Thermal 1,2-Acetyl Migration in Bicyclo[2,1,0]pentane

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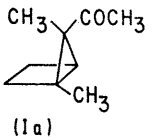
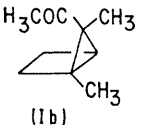
Summary Cyclopentenyl methyl ketones (II) and (III) are produced upon thermolysis of 5-acetyl-1,5-dimethylbicyclo[2,1,0]pentane (I); formation of ketone (III) entails a novel 1,2-acetyl shift.

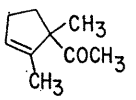
As part of our continuing efforts to elaborate the generality and mechanism of thermal 1,2 shifts of substituents located at the cyclopropane bridge of the bicyclo[2,1,0]pentane system, we have investigated the behaviour of the isomeric pair of ketones (Ia) and (Ib). Thermolysis of (I) leads to the formation of ketones (II) and (III) as principal products,



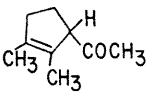
(Ia)



(Ib)



(II)



(III)

produced in comparable amounts. Rearrangement of (I) to (III) requires a novel 1,2-migration of an acetyl group. This 1,2-shift,† which has precedent in the related migration of an ethoxycarbonyl group previously reported by us for the corresponding ethyl ester,[1] occurs with greatly enhanced facility over that in the ester. Preliminary studies have established that (I) rearranges to (III) with appreciable rate at 200°, whereas temperatures above 300° are required for the corresponding rearrangement of ethyl 1,5-dimethylbicyclo[2,1,0]pentane-5-carboxylate.[1]

Bicyclo[2,1,0]pentanes (Ia) and (Ib) were derived from the corresponding esters[2-4] *via* reaction of the carboxylic acids with methyl-lithium.[5] Correct geometrical designations for the two ketones were secured from their relationship to the corresponding isomeric esters, for which we have assigned the stereochemistry.[4]‡ At 150°, reversible equilibration of (I) to give a 40 : 60 mixture of (Ia) and (Ib), favouring (Ib), proceeded at a rate comparable to that reported for the corresponding esters.[4] At this temperature, rearrangement to give (II) and (III), along with two minor products comprising less than 10% of product mixture, occurred at a slower rate than geometrical isomerization. Structural assignments for products (II) and (III) were afforded by spectral comparison with authentic samples of these ketones prepared from the corresponding ethyl esters, previously elaborated by us.[1,3,6]

Our results establish that acetyl migration proceeds more readily than ethoxycarbonyl migration. The finding that the cyclopentenyl ketone (II) is formed from (I) with much greater facility than the ester corresponding to (II) is formed from ethyl 1,5-dimethylbicyclo[2,1,0]pentane-5-carboxylate, despite comparable rates of 1,3-diradical formation, effectively rules out a mechanism for this reaction proceeding *via* a 1,3-hydrogen shift in the diradical generated upon scission of the central bond.

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† A thermal 1,2-acetyl migration has recently been noted for 5-acetyl-1,4,5-trimethylbicyclo[2,1,0]pentane (E. Baggiolini, K. Schaffner, and O. Jeger, *Chem. Comm.*, in the press). We thank Dr. Schaffner for communication of these results prior to publication.

‡ The stereochemical assignments are corroborated by the n.m.r. spectra of the 1-trideuteriomethyl derivatives of these esters. The isomer assigned the *exo*-geometry displays a resonance signal for its C-5 methyl group at τ 8.86, compared with 8·70 for the *endo*-isomer. (H. U. Gonzenbach, unpublished results from these laboratories). The higher chemical shift in the *exo*-isomer is expected by analogy with the data for the isomeric pair of ethyl 5-methylbicyclo[2,1,0]pentane-5-carboxylates[4] and due to the higher shielding effects by the *cis*-bimethylene bridge in the *exo*-isomer than by the adjacent *cis*-methyl group in the *endo*-isomer.

[1] M. J. Jorgenson and T. J. Clark, *J. Amer. Chem. Soc.*, 1968, **90**, 2188.
[2] M. J. Jorgenson, *J. Amer. Chem. Soc.*, 1966, **88**, 3463.
[3] M. J. Jorgenson, *J. Amer. Chem. Soc.*, 1969, **91**, in the press.
[4] M. J. Jorgenson, T. J. Clark, and J. Corn, *J. Amer. Chem. Soc.*, 1968, **90**, 7020.
[5] M. J. Jorgenson, *Org. Reactions*, 1969, **18**, in the press.
[6] M. J. Jorgenson and C. H. Heathcock, *J. Amer. Chem. Soc.*, 1965, **87**, 5264.