

A New Acetylene Rearrangement

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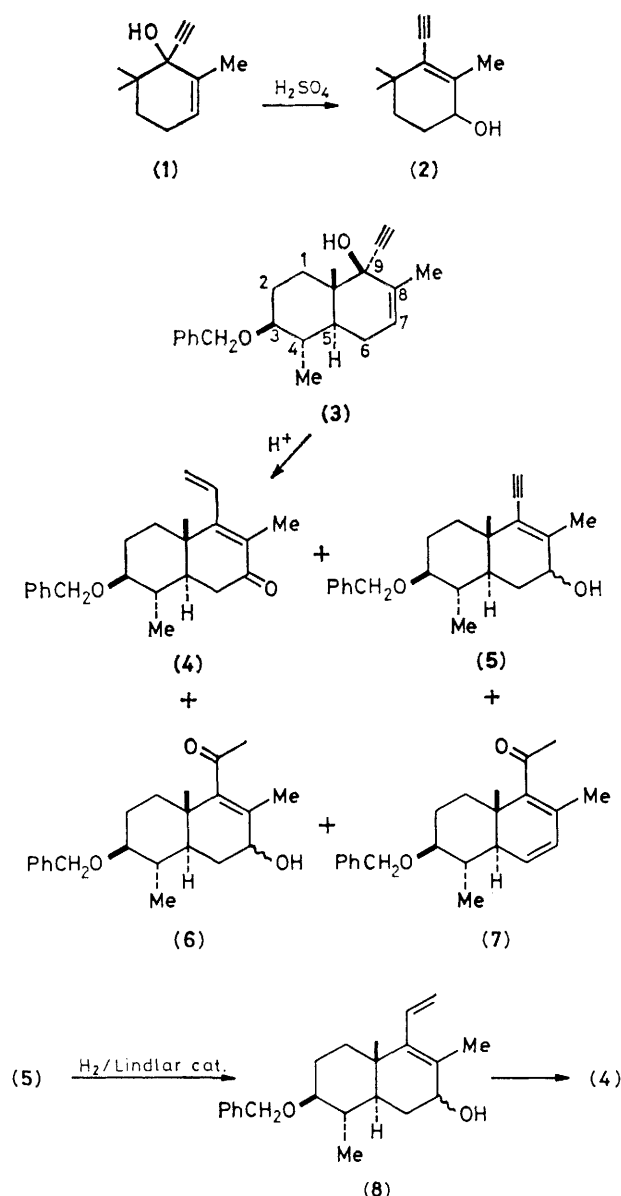
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Treatment of the enynols (**1**), (**2**), (**3**), and (**5**) with 35% perchloric acid in tetrahydrofuran produces, through a series of prototropic shifts, the corresponding dienones (**4**) and (**11**).

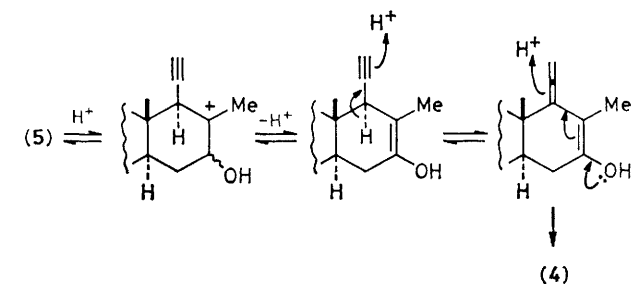
Central to the chemistry of acetylenes are their rich and diverse rearrangement processes.¹ Here we report an unexpected rearrangement of an acetylenic tertiary alcohol,

that has fortuitously provided a convenient route to potential di- and tri-terpene precursors.

The known acetylenic alcohol (**1**),² on treatment with 3%



Scheme 1



The unexpected conversion of (3) into (4) was confirmed by hydrogenation of (5) to give (8), which on oxidation with pyridinium chlorochromate gave (4). Interestingly, treatment of the dienol (8) with ethyl 2-nitroacrylate also gave (4) (67%).

In a formal sense, the conversion of (5) into (4) is related to the Meyer-Schuster rearrangement,³ except that in the latter migration of an oxygen atom occurs. The reason why (1) rapidly rearranges into (2), whereas the corresponding conversion of (3) into (5) is slow, is the anchimeric assistance to ionization provided by the triple bond. In (1), the tertiary -OH group can adopt an axial conformation that allows, in the rate determining ionization step, direct development of the π -orbital in the plane of the vinyl π -system and the triple bond. This accounts for a substantial acceleration compared to (3) in which the tertiary -OH group is rigidly constrained in an equatorial configuration. The conversion of (3)/(5) into (4) is best rationalized by a series of prototropic shifts (Scheme 1). The compound (9), without the 8-methyl group, cleanly rearranged on treatment with 35% HClO_4 -THF to give the enynol (10), without further rearrangement to a dienone, thus demonstrating the necessity of protonation leading to a tertiary carbenium ion rather than a secondary carbenium ion. Finally, when (1) or (2) was treated with 35% HClO_4 -THF it cleanly rearranged to the dienone (11) (48%).

The dienones (4) and (11) would be difficult to prepare by other routes and should find use as precursors to di- and tri-terpenoids.

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H_2SO_4 in ether for 24 h gave the expected rearranged enynol (2) (73%), whereas similar treatment of (3),[†] m.p. 82–83 °C, gave no reaction. Increasing the acid concentration to 10% HClO_4 -THF (48 h) gave (4) (34%), m.p. 84–85 °C[‡] and the expected enynol (5) (45%) as a mixture of epimers at C-7. Further increase in acid concentration, 35% HClO_4 -THF (2 h), gave (4) (85%). In an experiment where the mass balance was 98%, (3) on treatment with 35% HClO_4 -THF (5 h), gave (4) (74%), (5) (7.7%), (6) (15%), and (7) (2.2%); the latter two products being due to simple hydration of (5).

[†] The configuration at C-9 is assumed since (3) is made from the C-9 ketone, $\text{LiC}\equiv\text{CH}$, and $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$.

[‡] Selected spectroscopic data: i.r. ν_{max} 1660 cm^{-1} ; u.v. λ_{max} (EtOH) 260 nm; ^1H n.m.r. δ 7.45–7.29 (5H, m, aromatic), 6.5 (1H, ABX, J_{AX} 17.5, J_{BX} 10 Hz, vinyl group), 5.49 (1H, ABX, J_{AX} 17.5, J_{AB} 3 Hz, vinyl group), 5.1 (1H, ABX, J_{BX} 10, J_{AB} 3 Hz, vinyl group), 4.65 (1H, d, J 10 Hz, OCH_2Ph), 4.43 (1H, d, J 10 Hz, OCH_2Ph), 2.77–2.63 (1H, m, H^8), 2.43–2.33 (1H, m), 2.04–1.81 (2H, m), 1.79 (3H, s, C^8 -Me), 1.47–1.18 (5H, m), 1.13 (3H, s, C^{10} -Me), and 1.02 (3H, d, J 5 Hz, C^4 -Me).

References

- 1 'Chemistry of Acetylenes,' ed. H. G. Viehe, Marcel Dekker, New York, 1969.
- 2 C. Schmidt, *Can. J. Chem.*, 1976, **54**, 2310; S. Isoe, S. Katsumura, and T. Sakan, *Helv. Chim. Acta*, 1973, **56**, 1514.
- 3 R. A. Raphael, 'Acetylenic Compounds in Organic Synthesis,' Academic Press, New York, 1955; A. W. Nineham and R. A. Raphael, *J. Chem. Soc.*, 1949, 118.