PREPARATION OF THE PURE SODIUM SALT OF 1H-1,2,4-TRIAZOLE

M. Kazhemekaite, A. Yuodvirshis, and A. Vektarene

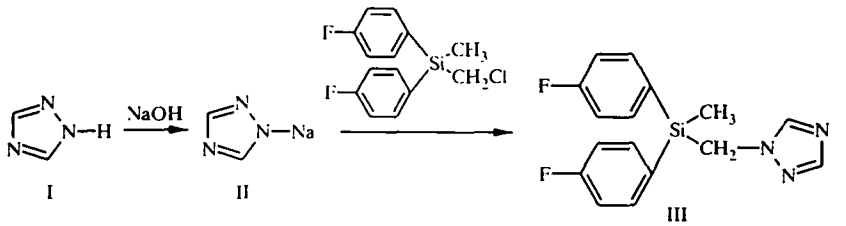
The sodium salt of 1H-1,2,4-triazole (I) serves as the starting material for the preparation of many of its N-substituted derivatives used for the protection of vegetation and in medicine.

Nevertheless, a preparation for the pure salt I has not yet been reported. Either the crude salt or a solution of its sodium salt without isolation has been employed. The synthesis of I has been complicated and involved costly reagents such as sodium methylate in methanol [1-4], sodium amide in liquid ammonia [5], or sodium hydride in anhydrous solvents [6, 7].

We have prepared an analytically pure sample of salt I by the action of excess NaOH in water on 1,2,4-triazole (II).

Samples of 1.2 g (0.03 mole) NaOH and 1.03 g (0.015 mole) triazole II were dissolved consecutively in 5 ml water. The solution was maintained at room temperature for 4 h. The reaction mixture was cooled to 4°C. The crystalline precipitate was filtered off and washed with cold methanol and then ether. The product was dissolved in dry methanol. The solution was filtered and the filtrate was evaporated to dryness. The residue was dried at 120-150°C to give 0.9 g (67%) sodium salt of 1H-1,2,4-triazole (II), mp 325-327°C. ^{1}H NMR spectrum in DMSO-d_6 at 200 MHz (TMS): 7.84 (2H, H-3, H-5). ^{13}C NMR spectrum in DMSO-d_6 at 50.3 MHz (TMS): 149.30 (C-2, C-3, C-5). Found: C, 26.59; H, 2.08; N, 46.19; Na, 25.54%. Calculated for $C_2H_2N_3Na$: C, 26.38; H, 2.21; N, 46.15; Na, 25.25%.

The use of pure salt I for the preparation of N-alkyl derivatives of 1,2,4-triazole markedly increases the yield of these products. For example, the well-known fungicide 1-[methylbis(4-fluorophenyl)silylmethyl]-1,2,4-triazole (III) was obtained in 49% yield using 90% sodium salt of 1,2,4-triazole [8]. In contrast, use of analytically pure sodium salt I gave pure III with mp 52-53°C in 75% yield. Fractionation in vacuum (0.05 mm Hg) was not required as in the procedure of Tacke and Becker [8].



Product III was entirely identical in its physical constants and NMR spectra to a sample of III prepared according to Tacke and Becker [8].

REFERENCES

1. U. Trust, P. Kemter, K. Ruehlmann, and F. Liebner, DE Patent 4,105,538; Chem. Abstr., **117**, 192068 (1992).
2. S. Scheithauer, R. Otto, U. Reitenbach, and J. Friese, DD Patent 284,225; Chem. Abstr., **114**, 207269 (1991).
3. R. Nyfeler, H. Zondler, and E. Strum, EP Patent 126,430; Chem. Abstr., **103**, 71319 (1985).
4. J. Curtze, R. Mendel, H. Becker, C. Drandarevski, and S. Lust, EP Patent 53,307; Chem. Abstr., **97**, 182426 (1982).

Institute of Biochemistry of the Lithuanian Republic, 2600 Vilnius, Lithuania. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 277-278, February, 1998. Original article submitted October 22, 1997.

 0009-3122/98/3402-0252$20.00

5. H. H. Strain, J. Am. Chem. Soc., **47**, 1995 (1927).
6. R. Lovey and A. Elliot, US Patent 4,737,508; Chem. Abstr., **109**, 110431 (1988).
7. J. Clough, GB Patent 2,143,523; Chem. Abstr., **103**, 215295 (1984).
8. P. Tacke and B. Becker, Appl. Organometall. Chem., **3(2)**, 133 (1989).