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SHORT COMMUNICATIONS

Thermal Transformation of 5-Substituted 2-Trityltetrazoles[*]

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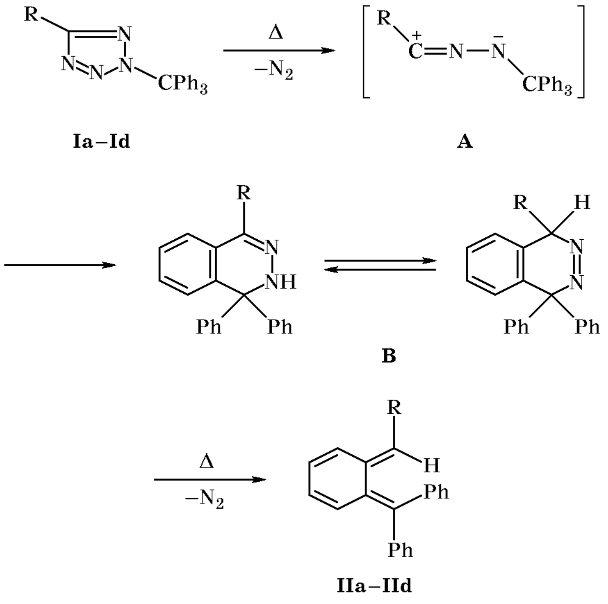
Thermolysis of 2,5-disubstituted tetrazoles is a classical example of generation of 1,3-dipoles. Such intermediates are readily involved in 1,3-dipolar cycloaddition reactions and are capable of undergoing 1,5- and 1,7-electrocyclizations. They are widely used in the synthesis of various heterocyclic compounds [1–6]. In continuation of our studies on thermal transformations of 2,5-disubstituted tetrazoles [7], we examined thermolysis of 5-substituted 2-trityltetrazoles in dodecane at 170–180°C and found that the process follows a mechanism which differs essentially from the generally accepted mechanism of such reactions. The thermolysis products were the corresponding *o*-quinodimethanes which were obtained in 35–68%. A possible reaction scheme is shown below:



R = Me (**a**), 4-MeOC$_6$H$_4$ (**b**), Ph (**c**), 4-ClC$_6$H$_4$ (**d**).

In the first stage, cleavage of the tetrazole ring and elimination of nitrogen molecule gives 1,3-dipole **A** which undergoes 1,6-electrocyclization with formation of 1,4-dihydrophthalazine **B**. *o*-Quinodimethane **II** is formed in the final stage as a result of thermal fragmentation of 1,4-dihydrophthalazine. This reaction is well known and is frequently used for generation of *o*-quinodimethanes having various structures [8, 9]. Thus the thermolysis of 5-substituted 2-trityltetrazoles can be regarded as a method for preparation of stable *o*-quinodimethanes.

5-Phenyl-2-trityltetrazole (Ic). A mixture of 2.5 mmol of 5-phenyltetrazole, 0.2 mmol of tetrabutylammonium bromide, 10 ml of 10% aqueous sodium hydroxide, and 10 ml of chloroform was stirred for 15 min at 20°C. A solution of 3 mmol of chlorotriphenylmethane in 20 ml of chloroform was added, the mixture was stirred for 2 h at 20°C, and the organic phase was separated, washed with 5 ml of 10% aqueous sodium hydroxide and water (2 × 10 ml), dried over sodium sulfate, and evaporated to dryness. Yield 0.9 g (93%), mp 155–156°C (from butyl acetate); published data [10]: mp 158–160°C. IR spectrum, ν, cm^{-1}: 930, 1005, 1030, 1050, 1160, 1195, 1285, 1330, 1380, 1455, 1480, 1500, 1605, 2870, 2930, 3050, 3075. ^{1}H NMR spectrum, δ, ppm: 7.08–7.48 m (18H, H$_{arom}$), 8.03 m (2H, H$_{arom}$). Found, %: C 80.32; H 5.12; N 14.52. $C_{26}H_{20}N_4$. Calculated, %: C 80.41; H 5.15; N 14.43.

Tetrazoles **Ia**, **Ib**, and **Id** were synthesized in a similar way.

5-Methyl-2-trityltetrazole (Ia). Yield 60%, mp 178°C [11] (from ethyl acetate). IR spectrum, ν, cm^{-1}: 890, 910, 930, 1010, 1030, 1040, 1090, 1170, 1190, 1290, 1330, 1360, 1390, 1450, 1500, 1520, 1600, 2970, 3040, 3070. ^{1}H NMR spectrum, δ, ppm: 3.1 s (3H, CH$_3$), 6.9–7.2 m (6H, H$_{arom}$), 7.3–7.45 m (9H, H$_{arom}$). Found, %: C 77.22; H 5.60; N 16.91. $C_{21}H_{18}N_4$. Calculated, %: C 77.30; H 5.52; N 17.18.

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5-(4-Methoxyphenyl)-2-trityltetrazole (Ib). Yield 55%, mp 186°C (from ethyl acetate). IR spectrum, ν, cm^{-1}: 910, 940, 1000, 1040, 1070, 1100, 1150, 1170, 1190, 1230, 1280, 1300, 1330, 1390, 1450, 1500, 1580, 1600, 2900, 2950, 2990, 3050. ^{1}H NMR spectrum, δ, ppm: 3.82 s (3H, CH_3O), 6.95–7.4 m (17H, H_{arom}), 8.0 m (2H, H_{arom}). Found, %: C 77.56; H 5.48; N 13.44. $C_{27}H_{22}N_4O$. Calculated, %: C 77.51; H 5.26; N 13.40.

5-(4-Chlorophenyl)-2-trityltetrazole (Id). Yield 51%, mp 187°C (from ethyl acetate). IR spectrum, ν, cm^{-1}: 910, 940, 1010, 1020, 1040, 1100, 1160, 1200, 1270, 1330, 1420, 1450, 1500, 1610, 2860, 2940, 3030, 3070. ^{1}H NMR spectrum, δ, ppm: 7.1–7.5 m (15H, H_{arom}), 8.2 m (4H, H_{arom}). Found, %: C 80.31; H 5.20; N 14.49. $C_{26}H_{19}N_4$. Calculated, %: C 80.62; H 4.91; N 14.47.

α,α′,α′-Triphenyl-*o*-quinodimethane (IIc). A mixture of 2.6 mmol of 5-phenyl-2-trityltetrazole and 10 ml of dodecane was heated for 3 h at 170–180°C and evaporated to dryness, and the solid tarry residue was treated with petroleum ether (3 × 10 ml). Yield 0.59 g (68%); yellow substance, mp 107–108°C (from 2-propanol). IR spectrum, ν, cm^{-1}: 755, 859, 907, 1043, 1069, 1352, 1440, 1490, 1559, 1600, 1636, 3013. UV spectrum (ethanol), λ_{max}, nm (log ε): 240.58 (4.18), 268.85 (4.02), 324.28 (3.76). ^{1}H NMR spectrum, δ, ppm: 6.15 m (1H, CH), 6.42–7.42 m (19H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 125.7, 125.9, 126.1, 126.2, 126.5, 126.8, 127.2, 127.3, 127.5, 127.9, 128.0, 128.7, 129.0, 129.3, 130.1. Found, %: C 94.10; H 5.91. M^+ 332. $C_{26}H_{20}$. Calculated, %: C 93.97; H 6.03. *M* 332.

o-Quinodimethanes **IIa**, **IIb**, and **IId** were synthesized in a similar way.

α-Methyl-α′,α′-diphenyl-*o*-quinodimethane (IIa). Yield 35%, mp 115–116°C (from 2-propanol). IR spectrum, ν, cm^{-1}: 700, 760, 780, 800, 850, 930, 980, 1030, 1080, 1450, 1500, 1610, 2860, 2930, 3030. ^{1}H NMR spectrum, δ, ppm: 1.7 s (3H, CH_3), 5.8–6.5 m (1H, CH, and 4H, H_{arom}), 7.0–7.4 m (10H, H_{arom}). Found, %: C 93.30; H 6.78. M^+ 270. $C_{21}H_{18}$. Calculated, %: C 93.33; H 6.67. *M* 270.

α-(4-Methoxyphenyl)-α′,α′-diphenyl-*o*-quinodimethane (IIb). Yield 45%, mp 133°C (from 2-propanol). IR spectrum, ν, cm^{-1}: 830, 870, 900, 1020, 1070, 1100, 1360, 1410, 1460, 1490, 1600, 1640, 3040, 3080. ^{1}H NMR spectrum, δ, ppm: 3.63 s (3H, CH_3O), 6.10 m (1H, CH), 6.20–7.40 m (18H, H_{arom}). Found, %: C 89.75; H 6.20. $C_{27}H_{22}O$. Calculated, %: C 89.50; H 6.08.

α-(4-Chlorophenyl)-α′,α′-diphenyl-*o*-quinodimethane (IId). Yield 35%, mp 127°C (from 2-propanol). IR spectrum, ν, cm^{-1}: 830, 870, 900, 1010, 1080, 1100, 1360, 1410, 1495, 1610, 1650, 3040, 3080. ^{1}H NMR spectrum, δ, ppm: 6.15 m (1H, CH), 6.25–7.40 m (18H, H_{arom}). Found, %: C 84.95; H 5.15. M^+ 367. $C_{26}H_{19}Cl$. Calculated, %: C 85.13; H 5.18. *M* 366.5.

The IR spectra of compounds **Ia**–**Id**, **IIa**, **IIb**, and **IId** were measured on a UR-20 spectrometer in KBr, and the IR spectrum of **IIc** was obtained on a Perkin–Elmer Spectrum-1000 instrument. The electron spectrum of **IIc** was recorded on a Perkin–Elmer Lambda 40 spectrophotometer. The mass spectra (70 eV) were run on an MKh-1321 instrument. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-200 spectrometer in $CDCl_3$ (**IIc**, **IId**) and DMSO-d_6 (**Ia**–**Id**, **IIa**, **IIb**).

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