A High Yield Method of Preparation of Pyridine-2-aldehyde

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Although pyridine-2-aldehyde is a compound of significant importance [1-3], however most of the reported methods of its preparation encounter a serious drawback of being relatively low yield [4-6]. In connection with preparation of aldehydes Barta-Szalai and Lempert [7] have reported a yield of 73% of 4-methoxybenzaldehyde by the reaction of 4-methoxybenzoic acid hydrazide with n-butylamine. This report encouraged us to attempt the reaction of pyridine-2-carboxylic acid hydrazide with n-butylamine in order to prepare pyridine-2-aldehyde. As a result of this reaction pyridine-2-aldehyde was isolated in the pure form in a yield of 97.9% with respect to pyridine-2-carboxylic acid hydrazide. The purity of the isolated product was established by the use of TLC technique against an authentic sample of pyridine-2-aldehyde in three different solvent systems. The characterization of the isolated pyridine-2-aldehyde was based on its observed boiling point, 38-39°/7 mm (lit.b.p. [8] 62-63°/14 mm), some positive chemical tests for aldehydes, preparation of phenyl hydrazone (m.p. obs. 181°, m.p. lit. [9] 182°) and 2,4-dinitrophenyl hydrazone (m.p. obs. 237°, m.p. lit. [9] 237°). Moreover, the IR spectrum (neat) of the isolated product showed a strong absorption at 1700 cm^{-1} and an absorption of moderate intensity at 2780 cm^{-1} corresponding to C=O stretching frequency of an aldehyde and the aldehydic C-H stretching frequency respectively.

The procedure used for the reaction of pyridine-2-carboxylic acid hydrazide with n-butylamine was a slight modification of the method reported [7] earlier for the same reaction of some substituted benzoic acid hydrazides. The modification consisted of using an almost saturated solution of pyridine-2-carboxylic acid hydrazide in n-butylamine rather than a 2% solution. The isolation of the aldehyde product was achieved by vacuum distillation rather than by preparative TLC as employed earlier [7]. To a 100 ml two-necked round bottom flask fitted with a reflux condenser and containing pyridine-2-carboxylic acid hydrazide (5.5g, 0.041 mole) was added n-butylamine (40 ml, 0.405 mole) in one lot. The mixture was slightly warmed and thoroughly stirred, using a magnetic stirrer, to yield a clear solution. This solution was subjected to reflux and the reaction was followed by TLC (silica gel, 1:1 acetone-petroleum ether) on the reaction mixture after each hour. After about twelve hours of reflux, the reaction mixture became reddish amber in colour and a new spot, in addition to the two spots of the reactants, was observed on the TLC plate. The fact that the new spot was due to the formation of pyridine-2-aldehyde was established by performing TLC against an authentic sample of pyridine-2-aldehyde. The reflux of the reaction mixture was continued till such time that the spot due to pyridine-2-carboxylic acid hydrazide on the TLC plate was no more visible. This required a total reflux time of forty eight hours. At this stage, most of n-butylamine was removed from the reaction mixture by distillation. Vacuum distillation of the concentrated reaction mixture, thus obtained, yielded pyridine-2-aldehyde at 38-39°/7 mm as a viscous oil (4.2g, 0.039 mole) in 97.9% yield with respect to pyridine-2-carboxylic acid hydrazide.

Pyridine-2-carboxylic acid hydrazide was prepared from pyridine-2-carboxylic acid by the same method as described [10] for preparation of pyridine-4-carboxylic acid hydrazide from pyridine-4-carboxylic acid. It was recrystallised from methanol, m.p. obs. 100°, m.p. lit. [11] 100-101°.

Further work on the reaction of some other heterocyclic carboxylic acid hydrazides with n-butylamine is in progress.

References

1. O. Fuchs, *Chem. Abstr.*, **53**, *7665d (1959)*.
2. W. Funke and K. Hamann, *Chem. Abstr.*, **53**, *9984a (1959)*.
3. C. Engler and F.W. Bauer, *Ber.*, **24**, *2530 (1891)*.
4. C. Harrios and G.H. Lenart, *Ann.*, **410**, *95 (1915)*.
5. C. Niemann, R.N. Lewis and J.T. Hays, *J. Am. Chem. Soc.*, **64**, *1678 (1942)*.
6. R. Iqbal and A.R. Ahmad, *J. Chem. Soc. Pak.*, **8**, *79 (1986)*.
7. G. Barta-Szalai and K. Lempert, *Period. Polytech. Chem. Engg.*, **24**, *253 (1980); Chem. Abstr.*, **95**, *13241h (1981)*.
8. J.R.A. Pollock and R. Stevens (Editors), "Dictionary of Organic Compounds", 4th ed. (1965), Eyre and Spottiswoode, London, p. 2815.
9. E.H. Rodd (Editor), "Chemistry of Carbon Compounds", Ist ed. (1957), Elsevier Publishing Co., London, **IVA**, p. 553.
10. S.P. Dutta and A.K. Acharyge, *Indian J. Appl. Chem.*, **29**, *99 (1966)*.
11. H.H. Fox and T.T. Gibas, *J. Org. Chem.*, **17**, *1653 (1952)*.