

## Short Communications

A Glutaconaldehyde Enol Ester with *cis* Configuration \*

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All enol esters of glutaconaldehyde (derivatives of 5-hydroxy-2,4-pentadienal) hitherto described have been shown<sup>1</sup> to have the thermodynamically stable all-*trans* structure inherited from the glutaconaldehyde anion<sup>2</sup> (*1*). These esters may be prepared by acylation of the glutaconaldehyde anion (*1*) with carboxylic acid anhydrides, acyl chlorides or with acyl isothiocyanates. In the case<sup>3</sup> of *N,N*-dimethyl carbamoyl chloride the usual all-*trans*-enol ester (*4*) was the reaction product, while *N,N*-dimethylcarbamoyl isothiocyanate yielded a 1-(*N,N*-dimethylcarbamoyl)-3-formyl-2-(1*H*)-pyridinethione (*5*).

We now report that reaction of the glutaconaldehyde anion (*1*) with ethoxycarbonyl isothiocyanate, when carried out at a higher temperature, unexpectedly gives a mixture of isomers. Thus *1* and ethoxycarbonyl isothiocyanate at 20°C in DMF yielded \*\* a mixture

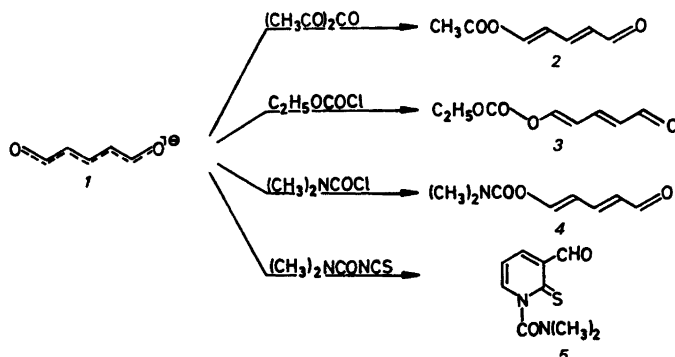
\* Part 10 in the series "Derivatives and Reactions of Glutaconaldehyde".

\*\* Higher temperature leads to decomposition. A control experiment with the reaction temperature at -50°C resulted in the formation of the all-*trans*-isomer *3* only.

of the two isomers *3* and *6* in the ratio 2.7:1. Repeated PLC was necessary for the separation. The structure depicted for *6* was assigned on the following basis.

When the UV spectra of the isomers were compared it was found (*cf.* Experimental) that *6* showed a significantly lower extinction coefficient than *3*. Correspondingly the <sup>1</sup>H NMR spectrum of *6* showed a coupling constant  $J_{4,5} = 6$  Hz, whereas  $J_{4,5} = 12$  Hz for the *trans* isomer *3*, the remaining coupling constants being identical. These results are in excellent agreement with results<sup>4</sup> for similar double bonds in other dienes. Furthermore the <sup>13</sup>C NMR spectra of *3* and *6* showed small differences in the shifts of carbons 3, 4 and 5, with the shift values for the *trans*-isomer (*3*) at a slightly lower field, as found in the <sup>13</sup>C NMR spectra of other *cis*- and *trans*-alkenes.<sup>5</sup> On this basis it can be concluded that the isomer *6* has the depicted structure with *cis*-configuration at the 4,5-enol double bond.

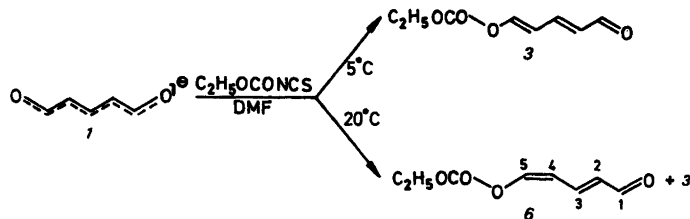
The formation of the *cis*-isomer *6* at higher temperature may be the result of a kinetically controlled reaction. In the reactions of *1* and organic alkyl or aryl isothiocyanates, formation of a stable intermediate anion has been demonstrated.<sup>6</sup> It therefore can be concluded that the course of the reactions of *1* with organic isothiocyanates is very dependent upon the reagent. It is worth mentioning that the ester (*3*) is much more stable than the corresponding acetate (*2*). This enhanced stability towards hydrolysis is probably due to the steric effect<sup>7</sup> of the methyl hydrogens.



Scheme 1.

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Scheme 2.

**Experimental.** Microanalyses were carried out at the Microanalytical Department of the University of Copenhagen by Mr. P. Hansen. Instrumentation: IR, Perkin Elmer 457. UV, Beckman ACTA III.  $^1\text{H}$  NMR, Jeol, JNM-PMX 60  $^{13}\text{C}$  NMR, Jeol FX 60. M.p. Büchi apparatus (uncorrected).

*O*-Ethoxycarbonyl-5-hydroxy-trans-2-trans-4-pentadienal (3). The all-trans isomer (3) was prepared as previously described.<sup>5</sup> To compare with the other isomer the detailed data for 3 are given here. Analytically pure 3 has m.p. 67–69°C (ether, pentane).

IR (KBr): 985 s (C=C trans), 941 s (absent in 6), 1745 s (ester CO)  $\text{cm}^{-1}$ .

UV abs. [ethanol ( $\epsilon$ ): 274 (36 900) nm.

$^1\text{H}$  NMR (60 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  9.46(H-1, d,  $J$  7.5 Hz), 7.36(H-3, dd,  $J$  12 and 15 Hz), 7.71(H-5, d,  $J$ , 12 Hz), 6.31(H-4, dd,  $J$  12 and 15 Hz), 6.11(H-2, dd,  $J$  15 and 7.5 Hz), 4.25 ( $\text{CH}_2$ , q,  $J$  6.8 Hz), 1.28 ( $\text{CH}_3$ , t,  $J$  = 6.8 Hz).

$^{13}\text{C}$  NMR[15.03 MHz,  $\text{CDCl}_3$ ]:  $\delta$  193.4(C1), 131.6(C2), 147.5(C3), 113.1(C4), 148.9(C5), 151.4(C6), 65.3(C7), 13.8(C8) Hz.

*O*-Ethoxycarbonyl-5-hydroxy-trans-2-cis-4-pentadienal (6). To glutacanaldehyde potassium salt (3 g), dissolved in DMSO (10 ml), was added ethoxycarbonyl isothiocyanate (3 ml) at 20°C while stirring was continued for 20 min, whereupon the reaction mixture was added to ice-cold water (100 ml). Extraction with ether, drying ( $\text{Na}_2\text{SO}_4$ ), filtration and concentration *in vacuo* yielded yellow crystals (1.79 g).  $^1\text{H}$  NMR and TLC showed the reaction product to be a mixture of isomers. Repeated PLC<sup>8</sup> (3 times) on silica gel (Merck Kieselgel 60 PF) with ether/pentane (4/6) as eluent resulted in the separation of two fractions. Isolation and extraction of these two fractions with ethyl acetate gave 0.22 g of the *cis*-isomer (6) with the highest  $R_F$  value followed by 0.59 g of all-trans-isomer (3). Redissolving the *cis*-isomer (6) in ether, addition of activated carbon, filtration and evaporation gave colourless crystals, m.p. 78–81°C. Anal.  $\text{C}_8\text{H}_{10}\text{O}_4$ : C, H.

IR (KBr): 985 s (C=C trans), 661 m (C=C *cis*, absent in 3), 1765 s (ester CO)  $\text{cm}^{-1}$ .

UV abs. [ethanol ( $\epsilon$ ): 275 (20 082) nm.

$^1\text{H}$  NMR (60 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.60 (H-1, d,  $J$  8 Hz), 7.56(H-3, dd,  $J$  15 and 12 Hz), 7.26 (H-5, d,  $J$  6 Hz), 6.20(H-4, dd,  $J$  15 and 6 Hz),

5.77(H-2, dd,  $J$  12 and 8 Hz), 4.33( $\text{CH}_2$ , q,  $J$  7 Hz), 1.38 ( $\text{CH}_3$ , t,  $J$  7 Hz).

$^{13}\text{C}$  NMR[15.03 MHz,  $\text{CDCl}_3$ ]:  $\delta$  193.4(C1), 131.6(C2), 141.8(C3), 109.9(C4), 142.8(C5), 151.5(C6), 65.3(C7), 13.8(C8) Hz.

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