

# Oxidation and the Hegershoff Reaction of *O*-Alkyl *N*-(3-Phenylpropenoyl)monothiocarbamates

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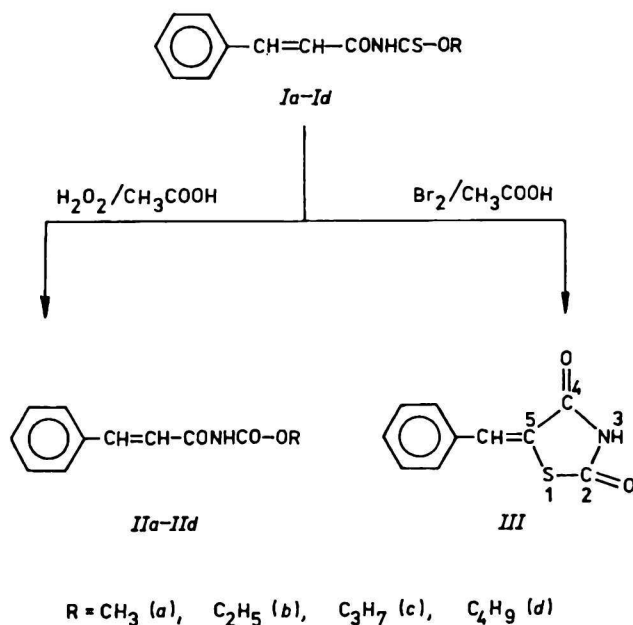
Oxidation and the Hegershoff reaction of *O*-alkyl *N*-(3-phenylpropenoyl)monothiocarbamates have been described. The structure of the synthesized products has been discussed on the basis of IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra.

In the previous paper [1] we dealt with synthesis of *O*-alkyl *N*-(3-phenylpropenoyl)monothiocarbamates and their cyclization in the presence of boron trifluoride and studied simultaneously the intermolecular rearrangement of *O*-methyl *N*-(3-phenylpropenoyl)monothiocarbamate to *S*-methyl ester by the method of crossed reactions.

The aim of the present work has been the oxidation of *O*-alkyl *N*-(3-phenylpropenoyl)monothiocarbamates *Ia—Id* with hydrogen peroxide in glacial acetic acid [2] under formation of *O*-alkyl *N*-(3-phenylpropenoyl)carbamates *Ila—Ild* (Scheme 1). In the IR spectrum of the presented compounds characteristic are the absorption bands belonging to stretching vibrations of the NH, C=O, and C=C groups. In the  $^1\text{H}$  NMR spectrum the most important signals are the two doublets for the  $-\text{CH}=\text{CH}-$  grouping at  $\delta = 7.58-7.91$

with the coupling constant  $J_{\text{AB}} = 16$  Hz, proving that derivatives *Ila—Ild* are all *trans* isomers.

We studied further the Hegershoff reaction [3] of *O*-alkyl esters *Ia—Id* with bromine in acetic acid. It was found that only one product, i.e. 5-benzylidene-1,3-thiazolidine-2,4-dione (*III*, Scheme 1) was formed by attack of sulfur on  $\alpha$ -carbon of the respective monothiocarbamic acid under simultaneous hydrolysis of the *O*-alkyl ester. The structure of compound *III* was confirmed by IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. Cyclization to thiazolidine *III* through  $\alpha$ -carbon was proved by the  $^{13}\text{C}$  NMR spectrum. The chemical shifts for alkene carbons C- $\alpha$  ( $\delta = 120$ ) and C- $\beta$  ( $\delta = 145$ ) of compounds *Ia—Id* [1] changed after cyclization as a consequence of attachment of the  $-\text{S}-\text{CO}-$  group to  $\alpha$ -carbon. While the signal for the C-5 carbon resonance of compound



Scheme 1

III (Scheme 1, analogue C- $\alpha$ ) was shifted downfield to  $\delta = 123.38$ , the signal for the benzylidene exocyclic  $-\text{CH}=\text{C}$  carbon (analogue C- $\beta$ ) was shifted upfield to  $\delta = 130.29$ . The changes presented correspond with the effect of the  $-\text{S}-\text{R}$  group on the  $^{13}\text{C}$  shifts of the  $\text{C}=\text{C}$  bond reported in [4].

## EXPERIMENTAL

O-Methyl (*Ia*), O-ethyl (*Ib*), O-propyl (*Ic*), and O-butyl (*Id*) N-(3-phenylpropenoyl)monothiocarbamates were prepared according to [1].

Infrared spectra were measured with a spectrometer IR 75 (Zeiss, Jena) in chloroform.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured with spectrometers BS 487 A (80 MHz) and 567 (25.15 MHz) (Tesla), respectively, in deuteriochloroform using tetramethylsilane as internal standard.

The reaction course was monitored by thin-layer chromatography on Silufol plates (Kavalier, Votice).

### O-Alkyl N-(3-Phenylpropenoyl)carbamates *Ila—Ild*

The compound *Ia—Id* (20 mmol) was dissolved in glacial acetic acid (4  $\text{cm}^3$ ) and a mixture of 30 % hydrogen peroxide (4  $\text{cm}^3$ ) in glacial acetic acid (6  $\text{cm}^3$ ) was added at continuous stirring. The reaction mixture was stirred at room temperature for 30 min. Then water was added until formation of a precipitate, which was sucked, dried, and crystallized from ethanol.

*O-Methyl N-(3-phenylpropenoyl)carbamate (Ila)*, yield 44 %, m.p. = 123—124 °C. For  $\text{C}_{11}\text{H}_{11}\text{NO}_3$  ( $M_r = 205.2$ )  $w_i(\text{calc.})$ : 64.38 % C, 5.40 % H, 6.83 % N;  $w_i(\text{found})$ : 64.53 % C, 5.48 % H, 6.97 % N. IR spectrum,  $\tilde{\nu}/\text{cm}^{-1}$ : 1610  $\nu(\text{C}=\text{C})$ , 1655 and 1735  $\nu(\text{C}=\text{O})$ , 3400  $\nu(\text{NH})$ .  $^1\text{H}$  NMR spectrum,  $\delta$ : 3.83 (s,  $\text{CH}_3$ ), 7.54 (m,  $\text{C}_6\text{H}_5$ ), 7.58 and 7.90 (d, d,  $\text{CH}=\text{CH}$ ),  $J_{\text{AB}} = 16$  Hz, 8.18 (s, NH).

*O-Ethyl N-(3-phenylpropenoyl)carbamate (Iib)*, yield 40 %, m.p. = 119—120 °C. For  $\text{C}_{12}\text{H}_{13}\text{NO}_3$  ( $M_r = 219.2$ )  $w_i(\text{calc.})$ : 65.74 % C, 5.98 % H, 6.39 % N;  $w_i(\text{found})$ : 65.86 % C, 6.08 % H, 6.47 % N. IR spectrum,  $\tilde{\nu}/\text{cm}^{-1}$ : 1605  $\nu(\text{C}=\text{C})$ , 1655 and 1730  $\nu(\text{C}=\text{O})$ , 3998  $\nu(\text{NH})$ .  $^1\text{H}$  NMR spectrum,  $\delta$ : 1.36 (t,  $\text{CH}_3$ ), 4.33 (q,  $\text{CH}_2$ ), 7.62 (m,  $\text{C}_6\text{H}_5$ ), 7.68 and 7.97 (d, d,  $\text{CH}=\text{CH}$ ),  $J_{\text{AB}} = 16$  Hz, 7.93 (s, NH).

*O-Propyl N-(3-phenylpropenoyl)carbamate (Iic)*, yield 37 %, m.p. = 125—126 °C. For  $\text{C}_{13}\text{H}_{15}\text{NO}_3$  ( $M_r = 233.3$ )  $w_i(\text{calc.})$ : 66.94 % C, 6.48 % H, 6.01 % N;  $w_i(\text{found})$ : 66.99 % C, 6.53 % H, 6.13 % N. IR spectrum,  $\tilde{\nu}/\text{cm}^{-1}$ : 1607  $\nu(\text{C}=\text{C})$ , 1667 and 1733  $\nu(\text{C}=\text{O})$ , 3400  $\nu(\text{NH})$ .  $^1\text{H}$  NMR spectrum,  $\delta$ : 0.96 (t,  $\text{CH}_3$ ), 1.71 (m,  $\text{CH}_2$ ), 4.17 (t,  $\text{CH}_2$ ), 7.51 (m,  $\text{C}_6\text{H}_5$ ), 7.58 and 8.87 (d, d,  $\text{CH}=\text{CH}$ ),  $J_{\text{AB}} = 16$  Hz, 7.98 (s, NH).

*O-Butyl N-(3-phenylpropenoyl)carbamate (Iid)*, yield 53 %, m.p. = 110—111 °C. For  $\text{C}_{14}\text{H}_{17}\text{NO}_3$  ( $M_r = 247.3$ )  $w_i(\text{calc.})$ : 68.00 % C, 6.93 % H, 5.66 % N;  $w_i(\text{found})$ : 68.12 % C, 7.04 % H, 5.78 % N. IR spectrum,  $\tilde{\nu}/\text{cm}^{-1}$ : 1610  $\nu(\text{C}=\text{C})$ , 1666 and 1733  $\nu(\text{C}=\text{O})$ , 3997  $\nu(\text{NH})$ .  $^1\text{H}$  NMR spectrum,  $\delta$ : 0.95 (t,  $\text{CH}_3$ ), 1.15—1.90 (m,  $\text{CH}_2-\text{CH}_2$ ), 4.23 (t,  $\text{CH}_2$ ), 7.58 (m,  $\text{C}_6\text{H}_5$ ), 7.62 and 7.91 (d, d,  $\text{CH}=\text{CH}$ ),  $J_{\text{AB}} = 16$  Hz, 8.05 (s, NH).

### 5-Benzylidene-1,3-thiazolidine-2,4-dione (III)

The compound *Ia—Id* (20 mmol) was dissolved in glacial acetic acid (15  $\text{cm}^3$ ) and bromine (20 mmol) was added dropwise. Then the mixture was stirred at room temperature for 1 h. After addition of water the formed precipitate was sucked, dried, and crystallized from ethanol. Yield 38—41 %, m.p. = 229—231 °C. For  $\text{C}_{10}\text{H}_7\text{NO}_2\text{S}$  ( $M_r = 205.2$ )  $w_i(\text{calc.})$ : 58.52 % C, 3.44 % H, 6.83 % N;  $w_i(\text{found})$ : 58.65 % C, 3.59 % H, 6.97 % N. IR spectrum,  $\tilde{\nu}/\text{cm}^{-1}$ : 1610  $\nu(\text{CH}=\text{C})$ , 1655 and 1715  $\nu(\text{C}=\text{O})$ , 3434  $\nu(\text{NH})$ .  $^1\text{H}$  NMR spectrum,  $\delta$ : 7.76 (m,  $\text{C}_6\text{H}_5$ ), 8.00 (s,  $\text{CH}=\text{C}$ ), 12.65 (s, NH).  $^{13}\text{C}$  NMR spectrum,  $\delta$ : 122.38 (s, C-5), 129.17 and 129.88 (d, d, *meta*-C, *ortho*-C), 132.90 (s, *ipso*-C), 131.78 and 130.29 (d, d, *para*-C,  $-\text{CH}=\text{C}$ ), 167.61 and 167.01 (s, s, C-2, C-4).

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