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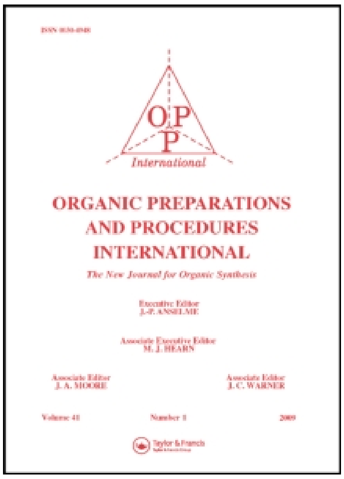

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A STEREOSELECTIVE APPROACH TO Z-ALLYLIC ALCOHOLS

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A STEREOSELECTIVE APPROACH TO Z-ALLYLIC ALCOHOLS

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(10/9/79)

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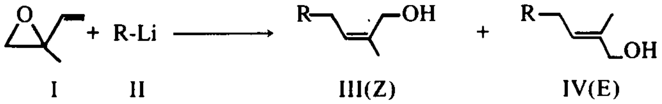
A detailed procedure for the synthesis of Z-allylic alcohols via the selective reaction of alkyllithium compounds with isoprene monoxide[1] is described.[2]



EXPERIMENTAL

Infrared spectra were recorded for carbon tetrachloride solutions with a Perkin Elmer 283 spectrophotometer. Gas chromatographic analyses were determined with a Perkin Elmer 3920 gas chromatograph. N.m.r. spectra were recorded with a Varian A60 spectrometer, and the data reported as δ in parts per million downfield from tetramethylsilane (internal standard, $\delta = 0$). Microanalyses were performed by Galbraith Laboratories.

General Procedure. 2-Methyl-2-octen-1-ol (III,IV, R = n-butyl). – To a stirred solution of 5.5 mmole n-butyllithium (1.6M in hexane) and 10 ml anhydrous ethyl ether, at -77°C under argon, was added 5 mmole isoprene monoxide (I).[3] After 12 hours at -77°C, the reaction mixture was warmed to room temperature over 15 minutes.[4] Saturated sodium dihydrogen phosphate (30 ml) was added and the mixture was extracted with 80 ml ethyl ether. The ether extract was dried over sodium sulfate, then the ether was removed at aspirator pressure, leaving 0.72 g residue. Purification of the crude product (0.63 g) by column chromatography on silica gel, using 3:1 petroleum ether:ethyl ether as eluent, gave 0.60 g (97% pure yield) of the conjugate addition products.

Anal. Calcd. for $C_9H_{18}O$: C, 75.99; H, 12.76

Found: C, 75.80; H, 12.97

IR (CCl_4, cm^{-1}): 3640-s, 3630-s, 3500, 2970-s, 2935-s, 2930-s, 2880-s, 2860, 2730, 1675, 1465-s, 1455-s, 1380-s, 1355, 1185, 1115, 1100, 1080, 1005-s, 100-s, 940, 910, 870, 860. NMR analyses of the 1,4 addition products were in agreement with those previously reported.[5] Glpc analysis (8 ft. x ¼ inch, 5% UCON LB 550X, 60/80 Chromosorb W, 120°C) showed the two distinct peaks of the isomeric alcohols: t_{rZ}20 minutes, t_{rE}23 minutes, with an E:Z ratio of 16:84.

In a similar manner was prepared:

2,5,5-Trimethyl-2-hexen-1-ol (III,IV, R = t-butyl) in 92% yield.

Anal. Calcd. for $C_9H_{18}O$: C, 75.99; H, 12.76

Found: C, 75.84; H, 12.68

IR (CCl_4, cm^{-1}): 3640-m, 3630-m, 3500, 3365, 2965-s, 2955-s, 2945-s, 2935-s, 2925-s, 2915-s, 2905-s, 2895-s, 2885-s, 2875-s, 2865-s, 2720, 1670, 1475-s, 1470-s, 1450-s, 1440-m, 1395-s, 1380-s, 1365-s, 1325, 1290, 1240-m, 1195-m, 1185-m, 1140, 1095-m, 1045, 1040, 1005-s, 1000-s, 940, 910, 900, 870, 860. NMR Z-isomer ($CDCl_3$, δ): 0.88 (9H, s), 1.53 - 2.07 (5H, m), 4.03 (2H, s), 5.30 (1H, t, 7Hz); NMR E-isomer ($CDCl_3$, δ): 0.88 (9H, s) 1.53 - 2.07 (5H, m), 3.93 (2H, s), 5.30 (1H, t, 7Hz). Glpc: t_{rZ} 17 minutes, t_{rE} 20 minutes, with an E:Z ratio of 13:87.

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2. For reviews see a) D. J. Faulkner, Synthesis, 175 (1971); b) J. Rewcroft and P. J. Sammes, Q. Rev. Chem. Soc., *25*, 135 (1971).
3. Electron donors, such as TMEDA and HMPA, did not improve yield, and no marked salt effect was observed when LiBr was added to the mixture.
4. Substantial reduction in yield was not observed when the length of time that the reaction was held at -77°C was decreased. When isoprene monoxide was stirred with n-butyllithium in ethyl ether at -77°C for 3½ hours the allylic alcohol was formed in 86% yield, while the E:Z ratio was unchanged.
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