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SHORT COMMUNICATIONS

Tritylation of Tetrazole and 5-Substituted Tetrazoles with Triphenylmethanol

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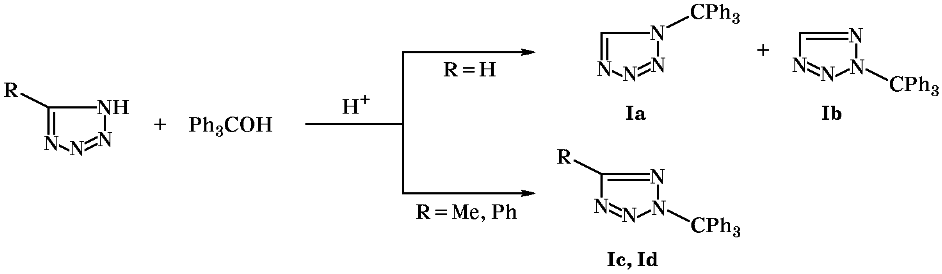
In the recent years, protection of N–H bonds in nitrogen-containing heterocycles by introduction of a triphenylmethyl (trityl) group has received increasing application. For this purpose, chlorotriphenylmethane or its functional derivatives are generally used, and the reaction is carried out in anhydrous solvents and in an inert atmosphere or, as recently proposed [1], under conditions of phase-transfer catalysis.

In continuation of our studies on alkylation of *N*-unsubstituted tetrazoles with alcohols [2] we now demonstrate the possibility of using triphenylmethanol as a more accessible and cheaper tritylating agent for tetrazole, 5-methyltetrazole, and 5-phenyltetrazole. The reaction smoothly proceeds in benzene or CH_2Cl_2 in the presence of an acid and with simultaneous removal of water as an azeotropic mixture with the corresponding solvent. From unsubstituted tetrazole, a mixture of two regioisomeric trityl derivatives **Ia** and **Ib** is formed. 5-Methyltetrazole and 5-phenyltetrazole are converted into the corresponding 2-trityltetrazoles **Ic** and **Id**. The ratio of isomers **Ia** and **Ib** was estimated at ~1 : 6 by ^{1}H NMR spectroscopy, taking into account that the 5-H signal of 1-substituted tetrazoles appears in a weaker field than the respective signal of the 2-substituted isomer [3]. Analysis of the IR spectra of the isomer mixture and the major isomer (which was isolated in the pure state) also indicates that the tritylation of tetrazole occurs mainly at N^2.

The structure of 2-trityl-5-methyl- and 2-trityl-5-phenyltetrazoles **Ic** and **Id** was confirmed by comparing their properties with those reported in [4, 5].

1- and 2-Trityltetrazoles Ia and Ib. A mixture of 3.5 g (0.05 mol) of tetrazole, 13.8 g (0.053 mol) of triphenylmethanol, and 2 drops of concentrated sulfuric acid in 50 ml of benzene was refluxed for 3 h with simultaneous distillation of water–benzene azeotrope. The mixture was cooled, and the precipitate was filtered off, thoroughly washed with ether and water, and dried under reduced pressure at 80°C. We isolated 12 g of a colorless amorphous powder with mp 204–205°C (decomp.), which was a mixture of tetrazoles **Ia** and **Ib** at a ratio of ~1 : 6. From the filtrate, an additional amount of isomer mixture **Ia**/**Ib** (~1 : 1), 1 g, was isolated; mp 199–203°C. Overall yield 86%. IR spectrum, ν, cm^{-1}: 638, 679, 702, 751, 767, 852, 866, 904, 967, 1000, 1022, 1034, 1095, 1130, 1170, 1188, 1263, 1323, 1374, 1444, 1491, 1595,



R = Me, (**c**) Ph (**d**).

3030, 3063, 3156. ^{1}H NMR spectrum, δ, ppm: 6.93–7.48 m (15H, H_{arom}), 8.48 s (0.85H, 5-H), 8.59 s (0.15H, 5-H).

2-Trityltetrazole. mp 206–207°C (from toluene); published data [6]: mp 217–219°C. The IR spectrum was identical to that given above. ^{1}H NMR spectrum, δ, ppm: 6.93–7.48 m (15H, H_{arom}), 8.48 s (1H, 5-H).

Tetrazoles **Ic** and **Id** were synthesized in a similar way.

5-Methyl-2-trityltetrazole (Ic). Yield 76%, mp 178–181°C (from toluene) [4]. IR spectrum, ν, cm^{-1}: 639, 669, 698, 750, 764, 889, 903, 929, 1002, 1025, 1085, 1155, 1184, 1285, 1323, 1356, 1386, 1445, 1494, 1508, 1595, 3045, 3058. ^{1}H NMR spectrum, δ, ppm: 2.52 s (3H, CH_3), 6.98–7.42 m (15H, H_{arom}).

5-Phenyl-2-trityltetrazole (Id). Yield 88%, mp 157–159°C (from toluene) [5]. IR spectrum, ν, cm^{-1}: 635, 673, 698, 730, 748, 764, 788, 876, 906, 924, 999, 1026, 1072, 1155, 1189, 1279, 1325, 1371, 1449, 1467, 1492, 1528, 1597, 3047, 3061. ^{1}H NMR spectrum, δ, ppm: 7.03–8.20 m (H_{arom}).

The IR spectra were measured on a Perkin–Elmer Spectrum 1000 Fourier spectrometer from samples pelleted with KBr. The ^{1}H NMR spectra were obtained from solutions in CD_2Cl_2 using a Tesla BS-567A instrument (100 MHz).

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