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PINACOL REARRANGEMENT OF TRICYCLO(3,3,1,$0^{2,6}$)NONANE-2,6-DIOL

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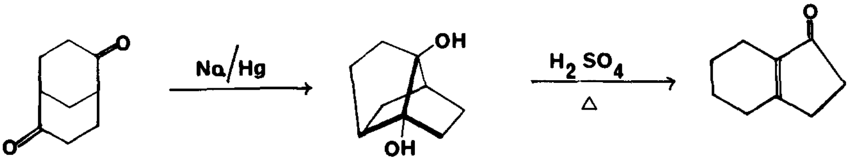
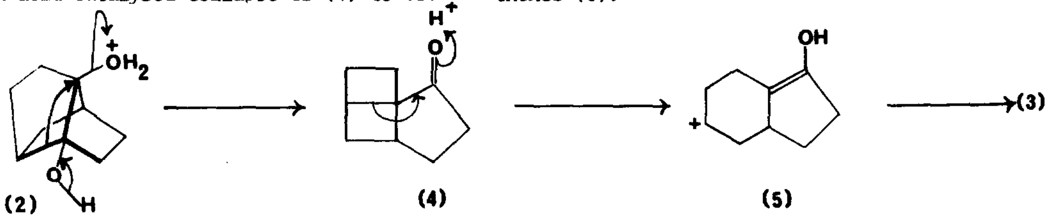
In 1922 Meerwein et al.[1] reported the reduction of bicyclo(3,3,1)nonan-2,6-dione (1) with sodium amalgam to a 1:1 mixture of bicyclo(3,3,1)nonane-2,6-diol and tricyclo(3,3,1,$0^{2,6}$) nonane-2,6-diol (2). The formation of the tricyclic diol remains one of only two examples(1,2) of a 2,6-transannular reaction in the bicyclo(3,3,1)nonane skeleton, although intramolecular reactions between other ring positions (particularly 3,7) are well known[3]. Treatment of (2) with hot concentrated sulphuric acid was reported[1] to cause apparent dehydration to a single volatile compound of unknown structure.



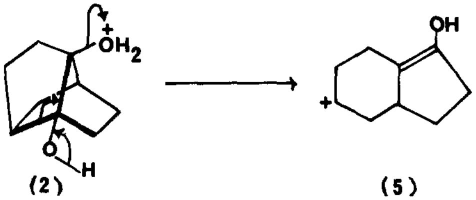
(1) (2) (3)

A 40% yield of this dehydration product was obtained by heating (2) in H_2SO_4(80%) for 1 hour at 160°. The resultant oil ($C_9H_{12}O$) was pure to T.L.C. (SiO_2/CH_2Cl_2) and G.L.C. (SE-30, 200°) and exhibited ν_{max}(liquid film) 1698 and 1648 cm^{-1}; λ_{max}^{EtOH} 237 nm (ε = 12,260) and two ^1H multiplets at 7.4 - 8.2 τ (2H) and 8.2 - 8.6 τ (1H) respectively in CCl_4 solution. The mass spectrum exhbited peaks at m/e = 136(87%; M^+), 108(28%), 94(81%), 93(55%), 91(28%), 80(29%), 79(100%), 77(37%), 51(22%), 41(21%), 39(39%) with metastable peaks at 107.6(136 $\rightarrow$ 121) and 66.4 (94 $\rightarrow$ 79). The corresponding 2,4-dinitrophenylhydrazone crystallised from ethanol-ethyl acetate with m.pt. 235-236°. This data suggested (3), viz. 4,5,6,7-tetrahydroindan-1-one[4], and was confirmed by direct comparison of the product (I.R., N.M.R. and co-injection G.L.C.) and its 2,4,-D.N.P. (mixed m.pt.) with authentic samples[5].

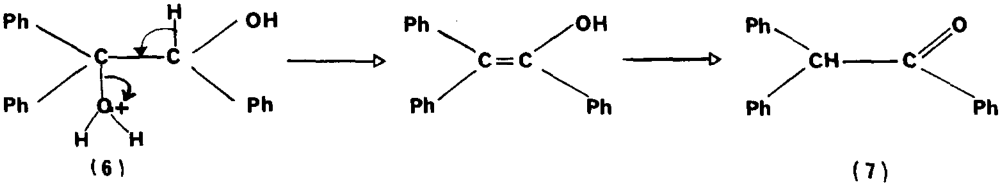
The formation of (3) can be rationalised by Pinacol rearrangement (2→4) followed by an acid-catalysed collapse of (4) to (5) and thence (3).



Alternatively, the intermediate carbocation (5) could be derived directly by the fragmentation shown below which circumvents the strain involved in the conversion of the bicyclo(2,2,1)heptane moiety of (2) into the bicyclo(2,2,0)hexane of (4).



This latter alternative to the normal pinacol rearrangement mechanism is reminiscent of the "vinyl dehydration" mechanism proposed (and later disproved) for conversions such as (6) to (7)[6].



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