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# DIMSYLSODIUM-INDUCED REARRANGEMENT OF ALKYLIMIDATES TO N-ALKYLLACTAMS

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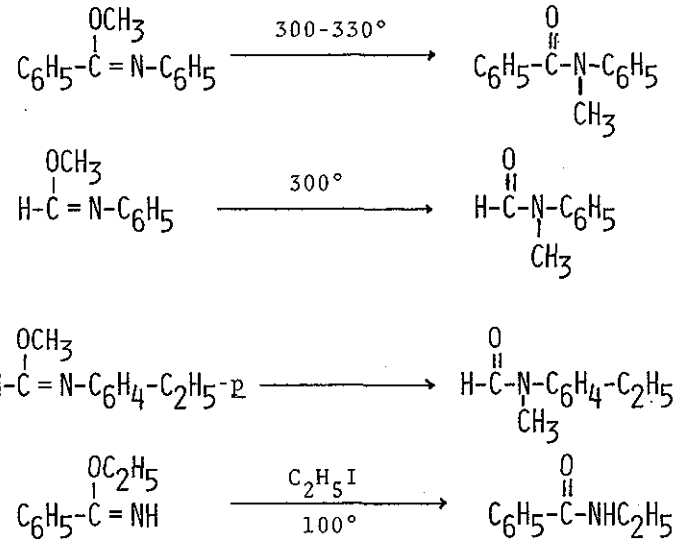
Treatment of 1-ethoxy-3,4-dihydro-6,7-dimethoxyisoquinoline (1) with dimsylsodium yielded 2-ethyl-1,2,3,4-tetrahydro-6,7-dimethoxy-1-oxoisoquinoline (2). Similarly, 2-ethoxy-4,5-dihydro-3H-pyrrole (3), 2-ethoxy-3,4,5,6-tetrahydropyridine (5), 7-ethoxy-3,4,5,6-tetrahydro-2H-azepine (7), and 7-ethoxy-3,4,5,6-tetrahydro-4-methyl-2H-azepine (9) were allowed to react with dimsylsodium to give the corresponding N-ethyllactams (4), (6), (8), and (10), respectively, through O to N migration of ethyl group by the catalytic action of dimsylsodium.

A variety of N-alkylamide have been prepared by the rearrangement of O-alkylimidates by many research groups[1], in an apparently uncatallyzed thermal rearrangement, frequently treated as a special case of the Chapman-Mumm rearrangement. The temperatures required for the rearrangement of alkyl group are generally quite high. Catalysis by Lewis and Brönsted acid[2], alkyl halide[3], or metal salt[4]

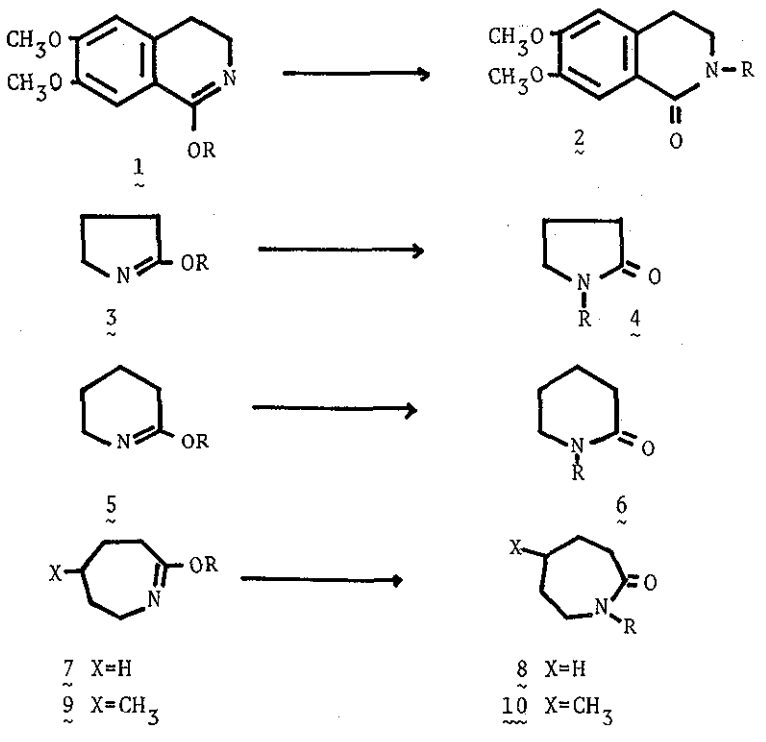
have been useful for the O to N migration of the alkyl group of imidates. Following examples would suffice as illustrations.



However, there is no survey on the base catalyzed migration of alkyl group leading to N-alkylamides. We have found that N-alkyl-lactams were formed from alkylimidates by the catalytic action of dimsylsodium. We wish to report these results in this paper.

1-Ethoxy-3,4-dihydro-6,7-dimethoxyisoquinoline (1), prepared from 1,2,3,4-tetrahydro-6,7-dimethoxy-1-oxoisoquinoline by treatment with triethyloxonium fluoroborate, was allowed to react with dimsylsodium in THF-DMSO at room temperature for 1 hr resulted in formation of 2-ethyl-1,2,3,4-tetrahydro-6,7-dimethoxy-1-oxoisoquinoline (2), mp 81-83° (MeOH-$Et_2O$), in quantitative yield. The spectral data [IR ($CHCl_3$) $cm^-$ 1630 (-N-CO), NMR δ ($CDCl_3$) 1.43 (3H, t, J=7 Hz, $\underline{CH_3}CH_2$),

3.90 (6H, s, 2x$OCH_3$), 4.22 (2H, q, $CH_3\underline{CH}_2$), 6.63 (1H, s, 5-H), 7.17 (1H, s, 8-H), mass (m/e) 235 ($M^+$), 220 ($M^+$-15), 207 ($M^+$-28), 178 ($M^+$-57)] were in good agreement with the assigned structure. Similar results were also obtained by the use of alicyclic imidates. The reaction of 2-ethoxy-4,5-dihydro-3H-pyrrole (3), 2-ethoxy-3,4,5,6-tetrahydropyridine (5), 7-ethoxy-3,4,5,6-tetrahydro-2H-azepine (7), and 7-ethoxy-3,4,5,6-tetrahydro-4-methyl-2H-azepine (9) with dimsyl-sodium afforded 1-ethyl-2-pyrrolidone (4)[5], 1-ethyl-2-piperidone (6)[6], 1-ethylcaprolactam (8)[7], and 1-ethyl-hexahydro-5-methyl-2H-azepin-2-one (10), respectively, in a similar fassion, in good yield.



The ethyl migration was not observed on standing imidates in a solution of DMSO without dimsylsodium. It is of interest that O-alkylimidates were converted to N-alkyllactams by a catalytic action of dimsyl anion under very mild conditions. The application and limitation of this reaction are under further investigation.

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