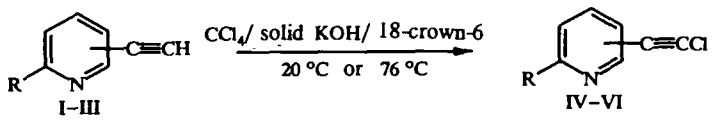
Chemistry of Heterocyclic Compounds, Vol. 34, No. 1, 1998

CHLORINATION OF PYRIDYLACETYLENES IN THE PHASE TRANSFER CATALYTIC SYSTEM CCl_4/KOH/18-CROWN-6

É. Abele, R. Abele, K. Rubina, and E. Lukevics

Chlorination of terminal aliphatic and aromatic acetylenes is usually carried out by chlorination of the corresponding acetylene in the system n-BuLi/N-chlorosuccinimide/THF [1, 2] or n-BuLi/Cl_2 [3] or in the presence of hypochlorites [4, 5]. A phase transfer catalytic method for the preparation of phenylchloroacetylene from phenylacetylene in the system CCl_4/50% NaOH/benzyltriethylammonium chloride has been described [6]. The only known method for the preparation of 3-chloroethynylpyridine is based on the reaction of 3-ethynylpyridine with KOCl in aqueous KOH [7].

We have developed a new method for the preparation of the chloroethynylpyridines IV-VI from the corresponding ethynylpyridines in the system CCl_4/solid KOH/18-crown-6. The chlorination products were obtained in 40-52% yield. The chlorinating agent in these reactions is CCl_4, which readily gives the Cl^+ ion in the presence of carbanions generated under the influence of bases [8].



I–III IV–VI

I, IV R = H, 2-ethynyl II, V R = H, 3-ethynyl III, VI R =Me, 3- ethynyl

All of the products are very unstable and readily resinify at elevated temperature or in contact with air.

2-Chloroethynylpyridine (IV). Powdered KOH (0.168 g, 3 mmol) was added to a solution of 2-ethynylpyridine (0.103 g, 1 mmol) and 18-crown-6 (0.013 g, 0.05 mmol) in carbon tetrachloride (1 cm^3), the mixture was stirred for 3 h at room temperature (monitored GLC) and filtered through Al_2O_3. The solvent was removed from the filtrate at low pressure and the residue was chromatographed on silica gel (eluent benzene:ethyl acetate, 1:1). Yield 0.055 g (40%). ^1H NMR spectrum ($CDCl_3$/TMS): 7.25 (1H, m, 5-H), 7.38 (1H, m, 3-H), 7.61 (1H, m, 4-H), 8.54 ppm (1H, m, 6-H). Mass spectrum, *m/z* (I_{rel}, %): 137 (100, M^+), 110 (23), 102 (62), 84 (25), 75 (31), 50 (24), 37 (13).

3-Chloroethynylpyridine (V) was obtained from 3-ethynylpyridine [9] analogously. The reaction was carried out for 3 h. ^1H NMR spectrum ($CDCl_3$/TMS): 7.18 (1H, m, 5-H), 7.27 (1H, m, 4-H), 7.68 (1H, m, 6-H), 8.49 ppm (1H, m, 2-H). Mass spectrum, *m/z* (I_{rel}, %): 137 (100, M^+), 110 (19), 102 (60), 84 (27), 75 (31), 50 (26), 37 (13). Yield 49%.

2-Methyl-5-chloroethynylpyridine (VI). Powdered KOH (8.96 g, 0.16 mol) was added to a solution of 2-methyl-5-ethynylpyridine (2.34 g, 20 mmol), 18-crown-6 (0.26 g, 1 mmol) and carbon tetrachloride (9.67 cm^3, 0.1 mol) in toluene (10 cm^3), and the mixture was stirred for 2 h at 76°C (monitored by GLC) and filtered through Al_2O_3. The solvent was distilled from the filtrate under reduced pressure and the residue was recrystallized from petroleum ether to give product VI (1.59 g, 52%), m.p. 65-66°C. ^1H NMR spectrum ($CDCl_3$/TMS): 2.56 (3H, s, CH_3), 7.07 (1H, m, 3-H), 7.58 (1H, m, 4-H), 8.51 ppm (1H, m, 6-H). Mass spectrum, *m/z* (I_{rel}, %): 151 (100, M^+), 116 (11), 89 (51), 84 (14), 63 (10).

Latvian Institute of Organic Synthesis, Riga, LV-1006. e-mail: kira@osi.lanet.lv. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 130-131, January, 1998. Original article submitted November 25, 1997.

 0009-3122/98/3401-0122$20.00

REFERENCES

1. W. Werboom, H. Westmijze, L. J. De Notten, P. Vermeer, and H. J. T. Bos, Synthesis, No. 4, 296 (1979).
2. G. Zweifel, W. Lewis, and H. P. On, J. Am. Chem. Soc., **101**, No. 7, 5101 (1979).
3. E. Kloster-Jensen, Tetrahedron, **22**, No. 3, 965 (1966).
4. H. Normant and T. Cuvigny, Bull. Soc. Chim. Fr., No. 11-12, 1447 (1957).
5. G. Zregler, C. A. Welch, C. E. Orzech, S. Kikkawa, and S. Miller, J. Am. Chem. Soc., **85**, No. 11, 1648 (1963).
6. M. Makosza and M. Fedorynski, Rocz. Chem., **49**, 1779 (1975).
7. A. N. Sinyako and N. S. Shvartsberg, Izv. Akad. Nauk SSSR, Ser. Khim., **10**, 2306 (1979).
8. M. Makosza, A. Kvast, E. Kwast, and A. Jonczyk, J. Org. Chem., **50**, No. 20, 3722 (1985).
9. É. Abele, R. Abele, K. Rubina, A. Gaukhman, and É. Lukevits, Khim. Geterotsikl. Soedin., No. 1, 46 (1998).