Interannular Dehydration as a Route to Novel Polycyclic Ring Systems

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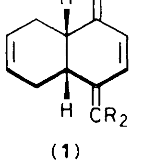
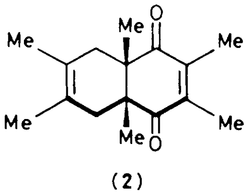
Treatment of the naphthoquinol (**3**) with zinc chloride and acetic anhydride results in the unexpected formation of the novel tricyclic and tetracyclic *exo*-methylene ketones (**5**) and (**6**); irradiation of (**5**) leads to a third unique polycyclic ketone (**7**).

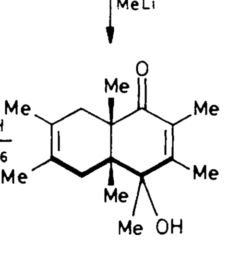
The work described in this communication arose out of a desire to synthesize trienones of general structure (**1**). To this end, the hexamethyldienedione (**2**)[1] was treated with methyllithium (1 mol. equiv.) and the resulting tertiary, allylic alcohol (**3**) (1 : 1 mixture of epimers) was exposed to a variety of acidic conditions. With toluene-*p*-sulphonic acid in benzene, excellent yields of the unrearranged dehydration product (**4**) were in fact obtained.† In contrast, treatment of (**3**) with zinc chloride and acetic anhydride provided the corresponding acetate (40%, mixture of epimers), a trace (<5%) of (**4**), and, unexpectedly, the rearranged dehydration products (**5**) (30%) and (**6**) (19%).‡ Compounds (**5**) and (**6**) can be derived, in a



(1)



(2)



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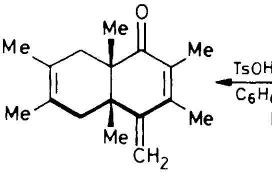

(4)

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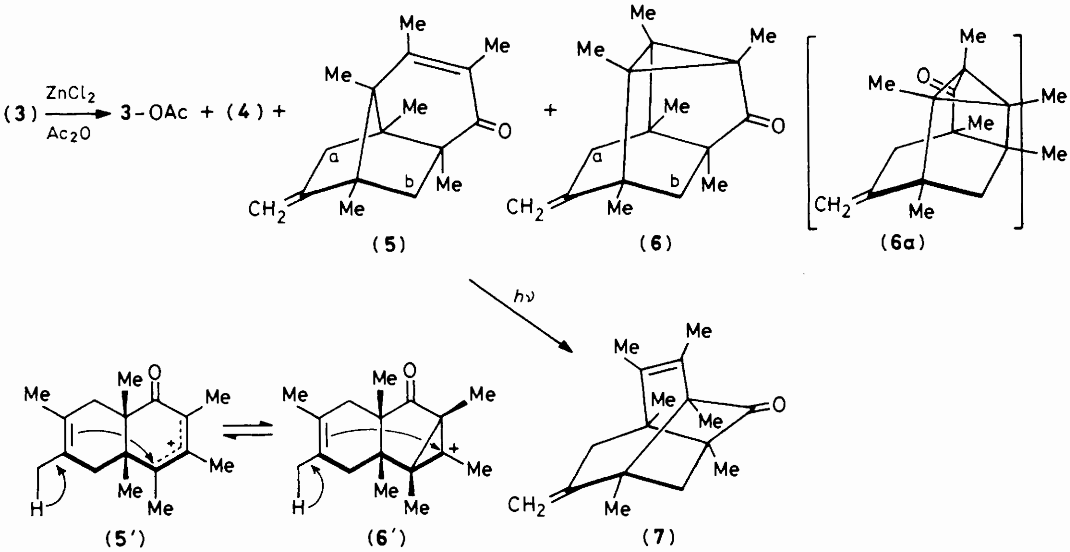
† All new compounds described gave satisfactory elemental analyses and exhibited spectra completely in accord with their assigned structures. The chemistry of (**4**) and related compounds will be described elsewhere.

‡ Compound (**5**): liquid; i.r. (film) 1660 (C=O) and 1620 cm^{-1} (C=C); 100 MHz ^{1}H n.m.r. ($CDCl_3$) δ 4.74 (m, 2H, *exo*-CH_2), 2.48 (br. d, 1H, J 17 Hz, H^a), 2.06 (br. d, 1H, J 17 Hz, H^a), 1.88 (s, 3H, vinyl Me), 1.83 (s, 3H, vinyl Me), 1.68 (d, 1H, J 13 Hz, H^b), 1.30 (d, 1H, J 13 Hz, H^b), and 1.06, 1.00, 0.94, 0.70 (each s, 3H, Me); mass spectrum, parent m/z 244; compound (**6**): liquid; i.r. (film) 1710 (C=O) and 1640 cm^{-1} (C=C); 400 MHz ^{1}H n.m.r. ($CDCl_3$) δ 4.68 (m, 2H, *exo*-CH_2), 2.35 (dt, 1H, J 3 and 17 Hz, H^a, assignment corroborated by spin decoupling), 2.22 (dt, 1H, J 3 and 17 Hz, H^a, assignment corroborated by spin decoupling), 1.45 (ABq, 2H, J 13 Hz, 2 × H^b), and 1.10, 1.03, 0.95, 0.90, 0.84, and 0.81 (each s, 3H, Me); mass spectrum, parent m/z 244. The alternative structure (**6a**), which would be formed *via* interannular bonding and proton loss from the other allylic methyl group, is ruled out on the basis of n.m.r. shift reagent studies which will be reported in the full paper.



formal sense, from interannular bonding and methyl group proton loss in ions (**5′**) and (**6′**) respectively (arrows).

The tricyclic dienone (**5**) exhibited interesting photochemical properties. Direct irradiation of (**5**) in benzene (Pyrex filter) afforded high yields of a single new photoisomer, assigned the novel structure (**7**) on the basis of a single crystal *X*-ray diffraction study, details of which have been published elsewhere.[2]

The photoproduct (**7**) is the result of a deconjugative 1,3-shift of the 1,5-diene central σ-bond in (**5**), a process for which literature precedent exists.[3]

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References

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