

ENANTIOSELECTIVE PHOTODECONJUGATION OF  $\alpha,\beta$ -UNSATURATED ESTERS IN  
 THE PRESENCE OF CATALYTIC AMOUNTS OF A CHIRAL-INDUCING ENTITY

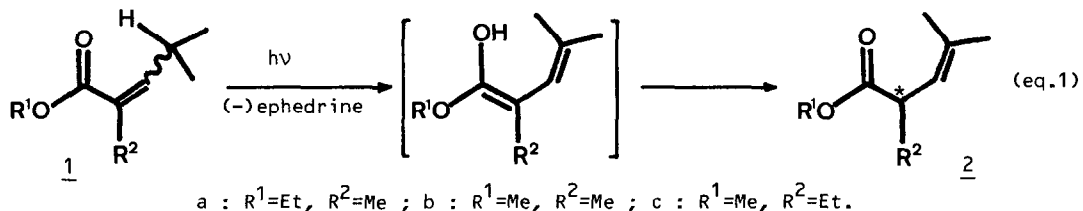
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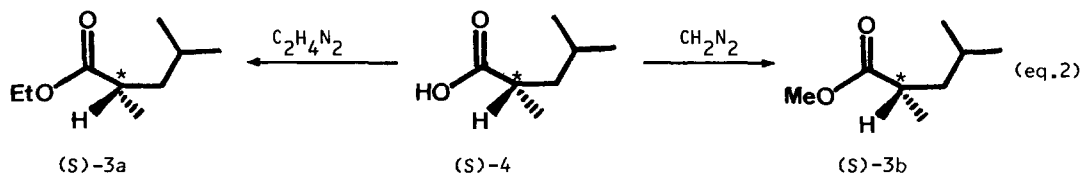
**Abstract :** In the presence of (-) ephedrine in small quantities, the photodeconjugation of  $\alpha,\beta$ -unsaturated esters is enantioselective and produces the R-enantiomer with an enantiomeric excess of up to 18%.

The photodeconjugation of  $\alpha,\beta$ -unsaturated esters<sup>(1)</sup> known for more than 20 years has recently been reinvestigated by several groups.<sup>(2)</sup> Very recently, we found that the photodeconjugation of  $\alpha$ -alkylidene lactones was enantioselective in the presence of small amounts of a chiral amino alcohol. When (-) ephedrine was used as the chiral-inducing entity, the configuration of the new asymmetric carbon was shown to be (R) for the major enantiomer.<sup>(3)</sup>

The conformational mobility of the  $\alpha$ -alkylidene lactones is restricted; we wondered if, in aliphatic esters, the mobility around the O-acyl bond might influence the enantioselectivity of the deconjugation. This communication describes the results obtained when esters 1a-1c were irradiated at  $\lambda = 254$  nm in the presence of (-) ephedrine.



When a solution of 1a ( $10^{-2}$  M) in  $\text{CH}_2\text{Cl}_2$  containing 0.1 equivalent of (-) ephedrine was irradiated at  $-78^\circ\text{C}$ , a fast E  $\rightleftharpoons$  Z isomerization of the starting ester was observed. For longer photolysis periods, 1a was cleanly transformed into 2a (yield = 68%;  $|\alpha|_D^{20} = -28.4 \pm 0.6^\circ$ ,  $c = 0.9$ , ether). An enantiomeric excess of  $16 \pm 3\%$  was determined from an NMR spectrum in the presence of  $\text{Eu}(\text{hfc})_3$ .<sup>(4)</sup> The R-configuration of the asymmetric center was established by comparison of the rotation of 3a obtained either from esterification of (S)-4<sup>(5)</sup> (eq. 2) or from hydrogenation of 2a.<sup>(6)</sup>



Irradiation of 1b under the same conditions produced 2b (yield = 67% ;  $|\alpha|_D^{20} = -15.1 \pm 0.4^\circ$ ,  $c = 0.9$ , ether) which showed an  $18 \pm 3\%$  enantiomeric excess from the NMR study. The R-configuration for the major enantiomer of 2b was established as precedently.<sup>(5,6)</sup>

Ester 1c possessed two types of  $\gamma$ -hydrogen atoms ; interestingly, irradiation of a hexane solution of 1c containing (-) ephedrine (0.1 eq.) led to a very clean deconjugation with formation of 2c (yield = 96% ;  $|\alpha|_D^{20} = -18.8 \pm 0.1^\circ$ ,  $c = 3.4$ , ether). The N.M.R. spectrum in the presence of  $\text{Eu}(\text{hfc})_3$  and the comparison of the specific rotation of the dihydro compound 3c ( $|\alpha|_D^{20} = -1.3 \pm 0.1^\circ$ ,  $c = 3.3$ , ether) with the rotation of an authentic sample of known optical purity<sup>(7)</sup> indicated an enantiomeric excess of  $12 \pm 2\%$  and a 2-R configuration for the major isomer.

In conclusion, photodeconjugation of  $\alpha,\beta$ -unsaturated esters in the presence of (-) ephedrine leads enantioselectively to the R-isomer as is the case for  $\alpha$ -alkylidene lactones. Work is presently in progress to generalize this reaction and to explain this enantioselectivity.

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#### References

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4.  $\text{Eu}(\text{hfc})_3 = \text{Tris} [3\text{-(heptafluoropropylhydroxymethylene)d-camphorato}] \text{europium}$ .
5. The acid(S)-4 ( $ee : 98 \pm 2\%$  ;  $|\alpha|_D^{20} = +20 \pm 0.5^\circ$ ,  $c = 0.86$ , ether) was obtained by resolution of the racemic acid ; the 2-S configuration of this enantiomer was known : D.A. Evans and J.M. Takacs, *Tetrahedron Lett.*, 1980, 20, 4233 ; P.A. Levene and R.E. Marker, *J. Biol. Chem.*, 1935, 111, 299. Esterification of this acid by  $\text{C}_2\text{H}_4\text{N}_2$  or  $\text{CH}_2\text{N}_2$  led respectively to (S)-3a ( $|\alpha|_D^{20} = +20.3 \pm 0.4^\circ$ ,  $c = 1.64$ , ether) or to (S)-3b ( $|\alpha|_D^{20} = +21.0 \pm 0.4^\circ$ ,  $c = 1.50$ , ether).
6. According to G. Suzukamo, M. Fukao and M. Tamura, *Tetrahedron Lett.*, 1984, 25, 1595, the hydrogenation on  $\text{PtO}_2$  does not affect the configuration at the allylic position. Hydrogenation of 2a and to 2b led respectively to 3a ( $|\alpha|_D^{20} = -4.2 \pm 0.2^\circ$ ,  $c = 0.95$ , ether) and to 3b ( $|\alpha|_D^{20} = -3.1 \pm 0.3^\circ$ ,  $c = 0.9$ , ether).
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