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†

SUSANTA SAMAJDAR, ANJAN GHATAK, SHYAMAPADA BANERJEE AND SUBRATA GHOSH*
Department of Organic Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700 032, India.
email: ocsg@mahendra.iacs.res.in; Phone: 91-33-4734971; Fax: 91-33-4732805.

Received on October 3, 2000.

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(PPh₃)₃Cl].¹ In the case of γ,δ-unsaturated aldehydes, an alternative path, viz. hydroacylation² 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 interest⁴ in the synthesis of cyclopentane derivatives, we undertook a synthesis⁵ 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-

¹Dedicated to Prof. S. C. Bhattacharyya.
*Author for correspondence
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\textsuperscript{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\textsuperscript{7} to the C\textsubscript{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 \textit{m}/\textit{z} 154 in the EIMS of the product also supported decarbonylation. \textsuperscript{1}H and \textsuperscript{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 \textsuperscript{1}H [0.82 (s), 0.93 (d, \(J = 7\) Hz) and 0.94 (s)] and \textsuperscript{13}C NMR (δ 13.5, 23.1, 23.7) chemical shifts of the methyls identical to those reported\textsuperscript{6a} for β-necrodol (5). The major component in this mixture displayed NMR spectra [\textsuperscript{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 \textsuperscript{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.
To determine whether the electronic nature of the C3-substituent (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) [1H NMR: 0.90 (3H, s), 1.14 (3H, d, J = 6.6 Hz), 1.27 (3H, s), 1.68 (3H, s)] along with the normal decarbonylation product (10) 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 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 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 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 crisscross 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 \( \gamma,\delta \)-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-\( \beta \)-necrodol and \( \beta \)-necrodol.

Acknowledgement

We are grateful to Professor Animesh Chakraborty of the Inorganic Chemistry Department of this Institute for valuable advice. Financial support from the Council of Scientific and Industrial Research (CSIR), New Delhi, is gratefully acknowledged. SPB thanks CSIR for a fellowship.

References


2. Larock, R. C., Oertle, K. and Potter, G. F.


3. Sattelkaul, T. and Eilbracht, P.


b. Patra, D. and Ghosh, S.


c. Ghosh, S., Patra, D. and Samajdar, S.


e. Samajdar, S., Patra, D. and Ghosh, S.


f. Ghosh, S., Patra, D. and Saha, G.


5. Samajdar, S., Ghatak, A. and Ghosh, S.


