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CARBONIUM ION REARRANGEMENT IN THE SYNTHESIS OF γ-LACTONES FROM (*E*)-β-ALKYLCINNAMIC ACIDS

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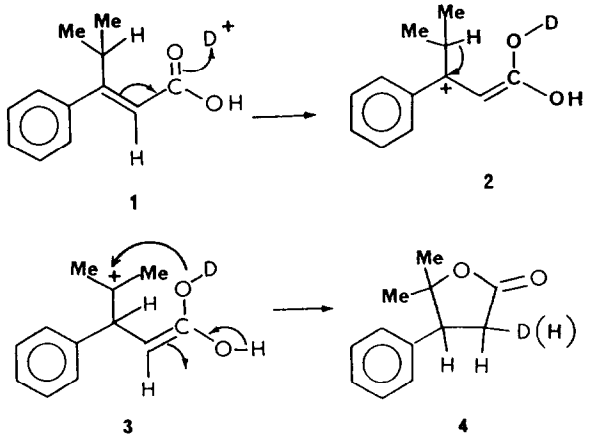
Abstract A possible formation of a bridged carbonium ion intermediate in the lactonization of (*E*)-β-*t*-butylcinnamic acid is discussed on the basis of deuteriation and ^{13}C NMR experiments.

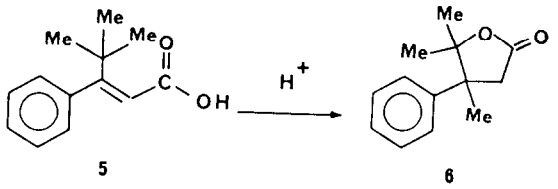
In a previous paper we presented a method for the synthesis of some γ-lactones and 3-alkylideneindanones starting from β-alkylated cinnamic acids.[1] We found that the *E*-isomers of the β-alkylcinnamic acids which contain a tertiary γ-carbon form γ-lactones and that the isomers with secondary γ-carbons does not cyclisize to lactones but to 3-alkylidene-1-indanones. The reaction mechanism for the formation of the lactones was discussed on the basis of deuteriation experiments. The results of these experiments indicate that an internal hydride shift is the dominating pathway (Scheme 1).



Scheme 1

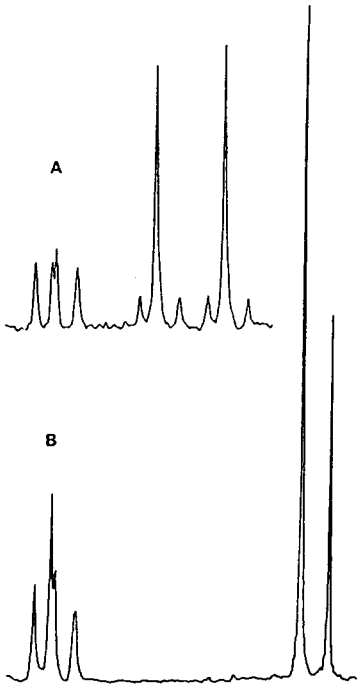
In the present study, the cyclization of (*E*)-β-*t*-butylcinnamic acid (5, Scheme 2), which contains a quaternary γ-carbon, is presented. The cyclization of the *E*-isomer gave 3,4-dimethyl-3-

-phenyl-γ-valerolactone (*6*, Scheme 2).



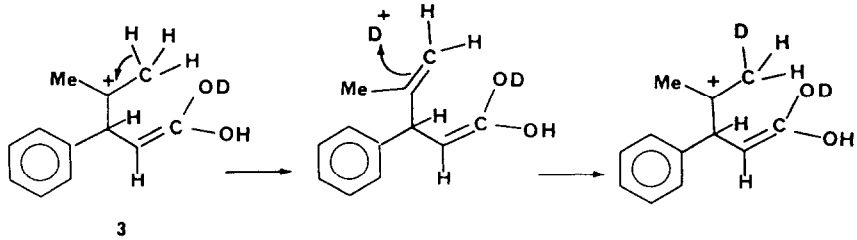
Scheme 2

This result provides further evidence for the hydride shift reported previously,[1] since the formation of *6* has to be the result of carbonium ion rearrangement in which the methyl group with its binding electrons acts as an internal nucleophile.



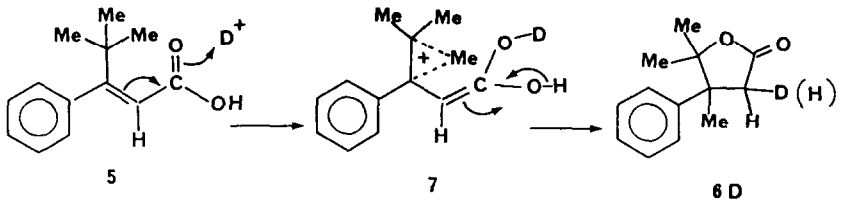
A deuterium exchange of the methyl hydrogens takes place when *1* is treated with deuteriated sulfuric acid which can be the result of "hyperconjugation". The deuterium exchange was established on the basis of the CD-triplets upfield from the undeuteriated methyl singlets in the ^{13}C NMR spectrum. The ^{13}C NMR spectrum (Fig. 1, B) shows that no deuterium exchange in the methyl groups took place in the lactonization of *t*-butylcinnamic acid although the same carbonium ion as that shown in Scheme 1 should be present in this reaction, provided that the lactonization proceeds by the mechanism shown in Scheme 1 and that the deuterium exchange is a consequence of double bond formation shown in Scheme 3.

Fig. 1. Proton decoupled 15.03 MHz ^{13}C NMR spectra of C-α and the methyl groups in the deuterium derivatives of *4* (spectrum A) and *6*D (spectrum B).



Scheme 3

The absence of deuterium exchange in the lactonization of *t*-butylcinnamic acid indicates a somewhat diverging reaction mechanism. I therefore propose that the methyl group transfer, contrary to the hydride transfer, might proceed through a bridged carbonium ion, resembling a nonclassical ion,[2] as shown in Scheme 4.



Scheme 4

In *7* the positive charge is spread across a three-carbon region with a two-electron three-center bond which should decrease the possibility for double bond formation in comparison with the more isolated positive charge in carbonium ion *3*. In *7*, if present in the reaction, deuterium exchange by double bond formation is scarcely likely because it would imply still one penta-coordinated carbon atom besides the one already involved in the bridged carbonium ion *7*.

Thus the deuterium exchange through "hyperconjugation" in the methyl group, in the lactonization of isopropylcinnamic acid, indicates that this reaction does not proceed through a hydrogen bridged carbonium ion. The deuterium exchange at C-α of *4* and *6D* was not complete which is seen from the CH_2 singlet of C-α in the ^{13}C NMR spectrum (Figure 1). This shows that a proton transfer from the hydroxyl group also operates. It is probable that the deuterium atom at C-α, which appears as a CD triplet in the ^{13}C NMR spectrum, originates from the OD group and not from secondary reactions after the cyclization because a deuterium exchange at C-α was not observed when *6* was treated with deuteriated sulfuric acid for 4 h at 20 °C. Deuterium at C-α was, however, completely interchanged to hydrogen when the lactone from a deuteriation experiment was hydrolyzed with sodium hydroxide and converted to the corresponding γ-hydroxy acid which spontaneously cyclisized back to the undeuteriated lactone when treated with hydrochloric acid.

Mass spectra were recorded on a VG-7070 E instrument (70 eV) equipped with a gas chromatograph (50 x 0,2 mm glass capillary column, stationary phase SE-30). ^1H NMR spectra were obtained on a Jeol FX-60 FT NMR spectrometer at 59.75 MHz and ^{13}C NMR spectra on the same instrument operating at 15.03 MHz. $CDCl_3$ was used as solvent and TMS as an internal standard.

(*E*)-3-*t*-butylcinnamic acid was prepared by alkaline hydrolysis of the corresponding ethyl cinnamate, which was prepared from ethyl (*Z*)-3-chloro-3-phenylpropenoate in a CuI catalyzed

Grignard reaction.[3]

3,4-Dimethyl-3-phenyl-γ-valerolactone (*6*). (*E*)-3-*t*-butylcinnamic acid (1 g) was added to 20 cm^3 concentrated sulfuric acid at 0 °C. After a reaction time of 4 h at 20 °C the mixture was poured into ice. The solid was filtered off and recrystallized from a mixture of light petroleum and diethyl ether. The yield was 0.72 g (72 %), mp. 88-90 °C.

MS *m/z* (% rel. int.): 189 (2), 176 (2), 146 (5), 145 (4), 118 (100), 103 (14), 91 (11), 78 (12), 77 (99), 43 (10).

^{1}H NMR: δ 1.01 (3H, s), 1.48 (3H, s), 1.60 (3H, s), AB-quartet centered at 2.95 (2H, q 16, 8 Hz), 7.32 (5H, s).

^{13}C NMR: δ 23.3 (CH_3), 25.2 ($2CH_3$) this signal was split into two singlets when analyzed in a mixture of $CDCl_3$:DMSO-d_6=1:1, 41.7 (C-2), 49.2 (C-4), 88.9 (C-3), 126.0, 127.3, 128.8, 142.3 (Ph), 175.0 (C=O).

The lactonization of (*E*)-3-*t*-butylcinnamic acid with deuteriated sulfuric acid was carried out in the same way as that with ordinary sulfuric acid. The main reaction product was a deuterio derivative of 3,4-dimethyl-3-phenyl-γ-valerolactone (*6*D) with varying degree of deuteriation in the phenyl ring.

^{1}H NMR: δ 1.01 (3H, s), 1.49 (3H, s), 1.61 (3H, s), AB-quartet centered at 2.96 (2H, q 16.8 Hz), 2.38 and 3.38 (1H, s), 7.26 (broad).

^{13}C NMR: δ 23.3 (CH_3), 25.2 ($2CH_3$), 41.5 (CD, t 21 Hz), 41.7 (C-2), 49.1 (C-4), 89.0 (C-3), 125.9-142.3 (Ph), 175.1 (C=O).

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