Rearrangements of the Gibbane Skeleton during Dehydrogenations with 2,3-Dichloro-5,6-dicyanobenzoquinone

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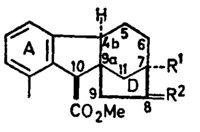
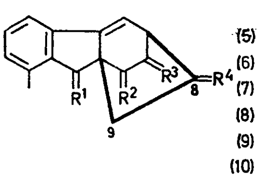
Summary Gibbanes in which ring A is aromatic react with 2,3-dichloro-5,6-dicyanobenzoquinone giving allylic carbonium ions (*via* Δ^{4b}-enes) which then undergo Wagner–Meerwein rearrangement; in 7-hydroxy-compounds, the 7,8-bond migrates to C-6 to give a 7-ketone, whereas in 7-deoxy-gibbanes, the 9,9a-bond migrates to position 4b to give a 9a,10-ene.

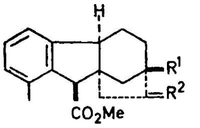
Treatment of the methyl ester (**1**) of dihydroallogibberic acid[1] with an excess of 2,3-dichloro-5,6-dicyanobenzoquinone (ddq) in boiling dioxan gave a 95% yield of a mixture of 8-epimeric keto-esters from which one pure epimer was isolated by chromatography. The latter, for which structure (**5**) or (**6**) was deduced from its u.v., i.r., and n.m.r. spectra, was shown to be the α-methyl epimer (**5**) because reduction with sodium borohydride, which took place from the less hindered α-face, gave the alcohol (**7**) in whose n.m.r. spectrum the methyl doublet had shifted downfield from τ 8·93 to 8·63. Structure (**5**) for the keto-ester was confirmed by (a) treatment with base in deuterium oxide which gave the trideuterio-derivatives (**8**) and (**9**) [*m/e* 299 (M^+) and 255 (M–CD$_2$=C=O); no peak at τ 5·95, ∴ 10-D] and (b) oxidation with selenium dioxide to the α-diketone (**10**) followed by heating with Pd–C gave methyl 1,7-dimethylfluorene-9-carboxylate.[2] Similarly, reaction of methyl allogibberate[3] (**2**) with ddq gave the rearrangement product (**11**) in 97% yield.



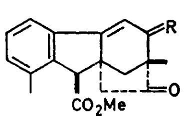
	R¹	R²
(1)	OH	H,Me
(2)	OH	CH$_2$
(3)	H	H,Me
(4)	H	OH,Me



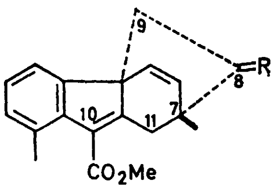
	R¹	R²	R³	R⁴
(5)	α-H,β-CO$_2$Me	H$_2$	O	β-H,α-Me
(6)	α-H,β-CO$_2$Me	H$_2$	O	α-H,β-Me
(7)	α-H,β-CO$_2$Me	H$_2$	α-H,β-OH	β-H,α-Me
(8)	α-D,β-CO$_2$Me	D$_2$	O	β-H,α-Me
(9)	β-D,α-CO$_2$Me	D$_2$	O	β-H,α-Me
(10)	α-H,β-CO$_2$Me	O	O	β-H,α-Me
(11)	α-H,β-CO$_2$Me	H$_2$	O	CH$_2$



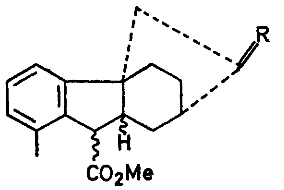
	R¹	R²
(12)	Me	O
(13)	Me	H$_2$



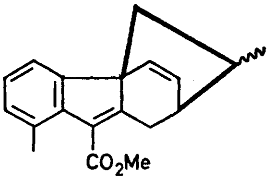
	R
(14)	H$_2$
(15)	α-H,β-OEt
(16)	β-H,α-OEt



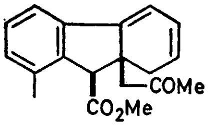
	R
(17)	O
(18)	H$_2$



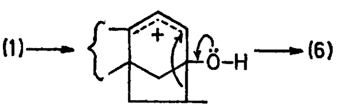
	R
(19)	O
(20)	H$_2$



(**21**)



(**22**)



(**23**)

As expected, treatment of methyl gibberate[1] (**12**) with ddq did not give the above type of rearrangement. The reaction yielded methyl dehydrogibberate[2] (**14**), and a high yield of products resulting from substitution at C-6 of the latter, *e.g.* the ethyl ethers (**15**) and (**16**) derived from traces of ethanol present in the dioxan. However a rearrangement product, which was identified as the keto-ester (**17**) by u.v., i.r., and n.m.r. spectroscopy was isolated in low yield. Structure (**17**) was confirmed by hydrogenation to the tetrahydro-derivative (**19**) and by oxidation with selenium dioxide in ethanol which gave methyl 1,7-dimethylfluorene-9-carboxylate. Analogous rearrangements took place when methyl deoxogibberate (*cf.* ref. 2) (**13**) and the ester (**3**)† were treated with ddq, the products (*ca.* 25%) being the esters (**18**) and (**21**) respectively. Hydrogenation of the former gave the tetrahydro-compound (**20**).

Treatment of the 8-hydroxy-ester[4] (**4**) with ddq afforded the keto-ester (**22**).

These rearrangement products are believed to arise by initial formation of the Δ^{4b}-ester followed by removal of a hydride ion by ddq from C-6 to give an allylic carbonium ion,[5] *e.g.* (**23**), which, unlike the 2-methylene-3-norbornyl cation,[6] undergoes Wagner–Meerwein rearrangement in either of two ways. If a 7-hydroxy-group is present the lone pair on the oxygen aids [see (**23**)] migration of the 7,8-bond to C-6 to give products typified by structure (**6**) in high yield; similarly an 8-hydroxy-group assists rupture of the 7,8-bond. However, in the absence of either a 7- or an 8-hydroxy-group nucleophilic attack at C-6 predominates and rearrangement follows a more unusual course; the 9,9a-bond migrates to C-4b and the product is a 9a,10-ene. All new compounds gave satisfactory spectra and analytical data.

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† Derived from gibberellin A_7 by acid catalysed aromatisation of ring A[4] followed by hydrogenation of the ring D double bond.

[1] B. E. Cross, *J. Chem. Soc.*, 1954, 4670.
[2] B. E. Cross, J. F. Grove, J. MacMillan, and T. P. C. Mulholland, *J. Chem. Soc.*, 1958, 2520.
[3] T. P. C. Mulholland, *J. Chem. Soc.*, 1958, 2693.
[4] B. E. Cross, R. H. B. Galt, and J. R. Hanson, *Tetrahedron*, 1962, **18**, 451.
[5] I. H. Sadler and J. A. G. Stewart, *Chem. Comm.*, 1969, 773; F. E. Lutz and E. F. Kiefer, *Tetrahedron Letters*, 1970, 4851.
[6] C. W. Jefford and W. Wojnarowski, *Chem. Comm.*, 1968, 129.