# Synthesis of Bicyclo[3,3,1]nonanes *via* Cope Reaction of an Enol

By Yvonne Bessiere-Chretien and Claude Grison

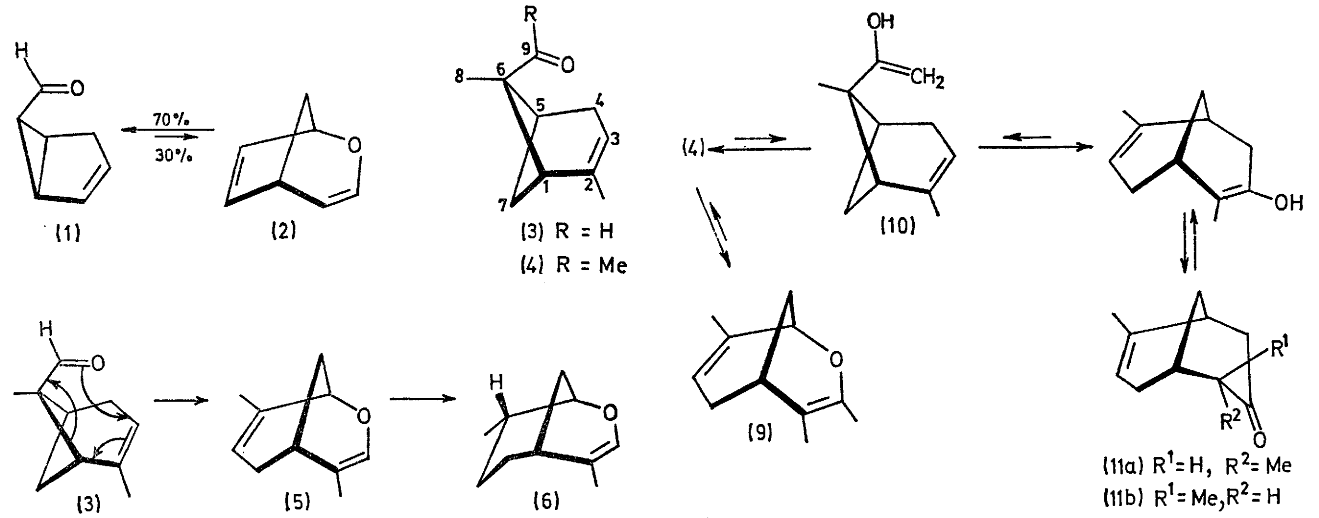
(*Laboratoire de chimie de l'Ecole Normale Superieure,* 24 *rue Lhomond,* 75005 *Paris*)

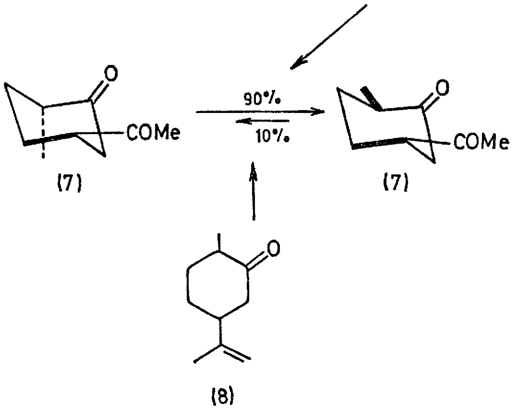
*Summary* The γδ-unsaturated ketone (**4**) rearranges thermally in two ways: above 200° a retro-Claisen reaction leads to practically quantitative conversion into the allyl vinyl ether (**9**), while between 150 and 180°, a Cope reaction of the enol (**10**) allows quantitative isolation of the bicyclo[3,3,1]nonenone (**11**); the non-enolisable aldehyde (**3**) gives only the ether (**5**) between 150 and 300°.

Claisen rearrangement equilibria are generally displaced in favour of γδ-unsaturated carbonyl derivatives unless the allyl vinyl ether is stabilized by conjugation,[1] or exhibits a lower steric strain than the carbonyl compound.[2] The latter appears not always to be sufficient by itself, since the equilibrium between *syn*-bicyclo[3,1,0]hex-2-ene-6-carbaldehyde (**1**) and the 2-oxabicyclo[3,2,1]octa-3,6-diene (**2**) favours the aldehyde.[3]

We have examined the thermal behaviour of pin-2-en-9-al (**3**) and 9-methylpin-2-en-9-one (**4**). The aldehyde (**3**) is quantitatively converted when heated in a sealed tube at 210° into the ether (**5**), the latter being stable up to 300°. The structure of (**5**) was supported by its spectra [δ (60 MHz; Me$_4$Si) 1·70 (d, *J* 1·5 Hz, 8-Me), 1·49 (d, *J* 1 Hz, 4-Me), 1·92—2·20 (4H), 4·13 (m, 1-H), 5·43 (m, 7-H), and 5·89 (d, *J* 1 Hz, 3-H); $M^+$ *m/e* 150; $\nu_{max.}$ 1665 cm$^{-1}$ (enol ether)], and by the following reactions. Partial reduction (Pd–C; MeOH) gave the enol ether (**6**), probably with an *endo*-Me at C-8, since it is likely that hydrogenation takes place from the *exo*-side[4] [δ 0·92 (d, *J* 5·5 Hz, 8-Me), 1·47 (d, *J* 1 Hz, 4-Me), 3·87 (m, 1-H), and 6·18 (d, *J* 1 Hz, 3-H); $M^+$ *m/e* 152; $\nu_{max.}$ 1665 cm$^{-1}$]; ozonolysis of (**6**), followed by reductive and oxidative work-up and base-catalysed equilibration, led to the isomeric diketones (**7**). The same diketones (**7**) are obtained after ozonolysis and equilibration of dihydrocarvone (**8**).

Ketone (**4**) isomerized similarly *via* a retro-Claisen reaction during 10 min at 210° to the ether (**9**) [δ 1·72 (d, *J* 1·5 Hz, 8-Me), 1·55br (s, 4-Me) 1·63br (s, 3-Me) 1·9—2·2 (4H), 4·15 (m, 1-H), and 5·42 (m, 7-H); $M^+$ *m/e* 164; $\nu_{max.}$ 1680 cm$^{-1}$] accompanied by 5—10% of the ketones (**11a** and **b**). At lower temperatures (12 h at 150° or 3 h at 180°) Cope rearrangement[5] of the enol (**10**) from the ketone (**4**) results in quantitative conversion into a mixture of the ketones (**11a**) (55%) and (**11b**) (45%), which can be equilibrated at room temperature in the presence of base to a mixture of (**11a**) (80%) and (**11b**) (20%) [δ 0·93 d, *J* 6 Hz, 2-Me in **11a**), 1·18 (d, *J* 7 Hz, 2-Me in **11b**), 1·59 (m, 6-Me), 5·17 (m, 7-H); $M^+$ *m/e* 164; $\nu_{max.}$ 1705 cm$^{-1}$]. The mixture [(**11a**) 55% and (**11b**) 45%] is unchanged after heating for 30 min at 220—230°. Heating of the ether (**9**) for 3 h at 180° causes partial conversion (20%) into ketones (**11a** and **b**), 80% of (**9**) being recovered.





So far as we are aware, this is the first reported example of a Cope reaction of the enol of a ketone; it is different from the thermal cyclizations of unsaturated ketones studied by Conia,[6] and provides a ready access to bicyclo[3,3,1]nonane derivatives. The precise nature of the enolization to (**10**) is not clear; it may be catalytic, and this is under study. It is not surprising that the rate of conversion of the enol ether (**9**) into the ketones (**11a** and **b**) is lower than that of the ketone (**4**), since the equilibrium between (**4**) and (**9**) strongly favours the latter.

(*Received*, 16*th May* 1973; *Com.* 690.)

---

[1] M. F. Ansell and V. J. Leslie, *Chem. Comm.*, 1967, 559; M. T. Hughes and R. O. Williams, *ibid.*, 1968, 587.

[2] B. C. Baumann, M. Rey, J. Markert, H. Prinzbach, and A. S. Dreiding, *Helv. Chim. Acta*, 1971, **54**, 1589; G. Maier and M. Wiessler, *Tetrahedron Letters*, 1969, 4987.

[3] M. Rey and A. S. Dreiding, *Helv. Chim. Acta*, 1965, **48**, 1985. See also the extensive literature in G. W. Klump, J. W. F. K. Barnick, A. H. Veefkind, and F. Bickelhaupt, *Rec. Trav. chim.*, 1969, **88**, 766.

[4] Catalytic hydrogenation of somewhat similar bicyclic systems has been described: R. T. Lalonde, J. Ding, and M. A. Tobias, *J. Amer. Chem. Soc.*, 1967, **89**, 665.

[5] We are grateful to A. F. Thomas, Firmenich SA, for suggestions about the mechanism for the formation of the bicyclo[3,3,1]-nonenone (**11**).

[6] J. M. Conia and M. Bortolussi, *Bull. Soc. chim. France*, 1972, 3402, and references therein.