A New Type of Olefinic Cyclization of Geraniol with Thallium(III) Perchlorate

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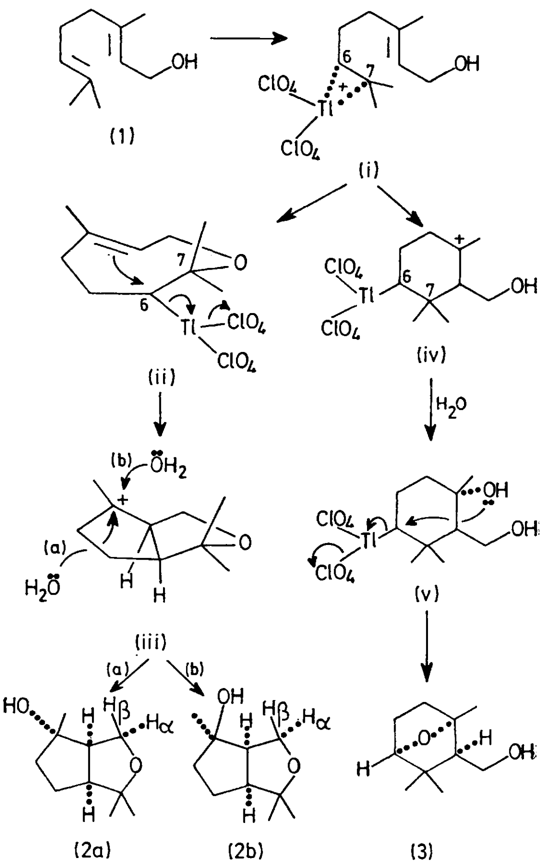
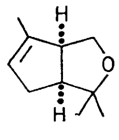
Summary A new type of olefinic cyclization was observed in the reaction of geraniol (**1**) with thallium(III) perchlorate to give three new carbocyclic products (**2a**), (**2b**), and (**3**).

RECENTLY we found that thallium(III) perchlorate in aqueous media was a useful reagent for the synthesis of *p*-quinols[1] from *p*-alkyl phenols. Although this reagent was also used for the ring contraction[2] and vicinal hydroxylation[3] of mono-olefins, little work has been reported on the reaction of polyolefins. We investigated the reaction of the terpene dienol geraniol (**1**) with $Tl(ClO_4)_3$ leading to three novel carbocyclic products, (**2a**), (**2b**), and (**3**). This is a new type of olefinic cyclization of geraniol (**1**).

The reagent was prepared[1] by dissolving Tl_2O_3 (6·0 g) in 60% perchloric acid (100 ml), followed by dilution with a tenfold volume of water in order to prevent acid-catalysed side reactions. Treatment of geraniol (**1**) (2·0 g) in CH_2Cl_2 (80 ml) with the diluted $Tl(ClO_4)_3$ solution (1150 ml, *ca.* 2 equiv.) at room temperature for 2 h with vigorous stirring gave (**2a**), (**2b**), and (**3**); we suggest mechanism indicated for their formation: (**2a**)† [49% yield;‡ m.p. 37 °C, ν_{max} ($CHCl_3$) 3600 and 3400 cm^{-1}, n.m.r. ($CDCl_3$) δ 1·20 (3H, s), 1·26 (3H, s), 1·33 (3H, s), 3·53 (1H, dd, *J* 10·0 and 5·2 Hz, H_β), and 3·85 (1H, t, *J* 10·0 Hz, H_α]; (**2b**) [11%; b.p. 85—90 °C at 18 mm Hg, ν_{max} ($CHCl_3$) 3400 cm^{-1}, n.m.r. ($CDCl_3$) δ 1·18 (3H, s), 1·27 (3H, s), 1·30 (3H, s), 3·72 (1H, dd, *J* 10·0 and 6·8 Hz, H_α), and 4·04 (1H, dd, *J* 10·0 and 2·0 Hz, H_β]; and (**3**) [31%; b.p. 140—150 °C at 18 mmHg, ν_{max} ($CHCl_3$) 3600 and 3400 cm^{-1}, n.m.r. ($CDCl_3$) δ 0·94 (3H, s), 1·12 (3H, s), 1·48 (3H, s), 3·64 (2H, m, $-CH_2-OH$), and 3·82 (1H, d, *J* 4·0 Hz, $-CH-O-$)].



The possibility of intramolecular hydrogen bonding in (**2b**), but not (**2a**), enables their stereochemistry to be assigned. *cis*-Fusion in (iii) favours the formation of (**2a**) rather than (**2b**). The stereochemistry of (**3**) is apparent from the reaction pathway *via* (iv) and (v). The formation of the key intermediate (ii) is supported by the fact that no five-membered carbocyclic product corresponding to (**2**) could be detected on treatment of geranyl acetate with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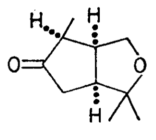
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† All new compounds gave correct elemental analyses and/or high resolution mass measurements.

‡ Yields were determined by g.l.p.c. (1·5% SE-30).

$Tl(ClO_4)_3$ (2 equiv.). Both epimeric alcohols (**2a**) and (**2b**) gave exclusively the same olefin (**4**) [b.p. 44—45 °C at 2 mmHg; n.m.r. ($CDCl_3$) δ 1·66 (3H, br. s) and 5·42 (1H, m)] on treatment with toluene-*p*-sulphonic acid. Hydroboration of (**4**) followed by Jones oxidation gave the five-membered ring ketone (**5**) [ν_{max} ($CHCl_3$) 1743 cm^{-1}, n.m.r. ($CDCl_3$) δ 1·02 (3H, d, *J* 8·0 Hz)].

In connection with the olefinic cyclization of polyclefins which has been extensively studied,[4] this particular olefinic cyclization is interesting because of the predominant formation of the five-membered carbocyclic compounds (60% total yield). These products, which possess the iridoid carbon skeleton, may be useful in the synthesis of iridoid monoterpenes,[5] and in the biogenesis of iridoids.

(*Received*, 1*st September* 1976; *Com.* 1008.)

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