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NEW OXIDATION–REDUCTION TRANSFORMATION OF DERIVATIVES OF 1,10b-DIHYDRO-1H-PYRAZOLO[1,5-*c*]-1,3-BENZOXAZINE AND 7,12-DIHYDRO-6H-[1]BENZOPYRANO[4,3-*d*]-1,2,4-TRIAZOLO[1,5-*a*]PYRIMIDINE

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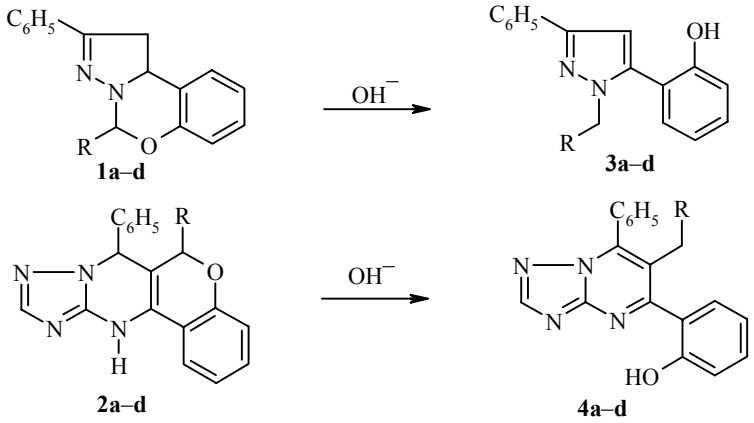
We have found that the action of a suspension of KOH in DMSO–DMF on 5-aryl-1,10b-dihydro-1H-pyrazolo[1,5-*c*]benzo[*e*]-1,3-oxazines **1a-d** and 6-aryl-7-phenyl-3-aryl-7,12-dihydro-6H-[1]benzopyrano-[4,3-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidines **2a-d** leads to reductive opening of the pyran or oxazine ring and concurrent dehydrogenation of azaheterocyclic fragment.



1-4 a R = C_6H_5, **b** R = *p*-$CH_3OC_6H_4$, **c** R = *p*-ClC_6H_4; **1, 3 d** R= *p*-$O_2NC_6H_4$; **2, 4 d** R = H

This reaction leads to the formation of 2-hydroxyaryl derivatives of pyrazoles **3a-d** and 1,2,4-triazolo[1,5-*a*]pyrimidines **4a-d**, respectively.

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A solution of 3.1 mmol **1** [1] or **2** [2] in a mixture of 5 ml DMF, 1 ml DMSO, and 0.1 g KOH was heated at reflux until the red color disappeared (1-1.5 h). The reaction mixture was filtered. The filtrate was washed with water and neutralized with dilute hydrochloric acid to pH 7. The product was filtered off and recrystallized from octane.

1-Benzyl-5-(2-hydroxyphenyl)-3-phenylpyrazole (3a) was obtained in 86% yield; mp 175-178°C. ^{1}H NMR spectrum at 200 MHz (DMSO-d_6), δ, ppm: 9.93 (1H, s, OH); 6.73 (1H, s, 4-H); 6.8-7.9 (14H, m, H_{Ar}); 5.26 (2H, s, CH_2). Found, %: C 80.3; H 5.7; N 8.5. $C_{22}H_{18}N_2O$. Calculated, %: C 81.0; H 5.6; N 8.6.

5-(2-Hydroxyphenyl)-1-(4-methoxybenzyl)-3-phenylpyrazole (3b) was obtained in 69% yield; mp 149-151°C. ^{1}H NMR spectrum at 200 MHz (DMSO-d_6), δ, ppm: 9.99 (1H, s, OH); 6.72 (1H, s, 4-H); 6.7-7.5 (13H, m, H_{Ar}); 5.17 (2H, s, CH_2); 3.67 (3H, s, CH_3O). Found, %: C 77.7; H 5.7; N 8.2. $C_{23}H_{20}N_2O_2$. Calculated, %: C 77.5; H 5.7; N 7.9.

5-(2-Hydroxyphenyl)-1-(4-chlorobenzyl)-3-phenylpyrazole (3c) was obtained in 91% yield; mp 159-162°C. ^{1}H NMR spectrum at 200 MHz (DMSO-d_6), δ, ppm: 10.02 (1H, s, OH); 6.77 (1H, s, 4-H); 6.8-7.9 (13H, m, H_{Ar}); 5.25 (2H, s, CH_2). Found, %: C 73.0; H 4.7; Cl 10.0. $C_{22}H_{17}ClN_2O$. Calculated, %: C 73.2; H 4.8; N 7.8.

5-(2-Hydroxyphenyl)-1-(4-nitrobenzyl)-3-phenylpyrazole (3d) was obtained in 85% yield; mp 183-185°C. ^{1}H NMR spectrum at 200 MHz (DMSO-d_6), δ, ppm: 9.95 (1H, s, OH); 6.79 (1H, s, 4-H); 6.9-7.9 (13H, m, H_{Ar}); 5.4 (2H, s, CH_2). Found, %: C 70.5; H 4.9; N 11.5. $C_{22}H_{17}N_3O_3$. Calculated, %: C 71.2; H 4.6; N 11.3.

6-Benzyl-5-(2-hydroxyphenyl)-7-phenyltriazolo[1,5-*a*]pyrimidine (4a) was obtained in 70% yield; mp 217-219°C. ^{1}H NMR spectrum at 200 MHz (DMSO-d_6), δ, ppm: 9.84 (1H, s, OH); 8.56 (1H, s, 2-H); 6.5-7.7 (14H, m, H_{Ar}); 3.93 (2H, s, CH_2). Found, %: C 76.5; H 5.0; N 14.6. $C_{24}H_{18}N_4O$. Calculated, %: C 76.2; H 4.8; N 14.8.

5-(2-Hydroxyphenyl)-6-(4-methoxybenzyl)-7-phenyltriazolo[1,5-*a*]pyrimidine (4b) was obtained in 77% yield; mp 233-236°C. ^{1}H NMR spectrum at 200 MHz (DMSO-d_6), δ, ppm: 9.84 (1H, s, OH); 8.54 (1H, s, 2-H); 6.6-7.6 (13H, m, H_{Ar}); 3.93 (2H, s, CH_2); 3.81 (3H, s, OCH_3). Found, %: C 73.3; H 5.2; N 13.9. $C_{25}H_{20}N_4O_2$. Calculated, %: C 73.5; H 4.9; N 13.7.

5-(2-Hydroxyphenyl)-6-(4-chlorobenzyl)-7-phenyltriazolo[1,5-*a*]pyrimidine (4c) was obtained in 70% yield; mp 262-265°C. ^{1}H NMR spectrum at 200 MHz (DMSO-d_6), δ, ppm: 9.86 (1H, s, OH); 8.54 (1H, s, 2-H); 6.6-7.7 (13H, m, H_{Ar}); 3.89 (2H, s, CH_2). Found, %: C 70.5; H 4.0; N 7.7. $C_{24}H_{17}ClN_4O$. Calculated, %: C 73.2; H 4.8; Cl 9.8; N 7.8.

5-(2-Hydroxyphenyl)-6-methyl-7-phenyltriazolo[1,5-*a*]pyrimidine (4d) was obtained in 55% yield; mp 173-175°C. ^{1}H NMR spectrum at 200 MHz (DMSO-d_6), δ, ppm: 9.76 (1H, s, OH); 8.98 (1H, s, 2-H); 6.9-7.7 (9H, m, H_{Ar}); 2.05 (3H, s, CH_3). Found, %: C 70.9; H 4.7; N 18.8. $C_{18}H_{14}N_4O$. Calculated, %: C 71.5; H 4.7; N 18.5.

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