BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47(5), 1305 (1974)

Synthesis of (4-Pyridyl)-1,2-ethanediol

Herbert S. Aaron and Jacob I. Miller

Chemical Research Division, Edgewood Arsenal, Aberdeen Proving Ground, Maryland, 21010 USA

(Received August 13, 1973)

Synopsis. A conflict in the literature regarding the physical properties of 4-(pyridyl)-1,2-ethanediol has been resolved. The melting point and solubility data of this compound are correct as reported in *J. Org. Chem.*, **30**, 1331 (1965).

Furuyama, Mori, and Wakasa[1] recently modified our procedure[2] for the synthesis of (4-pyridyl)-1,2-ethanediol (I) and obtained a liquid product reported to be insoluble in acetone, and which seemed to dissolve only in solvents with a Hildebrand solubility parameter greater than 12.7. Although no analytical data was offered to establish the purity of their product, they suggested that the melting point and solubility we reported for I were in error. However, their claim that Haas *et al.*[3] also indicated a similar doubt with respect to our results is incorrect. Actually, our paper was uncited by Haas *et al.*, and was probably unknown to them, since it appeared only shortly before their own publication. The fact that Haas *et al.* obtained I as a pasty mass that could not be readily purified (by unspecified means) does not disprove our results. Indeed, these workers recrystallized the corresponding 2-pyridylglycol from methylene chloride, which has a solubility parameter of only 9.8.[4]

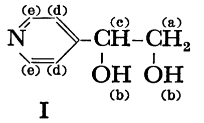
In view of the claim[1] that I was insoluble in acetone, we ran the reaction as described by Furuyama *et al.*, in order to evaluate their product. The solubility discrepancy is apparently resolved from the fact that the crude product thus obtained did give an initial appearance of being insoluble in acetone, but only because it contained about 18% of a mixture of acetone-insoluble magnesium and potassium salts of isonicotinic acid. In our hands, the modified procedure[1] gave a 54% yield of crude I (unrecrystallized), after separation from these salts. By our original procedure, a 35% yield of the purified product had been obtained.[2]

Experimental

(4-Pyridyl)-1,2-ethanediol (I) was obtained as a clear, viscous, yellow oil (22 g); as described.[1] A less-than-theoretical yield was signalled by the strong odor of 4-vinylpyridine on the inorganic filter cake. The crude product appeared, initially, to be insoluble in acetone. However, when a 1.1 g portion was stirred into 6 ml of acetone, it formed an opaque gum, which slowly dissolved, and left an insoluble, tan, solid residue II, 0.15 g, mp 265—320 °C. Combustion, NMR (in D_2O) and atomic absorption analysis (for K and Mg) indicated II was a mixture of inorganic salts of isonicotinic acid, consistent with a composition of four parts $C_5H_4NCOOK \cdot 1/2H_2O$ (IIA) and one part $C_5H_4NCOO(Mg)OH \cdot 1/2H_2O$ (IIB).

Found: C, 42.0; H, 3.0; N, 7.9; O, 25.2; Mg, 2.5; K, 19.3%. Calcd for 4/1 mixture of IIA/IIB: C, 42.4; H, 3.1; N, 8.2; O, 25.3; Mg, 2.8; K, 18.5%.

After II had been filtered off, the acetone solution was allowed to stand overnight, and an additional 0.03 g of solid precipitated. This material shriveled in a capillary tube at about 290 °C, but did not melt, even when heated to 340 °C; it was not further characterized. The acetone solution was then concentrated under reduced pressure to give 0.8 g of I as an oil, which slowly crystallized, when seeded.[2] A larger batch (14.5 g) of the initial liquid product (I), above, was similarly treated (60 ml of acetone, 10 min stirring) to give 2.3 and 0.4 g of insoluble salts, respectively, and 11.8 g (54%) of crude I, as a tacky, orange solid. The NMR spectrum of I, mp 69—71 °C (from CH_2Cl_2), was recorded in deuteroacetone, on a Varian A-60D Spectrometer (60 MHz, internal TMS reference, ambient probe temperature of 33 °C): δ 3.65, $2H_{(a)}$ m; 3.90, $2H_{(b)}$ s; 4.76, $H_{(c)}$ ~t; 7.40, $2H_{(d)}$ ~d; 8.48, $2H_{(e)}$ broad m. In D_2O, unless heated,[1] the $H_{(b)}$ and $H_{(c)}$ signals overlapped at about δ 4.88.



I

We thank Mr. Donald Hench, Mrs. Marjorie Buckles and Mr. John Corliss and staff for the analytical results, and Mrs. Linda Szafraniec for the NMR data.

References

1) T. Furuyama, K. Mori, and R. Wakasa, This Bulletin, **45**, 1924 (1972).

2) H. S. Aaron, O. O. Owens, P. D. Rosenstock, S. Leonard, S. Elkin, and J. I. Miller, *J. Org. Chem.*, **30**, 1331 (1965).

3) H. C. Haas, H. S. Kolesinski, and N. W. Schuler, *J. Polym. Sci. Part B*, **3**, 879 (1965).

4) J. H. Hildebrand and R. L. Scott, "Regular Solutions," Prentice Hall, Inc., Englewood Cliffs, N.J. (1962), p. 172.

Corrections

Volume 46, 1973

S. Takeuchi: A Kinetic Study on the Decomposition of Benzyl *N*-(Hydroxymethyl)carbamate in Alkaline Solution.
Transfer the figures of Fig. 3 and Fig. 4 in p. 1497 to those of Fig. 4, Fig. 3, respectively, keeping the factors in the both axes of the figures and the figure captions at the original locations.

K. Nakamura: The Structure of Ordered β V_2D as Determined by Means of the Deuteron Magnetic Resonance.
Page 2589. In col. 1, line 10, for "$(e^2qQ/h)^{\beta}_{\mathrm{oct}}$ and $(e^2qQ/h)^{\beta}_{\mathrm{oct}}$" read "$(e^2qQ/h)^{\beta}_{\mathrm{oct}}$ and $(e^2qQ/h)^{\beta}_{\mathrm{tet}}$."

A. Sera, C. Yamagami, and K. Maruyama: Effect of Pressure on the Rate of Solvolysis. Formolysis and Methanolysis of Secondary Alkyl Tosylates.
Page 3867. In experimental part, line 7, for "1-*t*-Butylethyl tosylate(8)" read "Di-*t*-butylmethyl tosylate(8)."