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Short Communication

An unusual reaction course in Rh(I)-induced decarbonylation of γ,δ-unsaturated aldehyde. Total synthesis of (±)-iso-β-necrodol and (±)-β-necrodol†

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Abstract

Decarbonylation of the γ,δ-unsaturated aldehydes (**4** and **9**), embodied in a sterically congested carbon network, with Wilkinson's catalyst followed a reaction course different from the normal decarbonylation or hydroacylation path. This investigation has led to the synthesis of iso-β-necrodol and the monoterpene β-necrodol.

Keywords: Monoterpene, decarbonylation, Wilkinson's catalyst, β-necrodol.

Decarbonylation of aldehydes is generally achieved by using Wilkinson's catalyst $[Rh(PPh_3)_3Cl]$.[1] In the case of γ,δ-unsaturated aldehydes, an alternative path, viz. hydroacylation[2] competes favourably with decarbonylation to form cyclopentanone derivatives. The reaction of γ,δ-unsaturated aldehydes with Rh(I) catalyst to form cyclopentanones has been extensively employed in natural products synthesis.[3] In connection to our interest[4] in the synthesis of cyclopentane derivatives, we undertook a synthesis[5] of the insect repellent monoterpene β-necrodol (**5**).[6] We envisioned that decarbonylation of the aldehyde functionality in the γ,δ-unsaturated aldehyde (**4**) would lead to the natural product. We now report that decarbonylation of the γ,δ-unsaturated aldehyde (**4**) with Wilkinson's catalyst follows an unprecedented reaction course different from hydroacylation or normal decarbonylation path leading to iso-β-necrodol (**6**) as the major product along with β-necrodol (**5**).

The γ,δ-unsaturated aldehyde (**4**) required for this purpose was obtained from the diol (**1**)[5] using the sequence delineated in Scheme 1. The diol (**4**) was converted to the divinyl ether (**2**) in 68% yield on treatment with excess of ethyl vinyl ether in the presence of $Hg(OAc)_2$ at room temperature. Heating a toluene solution of the vinyl ether (**2**) in a sealed tube at 180°C for 24 h effected smooth rearrangement to afford the aldehyde (**3**) along with its *cis*-isomer in ~8:1 ratio (from integration of the methyl signals in the ^1H NMR spectrum) in quantitative yield. Stereo-

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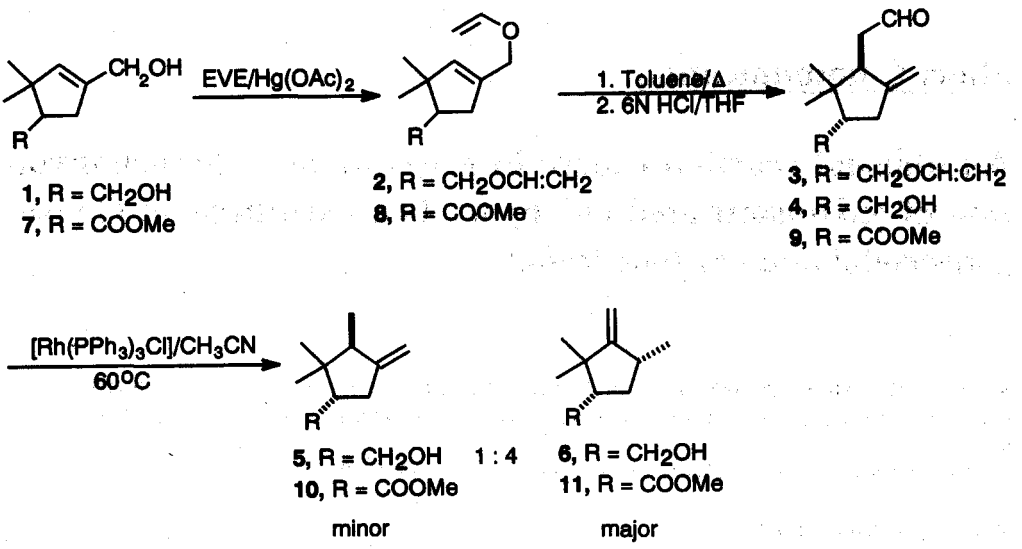
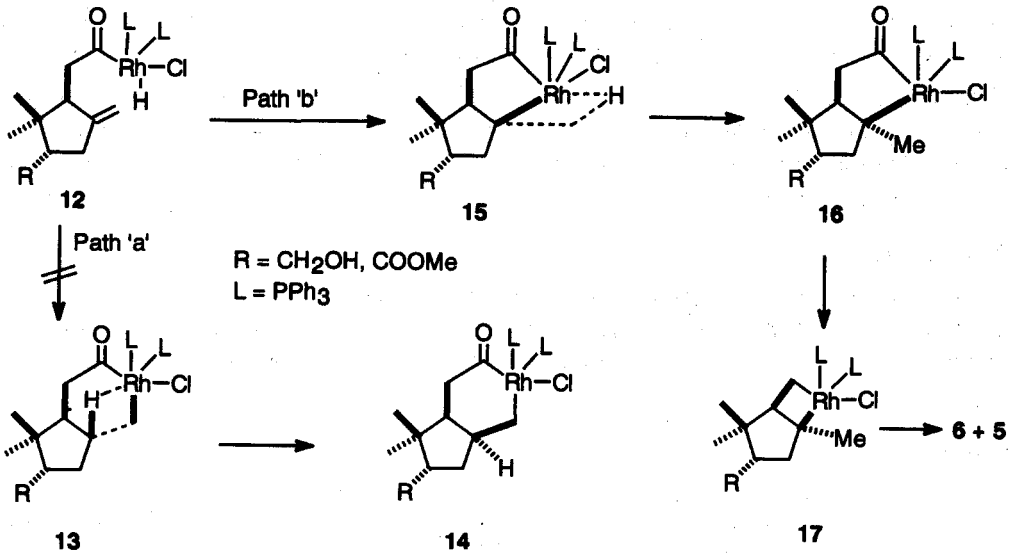


Scheme 1.

chemical assignment to the major isomer (**3**) as *trans* was based on comparison of the chemical shifts of the geminal methyls with those reported in the literature[6a] for β-necrodol (**5**) and epi-β-necrodol. Thus the chemical shifts of the geminal methyls in the major isomer (δ 0.88 and 0.97) were closely comparable to those reported for β-necrodol (δ 0.80 and 0.92). For the minor isomer the chemical shifts of the geminal methyls (δ 0.60 and 1.09) were comparable to those reported for *epi*-β-necrodol (0.51 and 1.04). Brief treatment of this mixture with 10% aqueous HCl led to the hydroxy aldehyde (**4**) along with its *cis*-isomer in 91% yield. The formation of the *trans*-isomer (**4**) as the major product from Claisen rearrangement of the vinyl ether (**2**) was attributed to be the result of the C–C bond formation from the face opposite[7] to the C_3-substituent. Decarbonylation of the aldehyde (**4**) was carried out by stirring a suspension of its acetonitrile solution with Wilkinson's catalyst at 60°C for 1½ h. The product obtained as a volatile liquid in 53% yield after chromatographic purification did not have a carbonyl absorption in IR indicating that complete decarbonylation had taken place without any hydroacylation. A molecular ion peak at *m/z* 154 in the EIMS of the product also supported decarbonylation. ^{1}H and ^{13}C NMR spectra of the product showed it to be a mixture of mainly two components in the ratio 4:1 from integration of the methyl signals. The minor one of these two components of the mixture had ^{1}H [0.82 (s), 0.93 (d, J = 7 Hz) and 0.94 (s)] and ^{13}C NMR (δ 13.5, 23.1, 23.7) chemical shifts of the methyls identical to those reported[6a] for β-necrodol (**5**). The major component in this mixture displayed NMR spectra [^{1}H 0.88 (s, 3 H), (1.11, d, J = 6.7 Hz, 3 H), 1.16 (s, 3 H), 3.56 (dd, J = 7.9 and 10.5 Hz, 1 H), 3.75 (dd, J = 5.8 and 10.5 Hz, 1 H), 4.76 (d, J = 2.5 Hz, 1 H), 4.80 (dd, J = 2.3 and 5.2 Hz) and ^{13}C 19.5, 24.5, 29.3, 64.1, 102.6 and 167.8] characteristic of two quaternary methyls, one secondary methyl, one hydroxy methylene and one exomethylene—all that required for β-necrodol but with different chemical shifts. Based on these data the major component in the mixture was assigned the structure **6**, which we named as iso-β-necrodol.



Scheme 2.

To determine whether the electronic nature of the C_3-substitutent (R) has any influence on the observed reaction course, the unsaturated aldehyde (**9**) was chosen. It was prepared in quantitative yield via Claisen rearrangement of the vinyl ether (**8**) derived from the hydroxy ester (**7**). The unsaturated aldehyde (**9**) on reaction with Wilkinson's catalyst afforded similarly the unexpected product (**11**) [^{1}H NMR: 0.90 (3H, s), 1.14 (3H, d, J = 6.6 Hz), 1.27 (3H, s), 3.68 (3H, s)] along with the normal decarbonylation product (**10**)[6a] in 3:1 ratio in ca. 50% yield. The stereochemical assignments to the products **6** and **11** are based on their mode of formation as delineated in Scheme 2.

An unsuccessful attempt[6a] to isomerise the double bond of pure β-necrodol (**5**) with Wilkinson's catalyst suggests the involvement of a different mechanism for the formation of the isomeric products. The unusual formation of iso-β-necrodol (**6**) and the ester (**11**) from Rh(I)-induced decarbonylation of the unsaturated aldehydes (**4** and **9**) may be explained by the well-established mechanisms for hydroacylation[2,8] and decarbonylation. The acylhydridorhodium (III) complex (**12**) first formed through oxidative addition of the catalyst into –CO-H bond undergoes an intramolecular *syn* Rh-H addition to the double bond presumably through the four center transition states (TS) (**13** or **15**) to form either a six-membered acylalkyl metallacycle (**14**) (path 'a') or a five-membered metallacycle **16** (path 'b'). The involvement of a six-membered metallacycle analogous to **14** has been invoked in hydroacylation of γ,δ-unsaturated aldehydes to produce cyclopentanones. The absence of any hydroacylation product in the present case suggests strong preference for the formation of the five-membered metallacycle **16** (path 'b'). Decarbonylation of **16** then leads to the rhodiacyclobutane derivative (**17**), which then collapses to the observed isomeric olefins. The involvement of an analogous rhodiacyclobutane has been invoked[8] to explain the formation of 1-pentene as a minor product during hydroacylation of 4-hexenal. The diversion of reaction course from path 'a' to path 'b' in the

present example is possibly due to the strain involved in criscross mode of addition of Rh-H as shown in TS **13** over the fused mode of addition in TS **15**.

In conclusion, we have demonstrated for the first time that decarbonylation of γ,δ-unsaturated aldehydes under steric constraint may follow a reaction course different from simple decarbonylation or hydroacylation. This investigation has led to the synthesis of iso-β-necrodol and β-necrodol.

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