

pound has an  $\omega$ -lactone ring with only one methyl side chain located on C-12, as in II.

The formation of the ions  $m/e$  171 and 153, analogues of which are not present in the spectrum of unbranched macrolides, can be rationalized as shown in scheme 1. McLafferty rearrangement of the C-12 hydrogen followed by cleavage of the bond  $\beta$  to the newly formed double bond would form a fragment of  $m/e$  171. Loss of water from this ion would produce the  $m/e$  153 ion.

**Experimental.** Gas chromatography was performed on a Hewlett-Packard 7620 A instrument with 6 mm  $\times$  3 m stainless steel columns packed with 10% FFAP or 5% SE-30 on Chromosorb W AW. IR spectra were recorded on a Perkin-Elmer 521 instrument. Mass spectra were run on a JEOL JMS-D 100 mass spectrometer at the Technical Research Center of Finland.  $^1\text{H}$  NMR spectra were determined in  $\text{CDCl}_3$  on a JEOL JMM PFT 100 spectrometer in the Department of Organic Chemistry, University of Helsinki.

The isolation of angelica root oil and separation of the fraction containing the oxygenated compounds have been described before.<sup>3</sup>

**12-Methyl- $\omega$ -tridecanolide.** About 0.2 mg of II was separated gas chromatographically from the oxygenated fraction of angelica root oil.

MS:  $m/e$  (%) 226 ( $\text{M}^+$ , 5), 211 (2), 208 (14), 198 (4), 196 (5), 193 (3), 190 (3), 171 (9), 160 (8), 165 (8), 153 (18), 152 (11), 139 (9), 124 (14), 111 (25), 98 (41), 97 (36), 84 (34), 83 (42), 69 (67), 56 (61), 55 (100), 41 (96). IR:  $\nu_{\text{max}}$  2920, 2875, 1735, 1458, 1375, 1345, 1235, 1170, 1145, 1105, 1060, 1007  $\text{cm}^{-1}$ . NMR:  $\delta$  ( $\text{CDCl}_3$ ) 0.92 (3 H, d,  $J$  6.8 Hz), 2.38 (2 H, m), 3.68 (1 H, doublet of doublets,  $J$  10.7 and 8.3 Hz), 4.20 (1 H, doublet of doublets,  $J$  10.7 and 3.4 Hz).

$\omega$ -Pentadecanolide was obtained from K&K laboratories.

The lactones were hydrolyzed using 10% alcoholic KOH at room temperature. The hydroxy acids were taken up into pentane and methylated with diazomethane.

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## Synthesis of Triallylmethane

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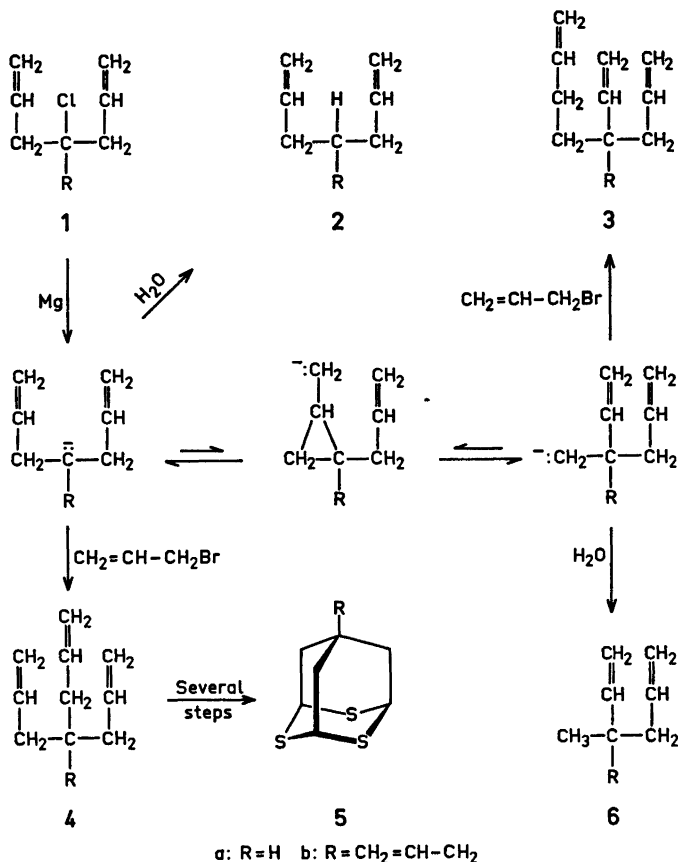
The aim of this note is to report the preparation of pure triallylmethane (**4a**), which was needed for the synthesis of 2,4,9-trithiaadamantane (**5a**).

In 1963, Shelden<sup>1</sup> treated the Grignard reagent from diallylmethyl chloride (**1a**) with allyl bromide. He obtained about equal amounts of **4a** and an isomer, believed to be 4-allyl-1,7-octadiene (**3a**), but failed to separate the products. In 1968, Reeve and Bianchi<sup>2</sup> obtained tetraallylmethane (**4b**) and 4-allyl-4-vinyl-1,7-octadiene (**3b**) from triallylmethyl chloride (**1b**) in the same way. They explained the formation of **3b** by the rearrangement shown in Scheme 1.

Following a suggestion by Shelden,<sup>1</sup> we have now prepared **4a** (= **2b**) by hydrolyzing the Grignard reagent from **1b**. 4-Methyl-4-vinyl-1,6-heptadiene (**6b**) was obtained as a by-product but the isomers **4a** and **6b** were cleanly separated by distillation through a spinning band column. Their purity was checked by GLC analysis, and their identity established by  $^1\text{H}$  NMR spectroscopy (see Experimental). Thus, the integration of either spectrum showed 7 paraffinic and 9 olefinic protons. The latter belong to three vinyl groups, since the elemental analyses and boiling points confirmed the molecular formula  $\text{C}_{10}\text{H}_{16}$ . Spin decoupling of the vinyl hydrogens revealed six allylic protons in **4a** and four in **6b**. The coupling of the remaining paraffinic proton in **4a** to all six allylic protons and the absence of further coupling in **6b** exclude alternative structures. As shown in Scheme 1, both **6b** and Shelden's product **3a** are the rearranged hydrocarbons predicted by the mechanism of Reeve and Bianchi.

As might have been expected, the mass spectrum of **4a** showed no molecular peak but was dominated by peaks due to the allyl cation ( $m/e$  41, 100%) and to the loss of an allyl radical ( $m/e$  95, 47%). In the spectrum of **6b**, the former peak (75%) was weaker than the latter (100%). This difference may be due to the fact that the fragmentations of **6b** are doubly allylic. Otherwise, the mass spectra as well as the IR spectra of the two isomers were quite similar.

**Experimental.** Freshly distilled triallylmethyl chloride (**1b**, 40 g, 0.23 mol) was prepared and converted to the Grignard reagent according to Reeve and Bianchi.<sup>2</sup> The resulting solution was poured on to a stirred mixture of ether (100 ml), 2 M hydrochloric acid (200 ml) and crushed ice (200 g). The organic layer was separated, washed with water and dried with magnesium sulfate. The ether was removed by rotary evaporation below 20°C and the residue



Scheme 1.

distilled *in vacuo* through a short column. GLC analysis of the distillate collected at 30–45 °C/10 mmHg showed **4a** (8 g, 25 %) and **6b** (3 g, 10 %). Redistillation through a 60 cm tall spinning band column (reflux ratio 20:1) yielded six fractions.

**4-Methyl-4-vinyl-1,6-heptadiene (6b)**. The second fraction consisted of pure **6b** (1.0 g, 3 %), b.p. 38–39 °C/10 mmHg,  $n_D^{20}$  1.4476. IR,  $\nu_{\max}$  (neat): 912vs (broad), 997s, 1375m, 1415m, 1440m, 1458m, 1620s, 2840w, 2920s, 2980s, 3000w, 3080s cm<sup>-1</sup>. <sup>1</sup>H NMR  $\delta$  (CCl<sub>4</sub>): 0.94 (3 H, s), 2.03 (4 H, broad d, *J* 7 Hz), 4.9 (6 H, m), 5.7 (3 H, m). (Found: C 88.2; H 11.9. Calc. for C<sub>10</sub>H<sub>16</sub>: C 88.2; H 11.8).

**4-Allyl-1,6-heptadiene (triallylmethane, 4a)**. The last fraction consisted of pure **4a** (6.4 g, 20 %), b.p. 43–44 °C/10 mmHg,  $n_D^{20}$  1.4520. IR,  $\nu_{\max}$  (neat): 912vs, 995s, 1344w, 1412m, 1442s, 1622s, 2840w, 2918s, 2980s, 3000w, 3080s cm<sup>-1</sup>. <sup>1</sup>H NMR,  $\delta$  (CCl<sub>4</sub>): 1.57 (1 H, septet, *J* 6.2 Hz), 2.04 (6 H, broad t, *J* 7 Hz), 4.96 (6 H, broad d, *J* 12 Hz), 5.7 (3 H, m). (Found: C 88.4; H 11.7. Calc. for C<sub>10</sub>H<sub>16</sub>: C 88.2; H 11.8).

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