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SHORT COMMUNICATIONS

3*H*-Naphtho[2,3-e]-1,2,4-triazepines

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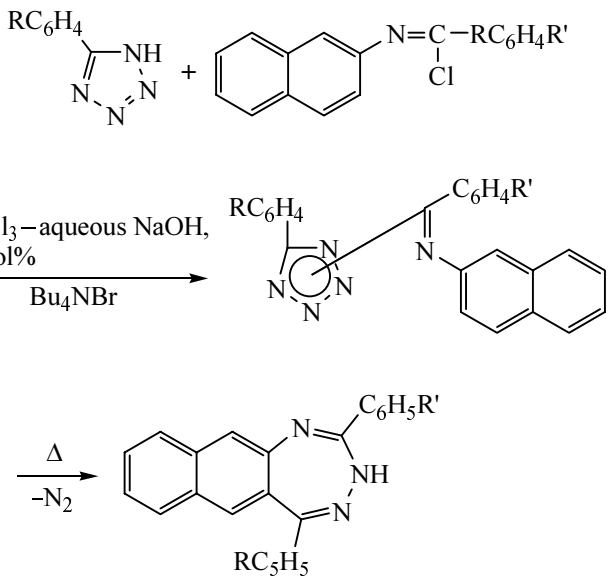
The thermal transformation of N-imidoyltetrazoles generated from 5-substituted tetrazoles and N-aryl(hetaryl)benzimidoyl chlorides may be regarded as one of the most promising ways of building up complex heterocyclic systems including one or several triazepine rings [1-8].

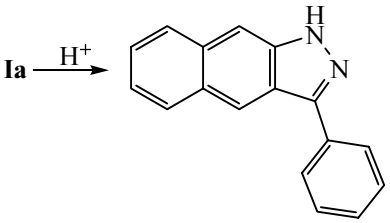
In extension of the study on the thermal transformation of disubstituted tetrazoles we found that the heating of N-imidoyltetrazoles prepared from 5-aryltetrazoles and N-(2-naphthyl)benzimidoyl chlorides under conditions of the phase-transfer catalysis gave rise to previously unknown 3*H*-naphtho[2,3-*e*]-1,2,4-triazepines. It should be noted that the reaction occurred 110–115°C and was accompanied with tarring resulting in decreased yield of the reaction product.



Ia–e

R = R' = H (**a**); R = H (**b, c**), R' = Me (**b**), 4-NO2 (**c**); R = 4-MeO, R' = H(**d**); R = 4-Cl, R' = H (**e**).

Unlike 3*H*-1,3,4-benzo- and 3*H*-pyrido[6,7-*e*]-1,2,4-triazepines that are readily hydrolyzed in water solutions of mineral acids to the corresponding aminobenzophenones [2, 8], 3*H*-naphtho-[2,3-*e*]-1,2.4-triazepines under the same conditions undergo more complicated transformations resulting in 3-arylbenzo-[*f*]indazoles.



2,5-Diphenyl-3*H*-naphtho-[2,3-*e*]-1,2,4-triazepine (Ia). To a mixture of 0.01 mol 5-phenyltetrazole, 0.001 mol of tetrabutylammonium bromide, 10 ml of 10% water solution of NaOH, and 30 ml of chloroform at 20°C while stirring was added within 30 min 0.01 mol of *N*-(2-naphthyl)benzimidoyl chloride in 10 ml of chloroform. The reaction mixture was stirred for 4 h at 20°C, the phases were separated, the organic layer was washed with 1% aqueous NaOH, with water (2×10 ml), and dried with magnesium sulfate. The chloroform was removed in a vacuum, to the solid residue 20 ml of toluene was added, the mixture was heated for 2 h at 110°C, cooled, the precipitate was filtered off and dried in air. Yield 0.714 g(36%), mp 300–302°C (from DMF). IR spectrum, Cm^{-1}: 920, 940, 949, 959, 977, 993, 1026, 1075, 1101, 1144,

1154, 1170, 1179, 1210, 1227, 1256, 1287, 1303, 1313, 1339, 1378, 1395, 1418, 1438, 1445, 1449, 1473, 1495, 1508, 1560, 1578, 1600, 1624, 2853, 2925, 3023, 3049, 3080, 3313. ^{1}H NMR spectrum, δ, ppm: 7.05– 8.08 m ($16H_{arom}$), 8.50 s (1H, NH). Found, %: C 83.05; H 4.98; N 12.07. $C_{24}H_{17}N_3$. Calculated, %: C 83.00; H 4.90; N 12.10.

Likewise were prepared and purified compounds **Ib–e**.

2-(4-Tolyl)-5-phenyl-3*H*-naphtho[2,3-*e*]-1,2,4-triazepine (Ib). Yield 0.235 g (17%), mp 283–286°C (from toluene). IR spectrum, cm^{-1}: 921, 936, 960, 997, 1028, 1075, 1097, 1155, 1187, 1213, 1228, 1254, 1301, 1313, 1378, 1420, 1439, 1474, 1511, 1556, 1577, 1602, 1624, 2854, 2921, 2954, 3028, 3057, 3317. ^{1}H NMR spectrum, δ, ppm: 2.36 s (3H, CH_3), 7.05–8.07 m ($15H_{arom}$), 8.45 s (1H, NH). Found, %: C 83.25; H 5.29; N 11.67. $C_{25}H_{19}N_3$. Calculated, %: C 83.10; H 5.26; N 11.64.

2-(4-Nitrophenyl)-5-phenyl-3*H*-naphtho[2,3-*e*]-1,2,4-triazepine (Ic). Yield 0.635 g (27%), mp 294–296°C (from toluene). IR spectrum, cm^{-1}: 922, 937, 959, 993, 1014, 1030, 1076, 1096, 1211, 1222, 1253, 1286, 1298, 1318, 1344, 1349, 1372, 1418, 1438, 1506, 1515, 1524, 1549, 1567, 1581, 1599, 1625, 2853, 2922, 3075, 3319. ^{1}H NMR spectrum, δ, ppm: 7.06–8.36 m ($15H_{arom}$), 8.73 s (1H, NH). Found, %: C 73.45; H 4.09; N 14.37. $C_{24}H_{16}N_4O_2$. Calculated, %: C 73.47; H 4.08; N 14.29.

5-(4-Methoxyphenyl)-2-phenyl-3*H*-naphtho[2,3-*e*]-1,2,4-triazepine (Id). Yield 0.651 g (31%), mp 296–298°C (from toluene). IR spectrum, cm^{-1}: 918, 935, 959, 1034, 1095, 1167, 1174, 1222, 1253, 1300, 1312, 1377, 1416, 1440, 1447, 1494, 1508, 1548, 1579, 1606, 1625, 2834, 2901, 2931, 2956, 3006, 3058, 3319. ^{1}H NMR spectrum, δ, ppm: 3.75 s (3H, CH_3), 6.85–8.07 m ($15H_{arom}$), 8.46 s (1H, NH). Found, %: C 79.66; H 5.16; N 11.14. $C_{25}H_{19}N_3O$. Calculated, %: C 79.58; H 5.04; N 11.14.

2-Phenyl-5-(4-chlorophenyl)-3*H*-naphtho[2,3-*e*]-1,2,4-triazepine (Ie). Yield 0.597 g (28%), mp 299–301°C (from toluene). IR spectrum, cm^{-1}: 937, 959, 1013, 1078, 1094, 1154, 1225, 1258, 1285, 1303, 1377, 1449, 1478, 1484, 1548, 1562, 1573, 1593, 1622, 2853, 2922, 3067, 3315. ^{1}H NMR spectrum, δ, ppm: 7.04–8.09 m ($15H_{arom}$), 8.56 s (1H, NH). Found, %: C 75.59; H 4.23; N 11.04. $C_{24}H_{16}N_3Cl$. Calculated, %: C 75.49; H 4.19; N 11.01.

Acid hydrolysis of 2,5-diphenyl-3*H*-naphtho-[2,3-*e*]-1,2,4-triazepine (Ia). A mixture of 5 mmol of triazepine **Ia** and 30 ml of concn. HCl was heated for 5 h at 100°C, then cooled to 20°C, the separated precipitate was filtered off and stirred with 50 ml of 10% water solution of K_2CO_3 for 30 min at 50°C, then cooled to 20°C, the separated precipitate was filtered off and dried in air. We obtained 1.044 g (86%) of 3-phenylbenzo-[*f*]indazole, mp 195–196°C (from ethanol) [9]. IR spectrum, cm^{-1}: 921, 971, 1001, 1029, 1049, 1071, 1089, 1130, 1159, 1177, 1204, 1259, 1270, 1286, 1325, 1367, 1418, 1436, 1445, 1451, 1468, 1485, 1510, 1544, 1601, 1621, 2754, 2849, 2913, 2944, 2992, 3042, 3117, 3139, 3174, 3193, 3197. ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 7.42–8.20 m ($11H_{arom}$), 12.76 s (1H, NH).

IR spectra were recorded on a spectrometer Shimadzu FTIR-8400S from KBr pellets, ^{1}H NMR spectra were registered on a Bruker AC-200 instrument in DMSO-d_6. The purity and homogeneity of compounds obtained was checked by TLC on Silufol UV-254 plates, eluent chloroform–petroleum ether–ethyl acetate, 10:15:3.

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