Rearrangement of Cross-conjugated Methylenecyclohexadienes

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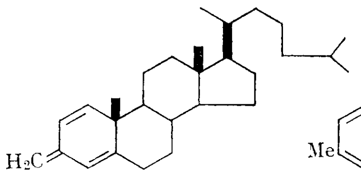
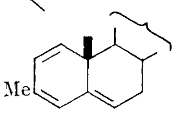
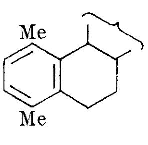
ACID-CATALYSED rearrangement of 3-methylene-cholest-4-ene yields 3-methylcholesta-3,5-diene.[1] It seemed of interest to examine the rearrangement of the related 3-methylenecholesta-1,4-diene (I) since several products appeared possible. Thus, by analogy with the above, the triene (II) (or a related isomer) could result or, alternatively, aromatic compounds (III) and (IV) could arise by reaction paths analogous to the dienone–phenol or dienol–benzene rearrangements.[2,3]



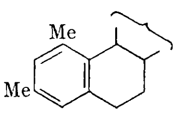
(I)



(II)



(III)



(IV)

[(IIIa) : Rings - A and - B only]

The Wittig reaction between 3-oxocholesta-1,4-diene and excess[1] of triphenylphosphonium methylide (generated from methyltriphenylphosphonium iodide and phenyl-lithium in tetrahydrofuran solution) proceeded normally and gave (I) in 72% yield. This appears to be the first example of a Wittig reaction on a cross-conjugated dienone. The colourless product, m.p. 60—63° ν_{max} 880, 1670 cm.$^{-1}$ ($CH_2=$), which was readily separated from a little unchanged ketone and coloured impurities by chromatography over silica gel, turned yellow within hours, even under nitrogen at −10°.

Rearrangement of the freshly chromatographed compound with warm aqueous or ethanolic hydrochloric acid, or boron trifluoride etherate in ether solution at room temperature, gave the same homogeneous (by t.l.c.) oil in nearly quantitative yield. The i.r. spectrum was consistent with an aromatic compound and the n.m.r. spectrum ($CDCl_3$) showed singlets at τ 2·12 (aromatic H) and 7·84 (CH_3–Ar) suggesting (III) to be the correct structure. It was thought that the chemical shifts of the aromatic methyl groups of (IV) would be significantly different and, in a similar case below, this was shown to be true.

Final proof of structure came about by carrying out the same rearrangement on the related bicyclic compound (Ia) (colourless unstable oil, ν_{max} 878, 1668 cm.$^{-1}$), similarly prepared from the corresponding ketone. Only one product was obtained (v.p.c. analysis) and was shown to be (IIIa) by comparison of its spectral and chromatographic properties with those of an authentic sample prepared[4] unambiguously from *p*-xylene by Friedel–Crafts succinoylation, Clemmensen reduction, polyphosphoric acid cyclization, and finally, Huang-Minlon reduction. Isomer (IVa) similarly prepared[4] from *m*-xylene was completely absent in the rearranged product (i.r. and v.p.c. analysis) and the n.m.r. spectrum ($CDCl_3$) showed two aromatic methyl peaks (τ 7·87 and 7·79).

Thus, by analogy, the rearranged product from (I) is undoubtedly (III), confirming the tentative assignment.

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[1] F. Sondheimer and R. Mechoulam, *J. Amer. Chem. Soc.*, 1957, 79, 5029.

[2] N. L. Wendler in "Molecular Rearrangements", Part II, (ed. P. de Mayo), Interscience, New York, 1964, p. 1028.

[3] R. H. Shapiro in "Steroid Reactions" (ed. C. Djerassi), Holden-Day, San Francisco, 1963, ch. 9, p. 371.

[4] E. de B. Barnett and F. G. Sanders, *J. Chem. Soc.*, 1933, 434.