AN APPROACH TO TAXANE DITERPENES. THE SYNTHESIS OF THE BICYCLO[5.3.1]UNDECAN-4-ONE DERIVATIVES.

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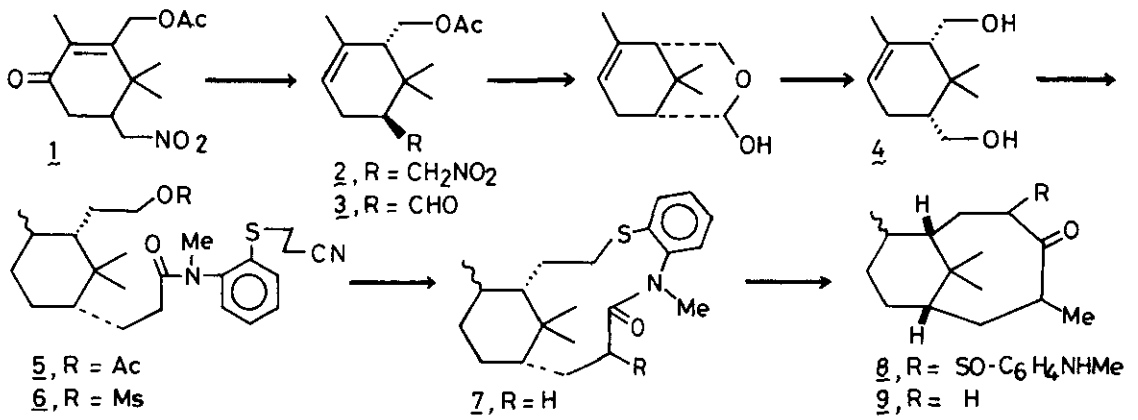
We previously reported a new method for formation of the medium-ring ketones by ring closure.[1,2] We now report the synthesis of the bicyclo[5.3.1]undecan-4-one 9 as a model for the synthesis of taxane diterpenes based on this new cyclization method.

Reduction of the tosylhydrazone of the enone 1 prepared from β-ionone with catecholborane afforded the trans-acetate 2. Epimerization of the aldehyde 3 with MeONa in MeOH followed by $NaBH_4$ reduction produced the cis-diol 4. This compound 4 was converted into the amide 5 by conventional methods.

When the mesylate 6 was treated with t-BuOK in t-BuOH, demasking of the thiol protecting group and the concomitant cyclization took place and the twelve-membered lactam sulfide 7 was obtained. After methylation, the LDA-promoted intramolecular cyclization of the corresponding sulfoxide proceeded quite smoothly affording the eight-membered keto sulfoxide 8 in quantitative yield. Reductive desulfurization of 8 gave the desired ketone 9.



1) Y. Ohtsuka and T. Oishi, Tetrahedron Lett., 1979, 4487; Chem. Pharm. Bull., 31, 454 (1983).

2) Syntheses of (±)-caryophyllene and (±)-isocaryophyllene: Y. Ohtsuka, S. Niitsuma, H. Tadokoro, T. Hayashi and T. Oishi, 4th Intr. Conf. Org. Synth. (IUPAC), 1982, Tokyo, Abstract p 69.