HETEROCYCLES, Vol. 4, No. 12, 1976

REACTION OF PICOLYL ETHER WITH DIMETHYLFORMAMIDE

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Reaction of 2- (I) and 4-ethoxymethylpyridine (VIII) with dimethylformamide in the presence of NaH afforded 2- (III) and 4-(1'-ethoxyvinyl)pyridine (IX). This type of reaction proceeded in 4-ethylpyridine to give 2,4-bis(2'-pyridyl)pentane (X).

In recent years, Suzuki reported the Hauser-Wittig type rearrangement[1] of picolyl ethers. For instance, 2-ethoxymethylpyridine (I) was transformed into 1-(2'-pyridyl)propanol (II)[2] under basic conditions in a 46% yield. During the course of the investigation to get more information on this reaction, a reductive condensation of picolyl ethers with dimethylformamide (DMF) was observed. In this communication we wish to report the reaction of picolyl ethers or alkylpyridines with DMF in the presence of NaH.

When I (2.8g, 0.02 mole) was heated with NaH (1g, 0.02 mole) in DMF (50ml) at 150° for 8 hr, colorless oil (III), bp 97° (11 mmHg), $C_9H_{11}ON$, was obtained in a 50% yield. In this reaction

violent evolution of dimethylamine was observed and II was not isolated.

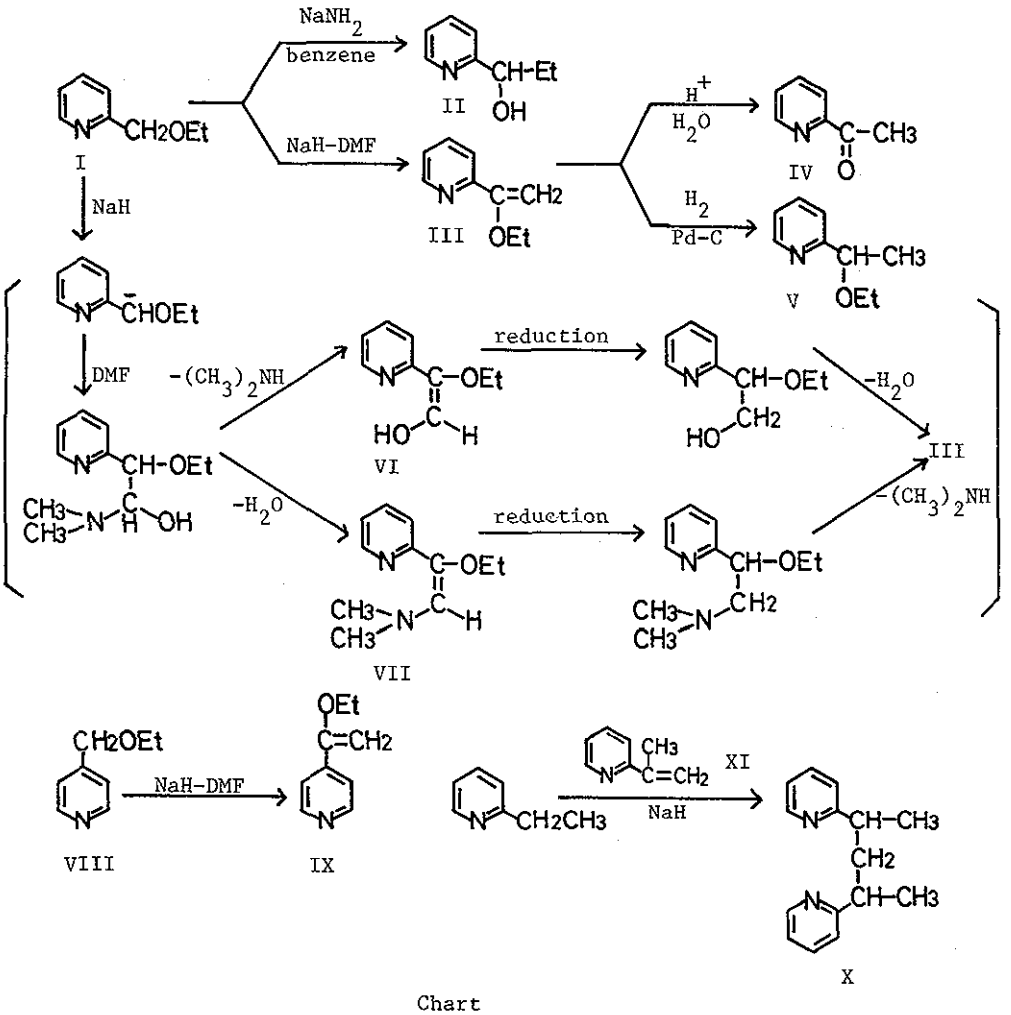
The IR spectrum of III ($CHCl_3$) shows an absorption band at 880 cm^{-1} due to an endo methylene group, and its NMR spectrum ($CDCl_3$) indicates the presence of ethyl protons at 1.42 ppm (3H, t, J=6Hz), 3.95 ppm (2H, q, J=6Hz), methylene protons at 4.25 ppm (1H, d, J=1.5Hz), 5.52 ppm (1H, d, J=1.5Hz) and four ring protons at 6.98-7.2 ppm (1H, m), 7.55-7.65 ppm (2H, m), and 8.45-8.55 ppm (1H, m). Based on these spectral data, the structure of III was assigned 2-(1'-ethoxyvinyl)pyridine.

Treatment of III with 10% hydrochloric acid at room temperature afforded 2-acetylpyridine which was identical with the authentic sample,[3] in an almost quantitative yield. Catalytic hydrogenation of III over Pd-C in methanol gave, in a 75% yield, 2-(1'-ethoxyethyl)pyridine (V), bp 79-80° (17mmHg), whose NMR spectrum [δ (CCl_4) ppm: 1.18 (3H, t, J=7Hz), 1.37 (3H, d, J=8Hz), 3.4 (2H, q, J=7Hz), 4.42 (1H, q, J=8Hz), 6.90-7.75 (3H, m), 8.40 (1H, m)] was consistent with its structure.

As shown in Chart, the formation of III may be reasonably explained by the course which involves the formylation of I followed by the reduction of the intermediate (VI or VII) with DMF or formic acid.

Similarly, 4-ethoxymethylpyridine (VIII) was allowed to react with DMF in the presence of NaH to give colorless oil of bp 97-99° (12mmHg), $C_9H_{11}ON$ (IX), in a 30% yield. The structure of this product was established as 4-(1'-ethoxyvinyl)pyridine (IX) from the following spectral data; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 880, NMR ($CDCl_3$) ppm:

1.30 (3H, t, J=7Hz), 3.92 (2H, q, J=7Hz), 4.32 (1H, d, J=3Hz), 7.4-7.55 (2H, m), 8.5-8.65 (2H, m).



Chart

The above condensation was applied to some alkylpyridines. Namely, treatment of 2-ethylpyridine (2g, 0.02 mole) with NaH (1g, 0.04 mole) in DMF (50 ml) at 157° for 5 hr gave a viscous, oily substance (X), bp 168-172°(11 mmHg), in a 70% yield (dipicrate, mp 204-206°). However, any significant product was not obtained from

the reaction of 2-picoline or 2-benzylpyridine under identical conditions. The structure of X was established as 2,4-bis(2'-pyridyl)pentane (X) from the elemental analysis of its dipicrate ($C_{15}H_{18}N_2 \cdot C_{12}H_6O_{14}N_6$) and the following NMR spectral data of X: $\delta(CCl_4)$ ppm: 1.18 (3H, d, J=6Hz), 1.24 (3H, d, J=6Hz), 1.8-2.3 (2H, m), 2.4-3.0 (2H, m), 6.65-7.15 (4H, m), 7.2-7.65 (2H, m), 8.35-8.6 (2H, m).

Although the details of the formation mechanism of X is not clear at present, a likely pathway is proposed as shown in Chart, that is, 2-(1'-methylvinyl)pyridine (XI) formed in the initial stage of the reaction may react with the starting material to give X.

Further investigations on chemical properties of the pyridine derivatives containing a vinyl ether group are in progress.

ACKNOWLEDGEMENT

The authors wish to thank Mr. Shigeru Ogawa for the technical assistance. Thanks are also due to the members of the central analytical room of this Institute for elemental analysis and NMR spectral measurements.

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Received, 30th September, 1976