SOME UNUSUAL TRANSFORMATIONS OF BISMESITYLDICHLOROMALONIMIDOYL DICHLORIDE UPON REACTION WITH SODIUM AZIDE

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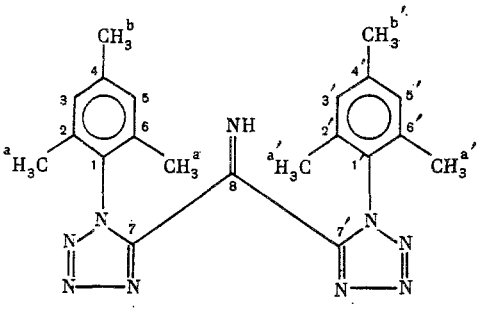
In previous work [1], we showed that bisaryldichloromalonimidoyl dichlorides react with excess sodium azide in acetone at 0-20°C to form previously unreported bis(1-aryl-5-tetrazolyl)dichloromethanes. In the present work, we found that the reaction of bismesityldichloromalonimidoyl dichloride (I) with excess sodium azide in purified, anhydrous DMF at 100°C gives bis(1-mesityl-5-tetrazolyl)iminoethane (II), whose structure was established by x-ray diffraction structural analysis, IR, ^1H and ^{13}C NMR spectroscopy, and mass spectrometry.

$(2,4,6\text{-}(CH_3)_3C_6H_2N{=}CCl)_2CCl_2$ (I) + NaN_3 →



(II)

A solution of 2 g (4.5 mmoles) (I) in 30 ml DMF was added to a suspension of 3.5 g (54 mmoles) NaN_3 in 30 ml DMF. The temperature of the reaction mixture was gradually raised to 100°C and the mixture was maintained at this temperature for 18 h. The mixture was poured onto ice. The precipitate formed was filtered off, washed with water, and dried to give 1.34 g (74%) (II), mp 210-212°C (from ethanol). Found: C 62.53; H 5.60; N 31.10%. Calculated for $C_{21}H_{23}N_9$: C 62.82; H 5.77; N 31.40%. Mass spectrum, m/z: 401 (M^+). IR spectrum (ν, cm^{-1}): 3225 (NH), 2980, 2920 (CH_3), 1630, 1600 (C=N), 1490 (C_6H_2), 1115, 1085 (tetrazole ring). PMR spectrum in $CDCl_3$ with TMS as the standard (δ, ppm): 1.74 s (6H, $CH_3{}^a$), 1.95 s (6H, $CH_3{}^{a'}$), 2.29 s (3H, $CH_3{}^b$), 2.33 s (3H, $CH_3{}^{b'}$), 6.94 s (4H, C_6H_2), 11.28 s (1H, NH). ^{13}C NMR spectrum in $CDCl_3$ with TMS as the standard (δ, ppm): 17.10, and 17.56 ($CH_3{}^a$ and $CH_3{}^{a'}$), 21.08 and 21.18 ($CH_3{}^b$ and $CH_3{}^{b'}$), 128.75 and 130.28 (C^2, C^6, $C^{2'}$, $C^{6'}$), 129.09 and 129.89 (C^3, C^5, $C^{3'}$, $C^{5'}$), 135.08 and 135.19 (C^4 and $C^{4'}$), 141.00 and 141.85 (C^1 and $C^{1'}$), 149.75 and 150.58 (C^7 and $C^{7'}$), 151.18 (C^8). Iminomethane (II) forms triclinic crystals with a = 10.056(2), b = 10.918(2), c = 11.114(3) Å, α = 115.07(2), β = 91.19(2), γ = 107.12(2)°, space group $P\bar{1}$. This molecule is asymmetrical. Dihedral angles 1-2, 1-3, and 2-4 are 81.8, 87.5, and 79.7°, respectively. The mean bond lengths in the heterocycles are: N=N, 1.293(3) Å; N=C, 1.312(4) Å; =N–N=, 1.354(3) Å; =N–N<, 1.349(3) Å; N–C, 1.336(4) Å. The N=C bond length in the iminomethane unit is 1.259(3) Å.

LITERATURE CITED

1. A. F. Shivanyuk, E. V. Dashkovskaya, and M. O. Lozinskii, Zh. Org. Khim., 22, 200 (1986).

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