Isomerisation of 4-Hydroxy-2-(prop-2-enyl)cyclopent-2-enones to 2-n-Propylcyclopent-2-ene-1,4-diones

By GERALD PATTENDEN* and RICHARD STORER
(*Department of Chemistry, The University, Nottingham* NG7 2RD)

Summary Treatment of 4-hydroxy-2-(prop-2-enyl)cyclopent-2-enones (**1**) with pyridine hydrochloride produces 2-n-propylcyclopent-2-ene-1,4-diones (**2**); the isomerisations probably proceed *via* intermediate 2-(prop-2-enyl)-cyclopentane-1,4,-diones (**5**).

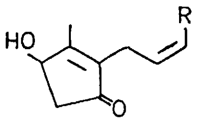
WE REPORT a novel acid-catalysed isomerisation of 4-hydroxy-2-(prop-2-enyl)cyclopent-2-enones (**1**) to 2-n-propylcyclopent-2-ene-1,4-diones (**2**). As depicted, this isomerisation formally involves oxidation of the cyclopentenolone hydroxy-function and synchronous reduction of the side-chain C–C double bond.

Thus, treatment of (**1a**) with pyridine hydrochloride (PHC) at 200° for 0·5h gave a single product which formed a bis-2,4-dinitrophenylhydrazone and showed spectral data, ν_{max} 1735 and 1700 cm^{-1}; τ 7·19 ($COCH_2CO$), 7·56 (t, J 8 Hz, $:C{\cdot}CH_2{\cdot}CH_2$), 8·0 ($:CMe$), 8·4 (m, CH_2), and 9·04 (t, *J* 6·5 Hz, CH_2Me); *m/e* 152·0837 ($C_9H_{12}O_2$) consistent with the cyclopent-2-ene-1,4-dione structure (**2a**). Similar reactions between PHC and the side-chain substituted homologues (**1b**) and (**1c**) led to the homologous diones (**2b**) and (**2c**) respectively, which both showed closely similar spectral data to those of (**2a**).

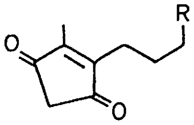
Cyclopent-2-ene-1,4-diones (**3**) are not intermediates in the isomerisations (**1**) → (**2**), since (**3a**)[1] produced only (**4b**) on treatment with PHC. Reduction of (**3a**) with ZnHg–HCl, or alternatively treatment of (**1a**) with NaOMe–MeOH led to the crystalline enol (**5a**),[2] m.p. 74—75°, which produced a comparable yield of (**2a**) with PHC. Although enols (**5**) could not be detected at any stage during the reactions between (**1**) and PHC (subsequent reactions too rapid), additional support for their probable intermediate role was obtained when it was found that the saturated side-chain analogue (**6c**) produced solely enol (**7c**) with PHC.

Analogue (**1e**) containing additional unsaturation in the prop-2-enyl side-chain produced largely cyclopentendione (**d4**) with PHC, accompanied by small amounts of positional isomers (**8**). The conversion (**1**) → (**5**) is envisaged as an acid-catalysed enone–dienol[3] type rearrangement. Isomerisation of (**5**) to (**2**) probably proceeds by initial protonation of the side-chain double bond and migration of the double bond along the side-chain to the ring position by a series of prototropic shifts.

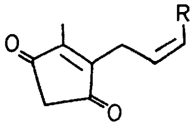
We thank the S.R.C. for financial support.



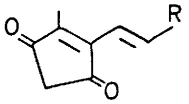
(1)



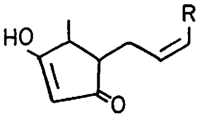
(2)



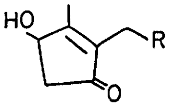
(3)



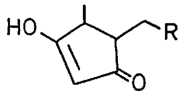
(4)



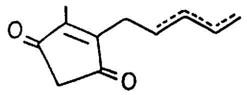
(5)



(6)



(7)



(8)

a; R = H
b; R = Me
c; R = Et
d; R = Pr^n
e; R = vinyl

(*Received, 3rd October* 1973; *Com.* 1377.)

---

[1] L. Crombie, J. A. Ellis, R. Gould, G. Pattenden, M. Elliott, N. F. Janes, and K. A. Jeffs, *J. Chem. Soc.* (*C*), 1971, 9.

[2] *Cf.* M. Elliott, *J. Chem. Soc.*, 1965, 3097.

[3] See E. N. Marvell and W. Whalley, 'Uncatalysed Rearrangements Involving the Hydroxyl Group,' in 'The Chemistry of the Hydroxy Group, Part 2,' p. 719, ed., S. Patai, Interscience, New York, 1971.