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A Facile Cyclization of an Enamine Nitrile to Dihydropyridinium Salts (1)

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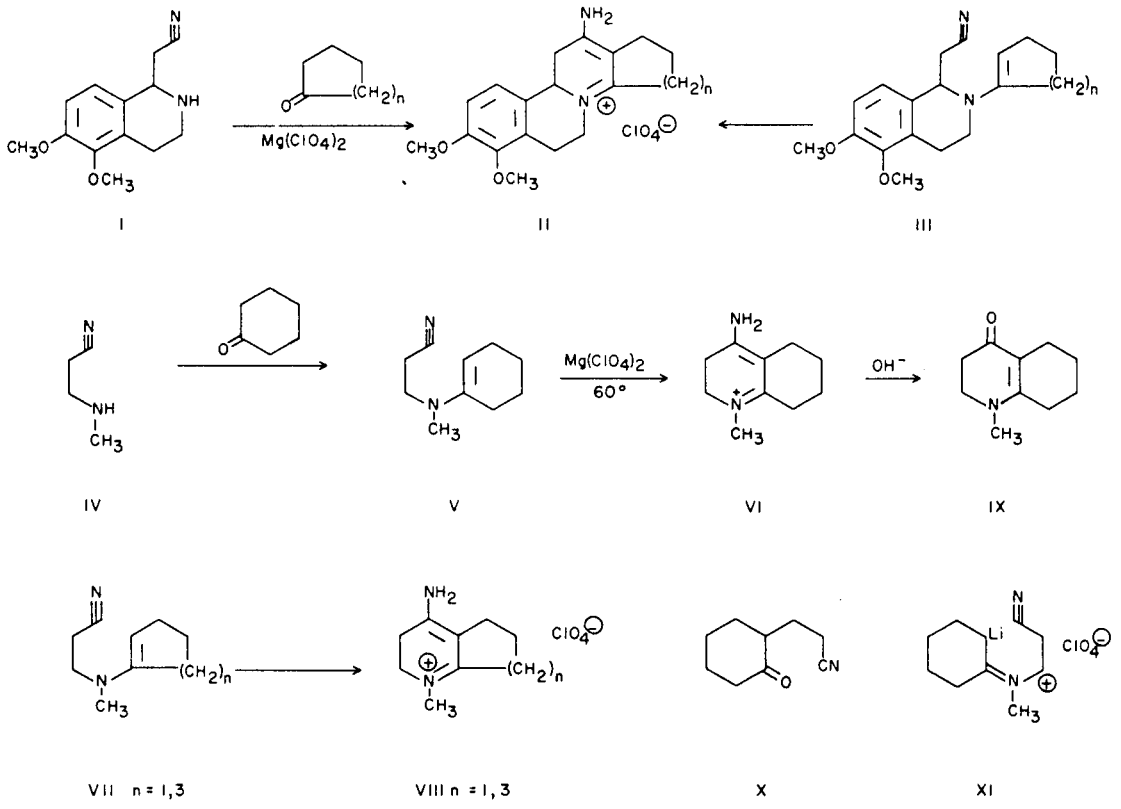
Sir:

A recent report (2) described the reaction of the aminonitrile (I) with cyclic ketones using magnesium perchlorate to produce II after prolonged heating (120°, 40 hours). Although the enamine, III, was postulated as an intermediate, no confirming proof was offered. We have now reexamined this reaction using simple systems and found that it proceeds through the enamine under unusually mild conditions (3).

The aminonitrile, IV (4), was treated in the usual manner (5) with cyclohexanone to give the enamine, V [b.p. 115° (1 torr); λ (film), 4.42, 6.08 μ; NMR (deuteriochloroform), τ 5.52, (triplet)]. A benzene solution of the enamine was treated with 1.1 equivalents of magnesium perchlorate and the mixture warmed to 55-65° for 2-3 hours with vigorous stirring. The powdered magnesium perchlorate had coagulated to a gummy residue during this time. The benzene was decanted and the "complex" treated with water producing essentially a quantitative yield of VI. Recrystallization of the perchlorate salt (EtOH) gave 85% of pure VI (m.p. 131-132°; λ (EtOH), 350 mμ (ε, 17,810); λ (nujol), 2.89, 2.96, 3.05, 6.05, 6.22, 6.60, 9.0 μ). Similar treatment of the enamine VII (n = 1) [b.p., 85° (0.1 torr); λ film 4.42, 6.13 μ; NMR (deuteriochloroform), τ 5.81 (diffuse triplet)] gave, after 2 hours VIII (n = 1) in 70% yield (m.p., 131-132°; λ (EtOH), 345 mμ (ε, 19,700); λ (nujol), 2.89, 2.96, 3.04, 6.01, 6.11, 6.47, 8.90 μ); The enamine VII (n = 3) [b.p., 110° (0.1 torr); λ (film), 4.41, 6.09 μ; NMR (deuteriochloroform), τ 5.21] gave, after 3 hours at 65-70°, VIII (n = 3) in 72% yield (m.p., 148-149°; λ (EtOH), 350 mμ (ε, 18,630); λ (nujol), 2.86, 2.94, 3.03, 6.06, 6.17, 6.56, 8.90 μ) (6). Structure proof of the cyclized products was obtained by alkaline hydrolysis of VI to the known (7) hexahydro-4-quinolone IX in 80% yield [b.p., 134° (1.5 torr); picrate 156°].

The use of lithium perchlorate with V in place of mag-



nesium perchlorate produced a liquid "complex" which upon treatment with cold water (24 hours) gave only the cyanoethyl ketone, X. The formation of the latter, was found to occur when a mixture of cyclohexanone, methyl amine and acrylonitrile was allowed to stand (24 hours) in aqueous solution. However, when the enamine V was treated with cold water (24 hours), only cyclohexanone and 2-(*N*-methyl)propionitrile was isolated. Thus the "complex" could be considered to exist as the iminium species, XI, which cleaves in water rapidly to cyclohexanone, methyl amine, and acrylonitrile. This behavioral difference between the lithium and magnesium ion is under investigation as well as the synthetic utility of the magnesium-ion induced cyclizations.

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