Tetrahedron Letters No. 49, pp 4505 - 4506, 1976. Pergamon Press. Printed in Great Britain.

A NEW APPROACH TO THE PREPARATION OF β-METHYL-α,β-CYCLOPENTENONES

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(Received in UK 11 October 1976; accepted for publication 18 October 1976)

Though already quite a number of methods are known for the preparation of various cyclopentenones of industrial importance[1], it appears to be of interest to present in this letter a novel synthetic approach to the preparation of some β-methyl-α,β-cyclopentenones, e. g. of cis-jasmone 6a and of cis-jasmololone 6c. The key step of the developed synthesis consists in the oxidative conversion of γ-exo-methylene-cyclopentanol systems of type 5 into β-methyl-α,β-cyclopentenones 6.

It was found that compounds of type 5 are easily available from the enantiomeric hydroxyacid 1b which is a residual by-product in Corey's famous prostaglandin synthesis[2]. For the resolution of the racemic hydroxyacid /1a + 1b/, /-/-threo-1-/p-nitrophenyl/-2-amino-1,3-propanediol was used[3]. In order to obtain optically pure 1b from the mother liquor, /+/--threo-1-/p-nitrophenyl/-2-amino-1,3-propanediol was applied according to the Marckwald principle.

For the preparation of cis-jasmone, the known bicyclic lactone alcohol 2a was prepared from 1b as reported previously[4,5]. From 2a through the intermediates 3a, 4a and 5a[6], cis-jasmone 6a identical in all respects with an authentic sample was obtained in 63 % overall yield.

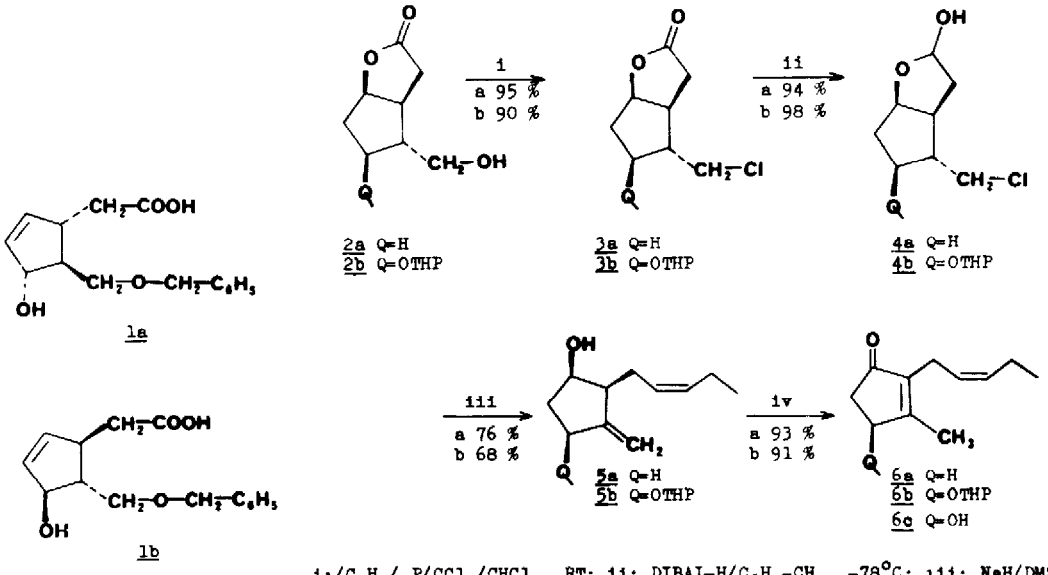
On considering that the isomerisation reaction does not affect the C_4 atom, the synthesis outlined above was extended to the preparation of rethrolones e. g. of cis-jasmololone 6c.

Compound 2b prepared from 1b in the course of the Corey synthesis[2,8] served here as starting material. On carrying out the above described sequence of reactions[6], 6b was obtained in 54 % overall yield.

Since the direct hydrolysis of 6b at room temperature in a 3 : 1 : 1 mixture of acetic acid : THF : water afforded 6c only in a moderate yield / 40 % /, the hydrolysis was carried out via the semicarbazide of 6b[9]. In that case 6c was obtained in 83.5 % yield / referred to 6b /, the spectroscopic data of the product being identical with the reported values whereas the $/\alpha/_D^{23.5}$ value was +9.2° / c = 10.3 in EtOH/.

Main attractive features of the developed synthesis especially in the case of 6c are its general usefulness /various rethrolones can be prepared

by choosing suitable Wittig partners[10]/, and the fact reported previously[11], namely the chirality of C_4 in 6c opposite to that of 1a which makes possible the preparation of /+/-cis-jasmololone of "natural configuration" from the enantiomer obtained as a so far useless by-product in Corey's prostaglandin synthesis.



i:/$C_6H_5/_3P/CCl_4/CHCl_3$, RT; ii: DIBAL-H/C_6H_5-CH_3, -78°C; iii: NaH/DMSO/ /$C_6H_5/_3P^+$-/$CH_2/_2CH_3$/ Br^-/, 40°C; iv: $CrO_3/H_2SO_4/H_2O$/ acetone, 0°C.

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