko, and A. A. Tolmachev, *Khim. Geterotsikl. Soedin.*, 852 (2001).