

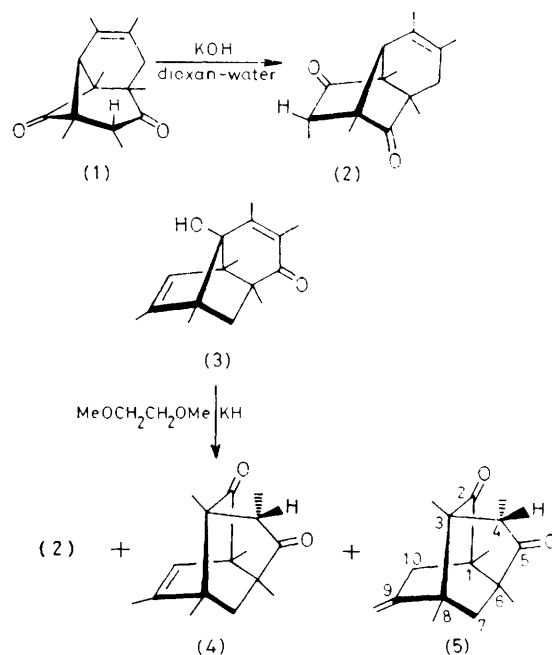
Formation of Twistane Derivatives *via* a Novel Base-catalysed Rearrangement. X-Ray Crystal Structure of 1,3,4,6,8-Pentamethyl-*exo*-9-methylene- tricyclo[4.4.0.0^{3,8}]decane-2,5-dione

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Summary A vinylogous, base-catalysed acyloin rearrangement leading to products (4) and (5) possessing the twistane (tricyclo[4.4.0.0^{3,8}]decane) ring skeleton is reported; an X-ray crystal structure analysis of (5) was performed.

As part of our investigation into the mechanism of the base-catalysed transformation of the diketone (1) into the diketone (2) (Scheme 1),¹ we have examined the base-induced chemistry of the tricyclic alcohol (3). There were two reasons for this: first, we knew from previous work² that thermolysis of (3) at 280 °C affords (in part) the diketone (2), and secondly, the alkoxide of (3) appeared to be a possible intermediate in the base-catalysed rearrangement of (1) to (2).

Accordingly, we treated the tricyclic alcohol (3) under the conditions which cause the conversion of (1) into (2), namely potassium hydroxide in refluxing aqueous dioxan. As there was no reaction, we used more vigorous conditions. Treatment of (3) with either potassium t-butoxide in refluxing dioxan or potassium hydride in dimethoxyethane (reflux) afforded a mixture of three products. The first of these was readily shown to be the diketone (2).² The other two were shown (*vide infra*) to have the interesting twistane (tricyclo[4.4.0.0^{3,8}]decane)-derived structures (4) and (5). In potassium t-butoxide-dioxan the (2):(4):(5)



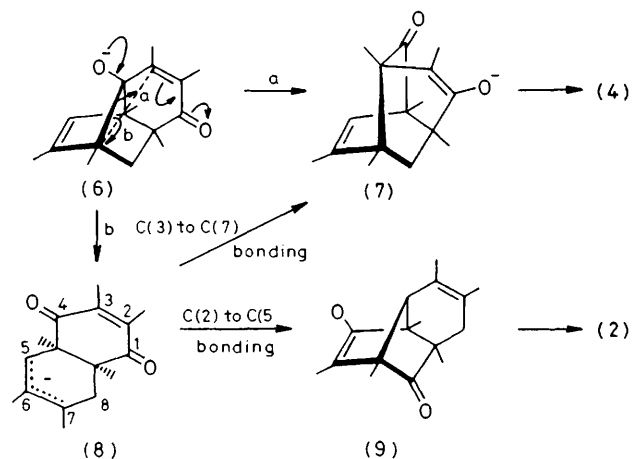
SCHEME 1

ratio was *ca.* 2:1:1. In potassium hydride-dimethoxyethane only a trace of the *exo*-methylene compound (5) was observed and the (2):(4) ratio was *ca.* 1:8.

The structures of compounds (4), m.p. 138.0–138.5 °C, and (5), m.p. 94.5–95.0 °C, were assigned on the basis of their spectra and, in the case of (5), on a single crystal X-ray diffraction study. *Crystal data:* (5), C₁₆H₂₂O₂; *M* = 246.4, monoclinic, space group *P*2₁/*c*, *a* = 13.7451(16), *b* = 8.9543(7), *c* = 12.5206(19) Å, β = 115.22(1)°, *U* = 1395.1(1) Å³, *D_c* = 1.173 g cm⁻³, *Z* = 4. Intensities were measured on a NONIUS CAD-4 diffractometer using Mo-*K*_α radiation out to 2θ = 52°, providing 1974 independent observed reflections. The structure was solved by direct methods using a *K* curve procedure³ and MULTAN⁴ and refined by full-matrix least-squares to the final *R* of 0.039. Anisotropic thermal parameters were used for C and O, and H atoms were refined isotropically. The C(1)–C(6) and C(3)–C(8) bridge distances are 1.585(3) and 1.584(3) Å, respectively; other bond distances are normal, and intermolecular contacts correspond to van der Waals interactions. All six-membered rings are in skew-boat conformations with the methyl group and the hydrogen at C(4) in pseudo-equatorial and pseudo-axial positions, respectively, with respect to the C(3) to C(8) ring. Full details of the structure determination will be published separately.^{5†}

In considering the mechanism, we can conclude that despite the fact that the alkoxide (6) (Scheme 2) does give some rearrangement to (2) (formally an alkoxy-Cope rearrangement⁶), our results indicate that this alkoxide is probably not a major intermediate in the base-catalysed rearrangement of (1) to (2) since neither (4) nor (5) is observed in this reaction. Elucidation of the mechanistic details of the conversion of (1) into (2) thus requires further experimental investigation.

The formation of twistane derivatives (4) and (5) is of mechanistic interest however. We view the formation of (4) as occurring *via* a vinylogous acyloin rearrangement (path a). This conversion has analogy in the base-catalysed



SCHEME 2

rearrangement of 4-substituted-4-hydroxycyclohexa-2,5-dien-1-ones (*p*-quinols) to 2-substituted hydroquinones.⁷ Interestingly, our results indicate that the success of this type of reaction is not dependent on an aromatic product driving force.

Alternatively, the formation of both (2) and (4) from (6) can be explained by ring-opening of (6) to the allyl anion (8) (path b) and re-closure (internal Michael addition) as indicated. Once formed, the twistane (4) slowly rearranges under the reaction conditions to its *exo*-methylene isomer (5), likely *via* a di-anion mechanism. This interconversion was verified by independent experiments on (4).

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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