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EQUILIBRATION OF METHYL 3-OXO-CIS-,10-OXO-CIS- AND 10-OXO-TRANS-CYCLOUNDEC-1-ENECARBOXYLATES

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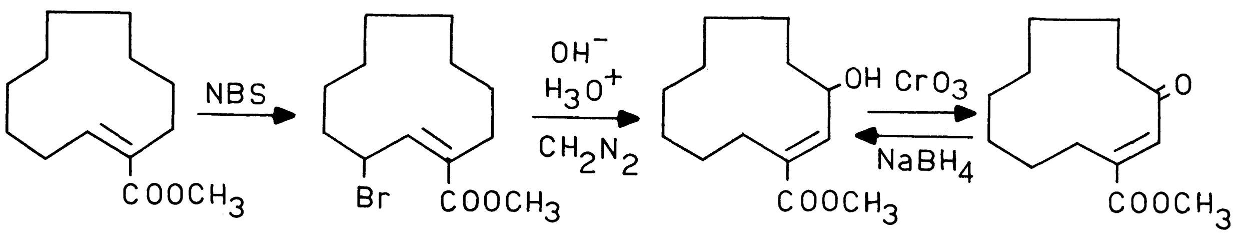
Methyl 3-oxo-cis-cycloundec-1-enecarboxylate (3) and the corresponding Δ^3-isomers,methyl 10-oxo-cis-and 10-oxo-trans-cycloundec-1-enecarboxylates (5) and (4),were synthesized.Equilibration using 1,5-diazabicyclo [4.3.0]non-5-ene as a basic catalyst gave very different results in comparison with those reported for analogous systems with 7-10 membered ring.

Equilibration of 3-methoxycarbonylcycloalkenones with ring sizes from 7 to 10 has been reported.$^{1)}$ The results of the equilibration experiments indicate that less od the Δ^2-isomer is present at equilibrium than for unsubstituted cycloalkenones.$^{2)}$

We report here the preliminary results of the equilibration experiments on methyl 3-oxo-cis-cycloundec-1-enecarboxylate (3) and the corresponding Δ^3-isomers,methyl 10-oxo-cis- and 10-oxo-trans-cycloundec-1-enecarboxylates (5) and (4).

The Δ^2-isomer (3) was prepared from methyl trans-cycloundec-1-enecarboxylate.$^{3)}$



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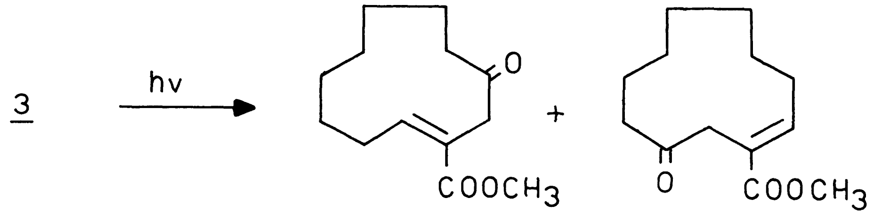
Allylic bromination,with NBS in CCl_4,afforded the 3-bromoderivative (1) $^{4)}$ in 45% yield.[(1),m.p. 64° from n-hexane; λ_{max}^{EtOH} 233 (9323);ir (nujol) ν_{CO} at 1712 cm^{-1},$\nu_{C=C}$ at 1635 cm^{-1};nmr (60 MHz,$CDCl_3$,δ) 6.7 (1H,d,J=12 Hz,vinyl proton) 4.9(1H,m,CHBr) 3.75(3H,s,$COOCH_3$)].Alkaline treatment of the bromoester (1) [(1), 20 g,KOH 16 g,H_2O 25 ml,DMSO 160 ml,1 h at 50°] gave the salt of the corresponding hydroxyacid, from which methyl 3-hydroxycycloundec-1-enecarboxylate (2) was obtained by acid treatment,extraction and CH_2N_2 esterification in an averall yield of 55%.[(2),m.p.54° from Et_2O-n-pentane; λ^{EtOH}_{max} 220(9038);ir(nujol)ν_{OH}at 3500 cm^{-1},ν_{CO} at 1695 cm^{-1},$\nu_{C=C}$ at 1640 cm^{-1};nmr (60 MHz,CCl_4,δ)6.55(1H,d,J=11 Hz,vinyl proton) 4.5(1H,m,CHOH) 3.72(3H,s,$COOCH_3$) 2.47(1H,s,OH) 2.45(2H,m,allylic methylene)].Jones oxidation$^{5)}$ of the hydroxyester (2) afforded the ketoester (3) in quantitative yield.[(3), m.p.64° from n-hexane; λ^{EtOH}_{max} 238 (7394);ir(nujol) ν_{CO} at 1710 and 1685 cm^{-1},$\nu_{C=C}$ at 1612 cm^{-1};nmr (60 MHz,$CDCl_3$,δ) 7.15(1H,s,vinyl proton) 3.78(3H,s,$COOCH_3$) 2.76(2H,m) 2.45(2H,m)].

The two Δ^3-isomers,(4) and (5),were obtained from (3) by photochemical reaction [high pressure Hg lamp, HPK 125 W Philips,pyrex filter,benzene solution]followed by separation by silica gel; the ratio (5)/(4) was 2.33.[(4),b.p.$_{0.2}$ 108-112°; λ^{EtOH}_{max} 217 (5823); ir (film) ν_{CO} at 1710 cm^{-1}(broad),$\nu_{C=C}$ at 1635 cm^{-1};nmr (100 MHz,$CDCl_3$,δ) 6.08(1H,t,J=7.6 Hz,vinyl proton) 3.83(3H,s,$COOCH_3$) 3.3(2H,s,$COCH_2$- C=C) 2.64(2H,m)2.39(2H,m). (5),m.p.57° from n-pentane; λ^{EtOH}_{max} 220 (7247);ir (nujol) ν_{CO} at 1715 and 1700 cm^{-1},$\nu_{C=C}$ at 1645 cm^{-1};nmr (100 MHz,$CDCl_3$, δ) 6.96(1H,t,J=8.5 Hz,vinyl proton) 3.79(3H,s,$COOCH_3$) 3.57(2H,s,$COCH_2$C=C) 2.37 (2H,m)].



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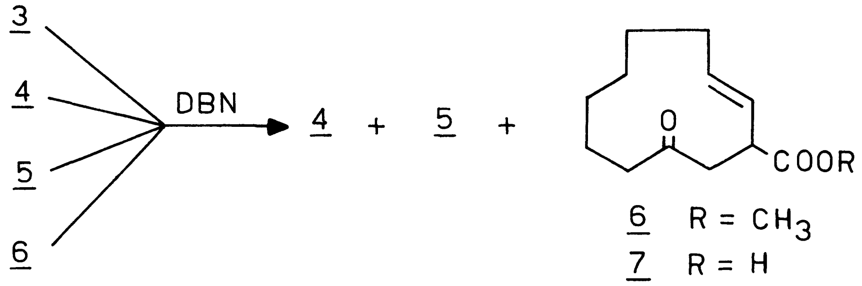
Stereochemical assignment rests only on the chemical shift of the vinyl protons in (4) and (5) as in the case of the corresponding cyclodecene derivatives.$^{1)}$ Analysis of the vinyl proton region of the nmr spectrum ($CDCl_3$) of the photolysate mixture obtained at short irradiation time shows the presence of four unsaturated compounds : the starting Δ^2-isomer (3) [40%, s at 7.15 ppm], the cis- Δ^3-isomer (5) [30%, t at 6.96 ppm],the trans- Δ^3-isomer (4) [10%, t at 6.08 ppm]and a "transient" compound [20%,s at 6.42 ppm] which we suggest to be a stereoisomer of the starting material (3). On the basis of the chemical shift of the vinyl proton of the two Δ^2-isomers,(3) was assigned to cis stereochemistry.$NaBH_4$ reduction of (3) affords the parent hydroxyester (2);therefore we tentatively suggest an inversion of the double bond configuration during nucleophilic bromine substitution of (1) in strong alkaline conditions.

Equilibration experiments were carried out using 1,5-diazabicyclo[4.3.0] non-5-ene [DBN] in refluxing benzene as described by Hirsch and Lin$^{1)}$, but the results were very different from those reported for analogous systems with 7-10 membered ring. From ($\underline{3}$),($\underline{4}$) and ($\underline{5}$)the same mixture [($\underline{4}$) 5%, a novel compound ($\underline{6}$) 39% and ($\underline{5}$) 56%[6]]was obtained.



The new isomer ($\underline{6}$) was isolated by crystallisation of the equilibrium mixture from n-pentane followed by column chromatography of the mother liquors[SiO_2,eluent n-hexane : n-hexane-Et_2O 10:1].Alkaline hydrolysis of the resulting crude ($\underline{6}$) afforded the corresponding acid ($\underline{7}$). [($\underline{7}$),m.p.100-102° from Et_2O].CH_2N_2 esterification of ($\underline{7}$) afforded ($\underline{6}$) in a pure state. [($\underline{6}$),b.p.$_{0.2}$ 110-112°;ir (film) ν_{CO} at 1730 and 1710 cm^{-1}, 980 cm^{-1} (-CH=CH-, trans); nmr (100 MHz,$CDCl_3$,δ) 5.5 (2H,m,vinyl protons) 3.68 (3H,s,$COOC\underline{H}_3$) 3.5 (1H,m,$C\underline{H}COOCH_3$)].

From ($\underline{6}$) also, the same equilibration mixture was obtained. The structure of methyl 10-oxo-trans-cycloundec-2-enecarboxylate ($\underline{6}$) was assigned on the basis of the analytical and spectral data. Spin decoupling experiments proved the structure by establishing coupling between the proton at C_1 and the olefinic protons.

In the case of methyl cis-and trans- cycloundec-1-enecarboxylate no double bond migration was observed under the above described experimental conditions.

The formation of ($\underline{6}$) can be reasonably explained by taking into account a proximity effect of the CO ketonic group on the hydrogen atoms at C_3 position of ($\underline{5}$). The Dreiding models examination also supports this hypothesis.

The kinetic study of the interconversion of ($\underline{3}$),($\underline{4}$),($\underline{5}$) and ($\underline{6}$) is in progress.

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