Dehydration of oximes and amides to nitriles is an important transformation in organic syntheses. In the last 40 years, a number of efficient methods have been developed for the dehydration of oximes and amides to nitriles,1a,1b and the search for better reagents is still continues.1c Also, it is reported that these conversions may be performed either by using bacterial enzymes with aldoximes1d or by employing oximes ethers under basic conditions.1e But the methods developed so far have their own limitations, for example, the use of extremely hazardous reaction conditions,1b volatile and moisture sensitive reagents,1c–1e use of toxic and hazardous chemicals,4,5 cumbersome workup procedures and problems associated with waste disposal,6,7 and lack of versatility in the transformations conducted in hydrated media.9,10

The chemistry and potentialities of AlCl3·6H2O as a reagent in organic synthesis has been less explored,8 particularly in the presence of KI in hydrated media.9 In continuation of our research in aluminum chemistry,1a,8,9 we now wish to report the AlCl3·6H2O/KI/CH3CN system as a new, efficient, and versatile alternate system for the dehydration of oximes and amides to nitriles and intramolecular cyclodehydration of amides to isoquinolines derivatives and keto oximes to anilides in hydrated media.

Aldoxime (Scheme 1, compound 1a) was reacted with the AlCl3·6H2O/KI/CH3CN system [1 equiv of AlCl3·6H2O/KI, 1 equiv of 1a] in a mixture of acetonitrile and water (5:1) at reflux temperature for 6 h, and after workup with 5% ammonium hydroxide solution, it produced p-methoxybenzonitrile (Scheme 1, compound 2a) in 95% yield without formation of triazine1c in the reaction mixture. It was observed that the acid-susceptible1d groups like methyl ether (Scheme 1, compound 1a) and furan (Scheme 1, compound 2h) were unaffected under the reaction conditions and both E and Z isomers of the oximes could be converted to nitriles (in most cases the oximes used were the mixture of E and Z isomers). Similarly, the amides (Scheme 1, compounds 5a,b) under the same reaction condition could be converted to its corresponding nitriles (in most cases the amides used were the mixture of E and Z isomers). Similarly, the amides (Scheme 1, compounds 5a,b) under the same reaction condition could be converted to its corresponding nitriles (Scheme 1, compounds 5a,b) in good yields in the hydrated media. Also, when the system was treated with the amides (Scheme 1, compounds 7a–c), intramolecular cyclodehydration (Bischler Naperalski reaction) occurred1d and resulted industrially important isoquinoline derivatives (Scheme 1, compounds 8a–c), the key intermediates for dextromethorphan [anti-tussive drug] and its analogues.14 Also, it was observed that when the...
The compounds were identified by IR, 1H NMR, and mass analyses and compared with authentic samples. \(^a\) The spectral data were compared with our reported results. \(^b\) The temperature was 80 °C for all experiments. \(^c\) Isolated yield.

**Experimental Section**

**General Experimental Procedure: Representative Procedure for Dehydration of p-Methoxybenzaldoxime.** AlCl\(_3\)-6H\(_2\)O (0.240 g, 1 mmol) and KI (0.498 g, 3 mmol) were stirred in acetonitrile and water (25 mL, 5:1) at room temperature for 0.5 h, and p-methoxybenzaldoxime (1a) (0.151 g, 1 mmol) was added. The reaction mixture was refluxed at 80 °C for 6 h, and the progress of the reaction was monitored by TLC. The solvent was distilled under reduced pressure, and the residue was obtained without side products; and (e) applications are versatile.

**Acknowledgment.** We sincerely thank the Director, Dr. J. S. Sandhu FNA, Dr. S. D. Boruah, Senior Scientist, Petroleum Division and the Analytical Division of the Regional Research Laboratory, Jorhat, Assam, for their help in carrying out this work.

\(\text{AlCl}_3\cdot6\text{H}_2\text{O}\) was treated with keto oximes, Beckmann rearrangement\(^{12}\) occurred and produced anilides in good yields (Scheme 1, compounds 4a, b). Besides, when reacted with cyclohexanone oximes (Scheme 1, compounds 9 and 11), it produced ring-enlargement products (Scheme 1, compounds 10 and 12). Acetonitrile was the best solvent among CHCl\(_3\), CH\(_2\)Cl\(_2\), and CCl\(_4\) in terms of yield and time. The reaction did not proceed at all in the absence of KI.

Regarding the mechanism of the reactions, it may be proposed that AlCl\(_3\cdot6\text{H}_2\text{O}\) is, in reality,9,15 \([\text{Al(H}_2\text{O})_6]\text{Cl}_3\), and reacts with KI to form \([\text{Al(H}_2\text{O})_3]\text{I}_3\), which can exist as \([\text{Al(H}_2\text{O})_4\text{OH}]_2\text{H}^+\) or \([\text{Al(H}_2\text{O})_6\text{OH}]_2\text{H}^+\). The liberated proton forms H\(_2\text{I}\) acid, which in the presence of aluminum dehydrated oximes and amides to nitriles as shown below (Scheme 2).

In conclusion, a new, efficient and versatile system for dehydration of amides and oximes in hydrated media is developed. The significant features of the system are as follows: (a) dehydration can be performed in hydrated media; (b) acid-susceptible groups are tolerated under the reaction conditions; (c) less toxic and hazardous chemicals can be used; (d) moderate to high yields are obtained without side products; and (e) applications are versatile.

**Experimental Section**

**General Experimental Procedure:** Representative Procedure for Dehydration of p-Methoxybenzaldoxime. AlCl\(_3\)-6H\(_2\)O (0.240 g, 1 mmol) and KI (0.498 g, 3 mmol) were stirred in acetonitrile and water (25 mL, 5:1) at room temperature for 0.5 h, and p-methoxybenzaldoxime (1a) (0.151 g, 1 mmol) was added. The reaction mixture was refluxed at 80 °C for 6 h, and the progress of the reaction was monitored by TLC. The solvent was distilled under reduced pressure, and the residue was obtained without side products; and (e) applications are versatile.

**Acknowledgment.** We sincerely thank the Director, Dr. J. S. Sandhu FNA, Dr. S. D. Boruah, Senior Scientist, Petroleum Division and the Analytical Division of the Regional Research Laboratory, Jorhat, Assam, for their help in carrying out this work.
