# Stereoselective Introduction of the Methoxycarbonyl Group into a Tetrahydrofluorenone 

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Summary Stereoselective introduction of the methoxycarbonyl group into the tetrahydrofluoren-9-one (1) giving the $9 \beta$-methoxycarbonyl derivative (5) has been achieved in high yield.

MuCh attention has been focused on the synthesis of hydrofluorenone derivatives which may serve as important intermediates in the total synthesis of gibberellins. ${ }^{1-4}$ Introduction of the methoxycarbonyl group into hydrofluorenones has also been studied., ${ }^{\mathbf{3} 4}$ We report here a stereoselective and efficient synthesis of the $9 \beta$-methoxycarbonyltetrahydrofluorene (5), which has a similar functionality to that of ring B in gibberellins, starting from the tetrahydrofluorenone (1a). ${ }^{1}$
Reaction of the trimethylsilyl ether (1b), m.p. $164^{\circ}$, with dimethylsulphonium methylide in anhydrous tetrahydro-furan(THF)-hexamethylphosphoric triamide $\left(-20^{\circ} \mathrm{C}\right.$; 30 min ) afforded stereoselectively the $\beta$-epoxide ( $\mathbf{2 b} \mathbf{b}) \dagger$ [m.p. $168{ }^{\circ} \mathrm{C}, \delta\left(\mathrm{CDCl}_{3}\right) 2 \cdot 87(1 \mathrm{H}, \mathrm{d}, J 4 \cdot 3 \mathrm{~Hz}, \mathrm{Hb}), 3 \cdot 41(1 \mathrm{H}, \mathrm{s}$, $9 \mathrm{a}-\mathrm{H}), 3 \cdot 66(1 \mathrm{H}, \mathrm{d}, J 4 \cdot 3 \mathrm{~Hz}, \mathrm{Ha})]$ in $90 \%$ yield as the sole product, while an epimeric mixture (3:1) of the $\beta$ - ( $2 \mathbf{b}$ ) and $\alpha$-epoxide (3b) [m.p. $155^{\circ}, \delta\left(\mathrm{CDCl}_{3}\right) 3 \cdot 13(1 \mathrm{H}, \mathrm{d}, J 4 \cdot 0 \mathrm{~Hz}$, $\mathrm{Ha}), 3.37(1 \mathrm{H}, \mathrm{s}, 9 \mathrm{a}-\mathrm{H})$, and $3.49(\mathrm{IH}, \mathrm{d}, J 4.0 \mathrm{~Hz}, \mathrm{Hb})]$ was obtained in $60 \%$ yield when the reaction was carried out in anhydrous $\mathrm{Et}_{2} \mathrm{O}-\mathrm{THF}$. Similar reactions of the acetate (1c) and the tetrahydropyranyl ether (1d) in anhydrous $\mathrm{Et}_{2} \mathrm{O}-\mathrm{THF}$ afforded a $1: 1$ epimeric mixture ( $30 \%$ yield) of (2c), m.p. 173-175 ${ }^{\circ}$, and (3c), m.p. 205-208 , and a $3: 2$ mixture ( $60 \%$ yield) of ( $\mathbf{2 d}$ ), m.p. $151-154^{\circ}$, and ( $\mathbf{3 d}$ ), m.p. $175-176^{\circ}$, respectively. The stereochemistry of the oxiran rings was assigned on the basis of NOE measurement.

Rearrangement of the $\beta$-epoxide (2b) with $\mathrm{BF}_{3}-\mathrm{Et}_{2} \mathrm{O}$ in anhydrous THF at $-20^{\circ}$ afforded exclusively the $\beta$-aldehyde (4b) [m.p. $\left.149^{\circ}, \delta\left(\mathrm{CDCl}_{3}\right) 9 \cdot 85(1 \mathrm{H}, \mathrm{d}, J 2 \cdot 2 \mathrm{~Hz})\right]$ in
$90 \%$ yield. A similar reaction of the acetate (2c) also gave the corresponding $\beta$-aldehyde (4c), m.p. $143^{\circ}$, in $70 \%$ yield; however, an epimeric mixture ( $6: 1$ ) of ( 4 c ) and its isomer was obtained ( $84 \%$ ) when the reaction was carried out in anhydrous $\mathrm{Et}_{2} \mathrm{O}$. A similar stereoselectivity was observed for the $\alpha$-epoxide (3c) : treatment of (3c) with $\mathrm{BF}_{3}-\mathrm{Et}_{2} \mathrm{O}$ in THF gave only the $\beta$-aldehyde ( 4 c ) ( $65 \%$ ), although reaction in $\mathrm{Et}_{2} \mathrm{O}$ gave a $1: 1$ epimeric mixture of the aldehydes.

(1)

(2)

(3)

(4) $\mathrm{R}^{2}=\mathrm{CHO}$
(5) $\mathrm{R}^{2}=\mathrm{CO}_{2} \mathrm{Me}$
$a ; R^{1}=H$
b; $\mathrm{R}^{1}=\mathrm{Me}_{3} \mathrm{Si}$
c; $R^{1}=A c$
d: $R^{1}=$ tetrahydropyranyl
$\dagger$ Satisfactory elemental analyses were obtained for all new compounds, and spectroscopic data obtained were in agreement with the structures shown. The product ratios indicated were estimated by n.m.r. spectroscopy.

Mild Jones oxidation ( $0^{\circ} ; \mathbf{3 0} \mathrm{s}$ ) of the $\beta$-aldehyde ( $\mathbf{4 b}$ ), and subsequent methylation and treatment with toluene- $p$ sulphonic acid yielded the $9 \beta$-methoxycarbonyl derivative (5a) [m.p. $145^{\circ}, m / e 332\left(M^{+}\right)$, $\nu_{\text {max }}\left(\mathrm{CHCl}_{3}\right) 3600,1775$, and $1745 \mathrm{~cm}^{-1}, \delta\left(\mathrm{CDCl}_{3}\right) 3.49(1 \mathrm{H}, \mathrm{d}, J 9 \cdot 2 \mathrm{~Hz}), 3.85(3 \mathrm{H}, \mathrm{s}), 3.88$ $(3 \mathrm{H}, \mathrm{s})$, and $3.88(1 \mathrm{H}, \mathrm{d}, J 9 \cdot 2 \mathrm{~Hz})]$ in $90 \%$ overall yield.

We thank Professor K. Nakanishi, Columbia University, for helpful advice, and Dr. S. Sato, Nichiden Varian Ltd., for NOE measurements.
(Received, 1st April 1974; Com. 373.)
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