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SYNTHESIS OF [4,4,4] PROPELLANE

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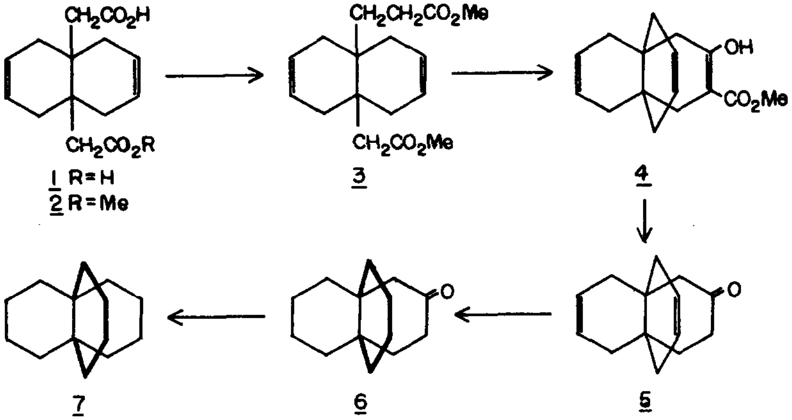
We wish to report the preparation of the title compound 7 by two distinctly different synthetic routes.

One route (J.A., D.G.) is summarized in Scheme I and uses as starting material the dicarboxylic acid 1, the usefulness of which has already been demonstrated for the synthesis of propellanes[1]:

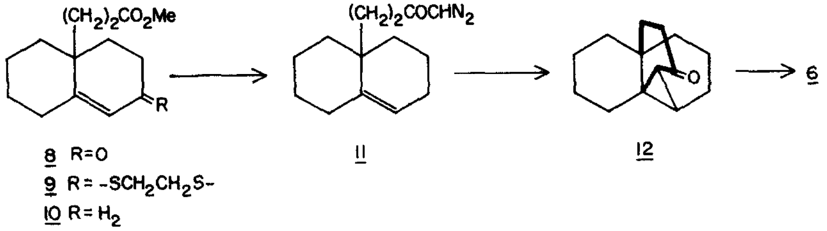
Scheme I



Arndt-Eistert homologation of the half-ester 2 (m.p. 72-73°) obtained from 1 via its anhydride[1] led to the diester 3, b.p. 156°/0.05 mm. Dieckmann cyclization of the latter gave smoothly the expected keto-ester in the form of its stable enolic tautomer 4 (as shown by n.m.r.), b.p. 100°/0.02 mm, ν_{max}^{chf} 1620, 1660 cm^{-1}. Alkaline hydrolysis followed by acidification led to the dienic ketone 5, m.p. 83-84°, ν_{max}^{chf} 1660, 1710 cm^{-1}, hydrogenation of which gave 4,4,4 propellan-3-one 6, m.p. 120-121°, ν_{max}^{chf} 1710 cm^{-1}.

Scheme II shows the alternative route (D.B., H.J.E.L.):

Scheme II



Addition of methyl vinyl ketone to 2-cyanoethylcyclohexanone, followed by acid treatment of the product and esterification, led to the keto-ester 8, b.p. 130°/0.1 mm, ν_{max}^{chf} 1660, 1730 cm^{-1}. Desulfurization of the derived ethylenedithioketal 9 gave the ester 10, ν_{max}^{chf} 1730 cm^{-1}. The corresponding acid was converted into the diazoketone 11, ν_{max}^{chf} 1680, 2110 cm^{-1}. Treatment of the latter with copper sulfate in refluxing cyclohexane afforded in 60% yield the cyclopropane ketone 12, ν_{max}^{chf} 1695 cm^{-1}, whose hydrogenation (Pd/C, n-propanol) led specifically in 90% yield (by GLC) to ketone 6, identical in all respects to that obtained by the first route.

Wolff-Kishner reduction of ketone 6 gave the propellane 7, m.p. 120°, n.m.r. ($CDCl_3$): single broad peak at τ, 8.50 above 60°C.

Analytical results obtained and additional spectroscopic evidence are in full accord with the proposed structures.

Reference

1. J. Altman, E. Babad, J. Itzchaki and D. Ginsburg, Tetrahedron, Suppl. 8, Part 1, 279 (1966).