A NOVEL CYCLIZATION FOR THE SYNTHESIS OF NITROGEN-CONTAINING HETEROCYCLES: THE SYNTHESIS OF (±)-HELIOTRIDANE, (±)-NUPHAR INDOLIZIDINE, AND (±)-DIHYDRODEOXYOTONECINE

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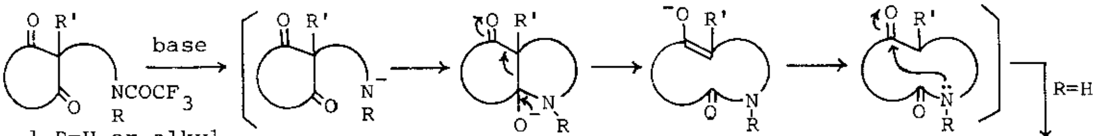
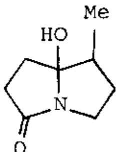
As shown in a general scheme, 1,3-diketone 1 bearing the appropriate protected amino side chain is readily converted into 6 in one pot from 1 under base-catalysed conditions. This sequential process involves a formation of carbinolamine 3 via 2, followed by a retroaldol type of ring-opening to give 4, and finally a transannular cyclization of 5(R=H). With an another point of view this sequence could be briefly depicted by a crisscross sign indicating reaction sites in formula 7, and thereby named as the *crisscross annulation*. Moreover, when the protected secondary amine 1(R=alkyl) is used as a substrate in this versatile annulation, it is of special significance to be able to intercept the strained medium-sized ketolactam 5, controlling the *crisscross annulation*. We have demonstrated a new approach to the synthesis of pyrrolizidine 8, indolizidine 9, azacyclooctanone 10, and azacyclononanone 11 by using this annulation. Further, these compunds were readily led to the alkaloids (±)-heliotridane(12), (±)-nuphar indolizidine(13), and (±)-dihydrodeoxyotonecine(14).



1 R=H or alkyl
2
3
4
5



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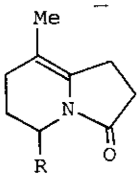
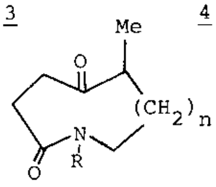
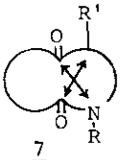


9 R=H or 3-furyl



10 n=1
11 n=2



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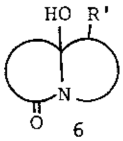

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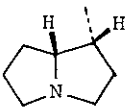

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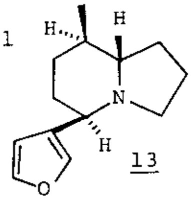

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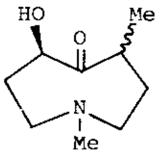

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