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An Ene-type Reaction of Thionyl Chloride with Linear Isoprenoids

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A diethylaluminium chloride-catalysed ene-type reaction of thionyl chloride with citronellyl, geranyl and linalyl acetates, followed by treatment of the reaction mixture with methanol, leads smoothly to the corresponding allylic methyl sulfinates.

To the best of our knowledge, thionyl chloride, unlike sulfinyl chlorides,[1,2] has never been used in an ene-type reaction with alkenes. Here we report such a transformation, involving linear monoterpenes **1a–c**.

In a typical experiment, a solution of **1a** in dichloromethane was treated at −40°C under argon with thionyl chloride (1.5 mol equiv.), followed by a solution of diethylaluminium chloride in heptane (3 mol equiv.). The reaction mixture was kept at −20°C for 30 min and then decomposed at this temperature with an excess of methanol in the presence of pyridine. Subsequent standard isolation of the final product, including column chromatography over silica gel, gave the methyl sulfinate **2a** in *ca.* 80% yield as an oil. The esters **2b,c** (Scheme 1) were obtained analogously in up to 75% isolated yield.

The structure of allylic sulfinates **2** as *ca.* 1:1 mixtures of the

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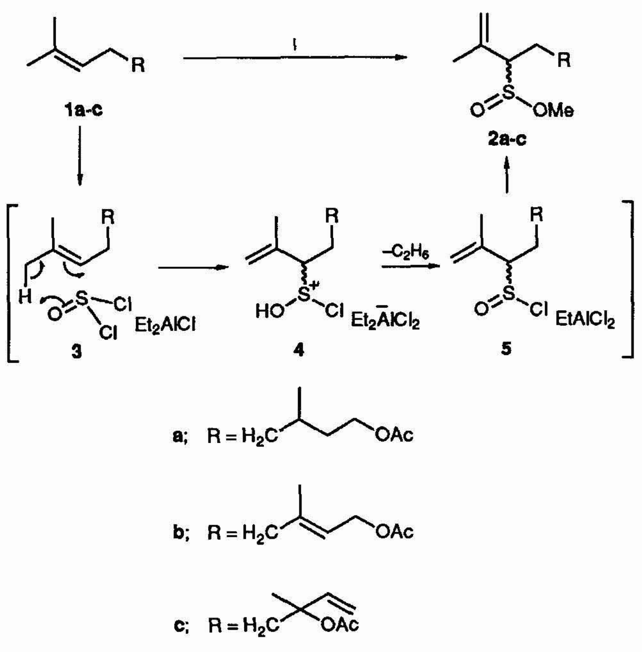

Scheme 1 *Reagents*: i, 1, $SOCl_2$–Et_2AlCl; 2, MeOH–Py (70–80%)

respective diastereoisomers in all cases was established on the basis of their combustion and spectral† analysis data. The formation of these compounds is thought to proceed *via* ethylaluminium chloride intermediates **3**–**5** (Scheme 1). It is noteworthy that geranyl acetate **1b** reacts with thionyl chloride as it does with benzenesulfinyl chloride,[2] chemoselectively with exclusive attack at its isopropylidene group.

References

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† ^1H *NMR data* (250 MHz, $CDCl_3$) for **2a**: δ 0.89 and 0.90 (3H, d, *J* 6 Hz, Me), 1.1–1.9 (7H, m, CH, CH_2), 1.76 and 1.78 (3H, br s, Me), 2.01 (3H, s, MeCO), 3.07 (1H, m, HCS), 3.74 and 3.76 (3H, s, MeO), 4.05 (2H, m, CH_2O), 4.93, 4.98, 5.10 and 5.15 (2H, br s, $H_2C{=}C$).

2b: δ 1.71 (7H, br s, Me-C^6), 1.80 and 1.82 (3H, br s, Me-C^2), 1.9–2.2 (4H, m, CH_2), 2.05 (3H, s, MeCO), 3.11 (1H, m, HCS), 3.77 and 3.79 (3H, s, MeO), 4.57 (2H, d, CH_2O), 4.96, 5.01, 5.14 and 5.19 (2H, br s, $H_2C{=}C$), 5.35 (1H, t, *J* 7 Hz, HC^7).

2c: δ 1.53 (7H, br s, Me-C^6), 1.6–2.0 (4H, m, CH_2), 1.75 and 1.77 (3H, br s, Me-C^2), 1.99 (3H, s, MeCO), 3.06 (1H, m, HCS), 3.73 and 3.75 (3H, s, MeO), 4.9–5.2 (4H, m, $H_2C{=}C$), 6.90 (1H, dd, *J* 17.7 and 10.7 Hz, $HC{=}CH_2$).