Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 1994, **4(3)**, 88
Mendeleev Communications

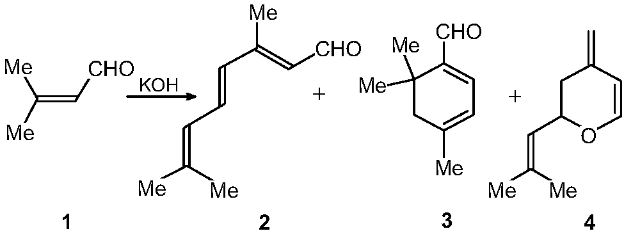
Alkali-catalysed Self-condensation of 3-Methylbut-2-enal: Formation of Novel Ros-oxide Dehydro Analogue

Irina A. Dyakonova, Georgii V. Cherkaev and Mark B. Erman*

Research Institute of Synthetic and Natural Fragrances, 117393 Moscow, Russian Federation. Fax: +7 095 334 7944

Alkali-catalysed self-condensation of 3-methylbut-2-enal **1** gives, along with the earlier reported products **2** and **3**, a novel rosoxide dehydro analogue **4**.

The base-catalysed self-condensation of 3-methylbut-2-enal **1** has for a long time been believed to give two aldehydes, **2** and **3**, in a ratio which depends on the reaction conditions.[1–3] Taking into account the growing availability of the starting aldehyde **1**[4] and the potential of this compound as a terpenic synthon, we have now revised its self-condensation and found that, besides the aforementioned products **2** and **3**, a hitherto unknown compound **4** is formed in considerable amounts over a wide range of reaction conditions (Scheme 1).



Scheme 1

For example, stirring 0.21 mol of freshly distilled aldehyde **1** with 0.021 mol of powdered KOH in 100 ml of dry ether for about 4 h at ±5 °C affords, upon neutralization and vacuum distillation, a mixture of **2**, **3** and **4** in the ratio ~2:3:5 (GLC), respectively, and total yield about 80%. At higher temperatures (> 15 °C), aldehydes **2** and **3** become predominant. A similar picture is observed, with but lower yields, in some other solvents as well, and even with an aqueous solution of KOH as the condensing agent. Compound **4** was isolated by column chromatography on silica gel and characterised comprehensively by elemental and spectral analyses.[†]

Despite two "extra" double bonds, compound **4** possesses an odour clearly resembling that of its well-known natural structural analogue – rosoxide[5] – and may therefore find a use in perfumery.

In our opinion, the formation of **4** can be attributed to cyclization of dehydrocitral **2**, probably *via* its enol form.

References

1 F. G. Fischer and K. Löwenberg, *Liebigs Ann. Chem.*, 1932, **494**, 263.
2 W. G. Young and S. L. Linden, *J. Am. Chem. Soc.*, 1947, **69**, 2912.
3 A. F. Thomas and R. Guntz-Dubini, *Helv. Chim. Acta*, 1976, **59**, 2261.
4 See, for example, M. B. Erman, Dr. Sci. Thesis, Moscow, 1991, p. 158.
5 See, for example, E. H. Eschinasi, *J. Org. Chem.*, 1970, **35**, 1097.

Received: Moscow, 31st January 1994
Cambridge, 18th February 1994; Com. 4/00751D

[†] ^{1}H NMR (250 MHz, $CDCl_3$, standard $SiMe_4$) and ^{13}C NMR (62.9 MHz, $CDCl_3$) data: δ_H 1.71 and 1.76 (3H and 3H, 2m, $Me_2C{=}$), 2.38 and 2.46 (1H and 1H, 2m, CH_2), 4.51 and 4.73 (1H and 1H, 2m, $CH_2{=}$), 4.61 (1H, m, CH–O), 5.28 (1H, dqq, *H*C=CMe$_2$), 5.39 and 6.46 (1H and 1H, 2br.d, HC=CH); δ_C 18.20 and 25.59 (2Me), 36.22 (–CH_2–), 73.42 (–CH–O), 105.47 and 146.01 (HC=CH), 106.67 and 137.49 ($CH_2{=}C$), 123.81 and 137.00 (*C*H=*C*Me$_2$).