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REACTIONS OF PYRIDINE DERIVATIVES BEARING SULFUR FUNCTIONAL GROUPS WITH NUCLEOPHILES

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Both the sulfinyl and sulfonyl groups on the pyridine nuclei have been found to be substituted quite readily by several nucleophiles such as alkoxides,thiolates, and cyanide anion to afford the corresponding ipso-substituted products in high yields. When EtONa was used as a nucleophile, 2-ethoxypyridine was obtained quantitatively together with sodium salts of various sulfinic acids in high yields. Furthermore, 2-and 4-sulfonylsubstituted pyridines also reacted with the Grignard reagents to afford regioselectively the corresponding substituted products respectively. However, the components of the products were dependent on the position of the sulfonyl group. For example, 2-phenylsulfonylpyridine reacts with alkyl or aryl Grignard reagents resulting in the formation of the ipso-substituted pyridine derivatives as sole products. Furthermore, when the reaction was carried out by using 5-hexenyl magnesium bromide, 2-(5-hexenyl)pyridine was obtained as a sole product and the formation of the ring closed product, 2-(cyclopentylmethyl)pyridine, was not obtained at all. These results suggest that the ipso-substitution would proceed via an ionic process and not via a radical process involving the initial one-electron transfer from the Grignard reagent to the substrate. On the other hand, 4-phenylsulfonylpyridine reacted with the Grignard reagent somewhat differently from that of the 2-derivative. In this reaction, the major product was 4,4'-bipyridine together with the 4-alkylpyridines except in the case of using phenyl Grignard reagent in where only 4-phenylpyridine was obtained. These results seem to demonstrate that the reaction of 4-phenylsulfonylpyridine with the Grignard reagents proceeds via an initial one-electron transfer giving rise to the anion radical which then generates the pyridyl radical by extrusion of phenyl sulfinate anion. Then, 4-pyridyl radical thus formed may couple with each other to result in 4,4'-bipyridine.