

DIMSILSODIUM-INDUCED REARRANGEMENT OF ALKYLIMIDATES
TO N-ALKYLLACTAMS

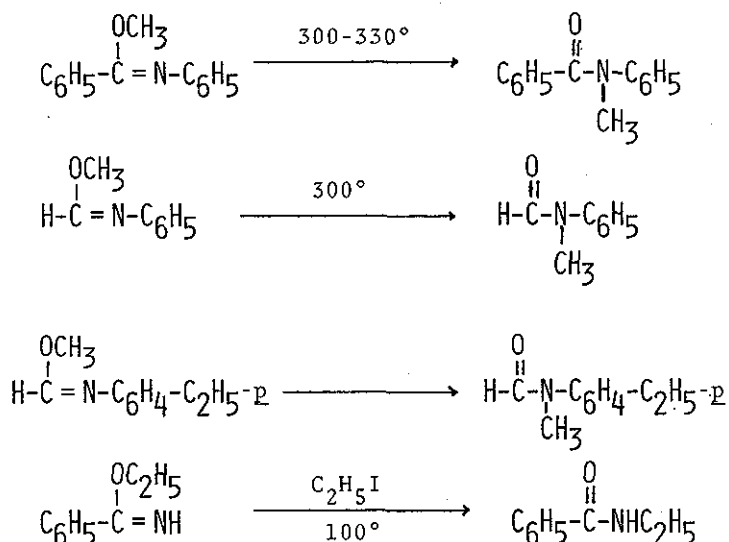
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Treatment of 1-ethoxy-3,4-dihydro-6,7-dimethoxyisoquinoline (1) with dimsilsodium yielded 2-ethyl-1,2,3,4-tetrahydro-6,7-dimethoxy-1-oxoisoquinoline (2). Similarly, 2-ethoxy-4,5-dihydro-3H-pyrrole (3), 2-ethoxy-3,4,5,6-tetrahydropyridine (5), 7-ethoxy-3,4,5,6-tetrahydro-2H-azepine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

A variety of N-alkylamide have been prepared by the rearrangement of O-alkylimidates by many research groups¹⁾, in an apparently uncatalyzed 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 acid²⁾, alkyl halide³⁾, or metal salt⁴⁾

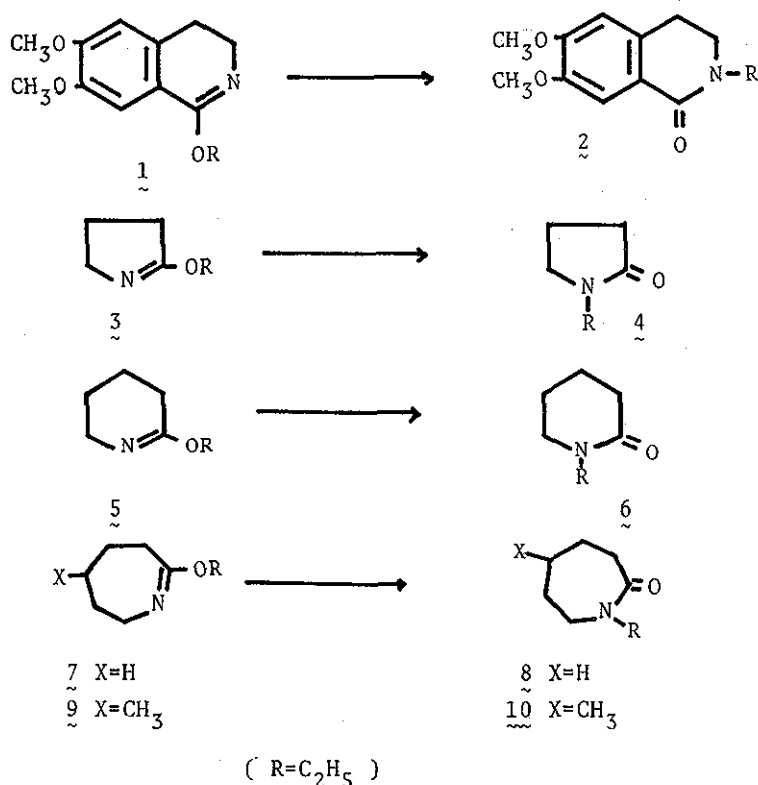
have been useful for the O to N migration of the alkyl group of imidates. Following examples would suffice as illustrations.



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 dimethylsodium. 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 dimethylsodium 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-Et₂O), in quantitative yield. The spectral data [IR (CHCl₃) cm⁻¹ 1630 (-N-CO), NMR δ (CDCl₃) 1.43 (3H, t, J=7 Hz, CH₃CH₂),

3.90 (6H, s, 2xOCH₃), 4.22 (2H, q, CH₂CH₂), 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 dimethylsodium 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 fashion, in good yield.



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

References

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