1,5-Hydrogen Migrations in Cyclopentenes

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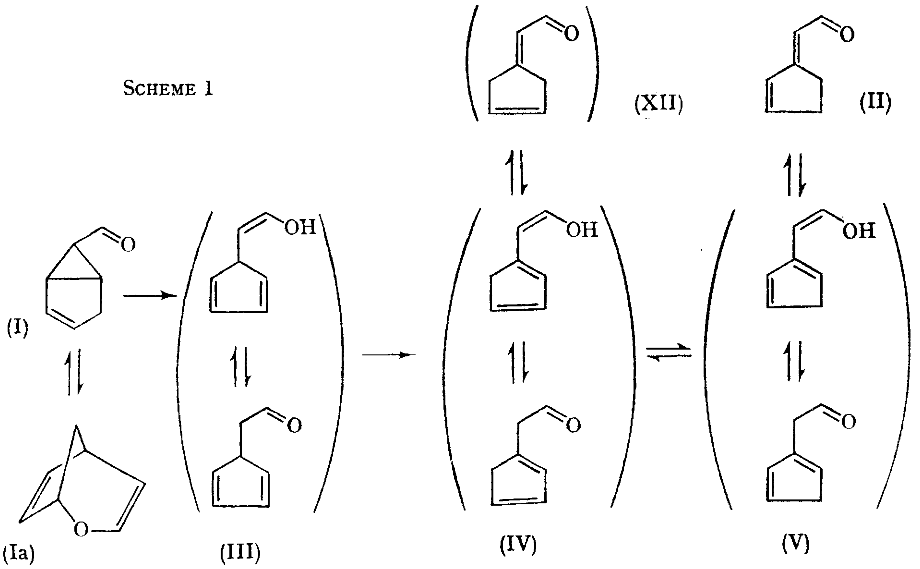
AMONG thermal "no-mechanism" reactions, the shift of an atom[1] or of a group of atoms[2] between the ends of a system of five unsaturated centres is taken as a general principle. We now report on several different varieties of 1,5-hydrogen shifts which take place consecutively when *endo*-6-formylbicyclo[3,1,0]hex-2-ene (I)[3] is heated; at least four new compounds are formed, on the energy surface, which is defined by the various C_7H_8O isomers, resulting ultimately from epoxidation of bicyclo-[2,2,1]hepta-2,5-diene.[4–7]

If compound (I) is heated in a nonpolar solvent to above 110° it is converted cleanly into its isomer (II). Scheme 1 outlines this conversion. When the reaction was followed by n.m.r. spectrometry, only signals due to (I), (Ia),[6] and (II) could be detected. The first step must therefore be rate-determining.

SCHEME 1



That compounds (IV) and (V) were involved as intermediates and that rearrangements connecting (IV), (V), and (II) were reversible, could be demonstrated by heating compound (I) or (II) in the presence of dimethyl acetylenedicarboxylate which led to compounds (VI) and (VII) (Scheme 2).†

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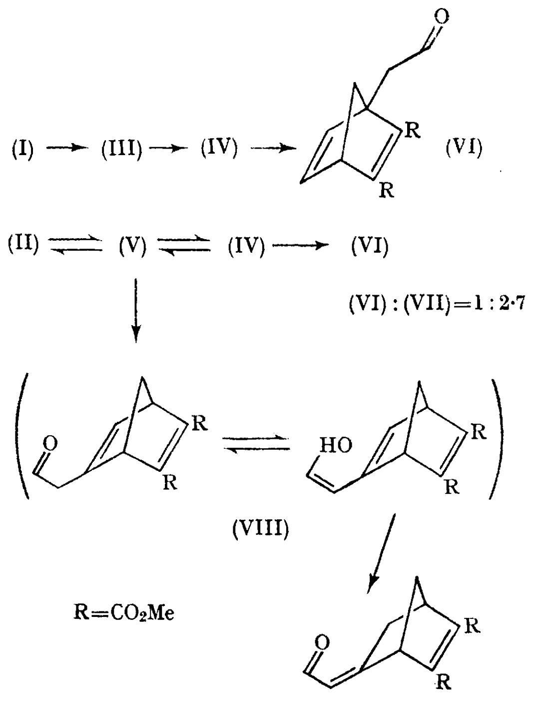
† All new compounds gave satisfactory analytical and spectral data. Compound (II) could be synthesized independently from cyclopenten-2-one and ethylidene cyclohexylamine by the method of G. Wittig and H.-D. Frommeld (*Chem. Ber.*, 1964, **97**, 3548).

By following the rearrangement (I) → (II) with n.m.r. spectrometry, disappearance of (I) was found to obey the first-order rate law with a rate constant $k = 10^{9\cdot92}\exp(-25\cdot5 \pm 0\cdot6\ \text{kcal. mole}^{-1}/\boldsymbol{R}T)$ sec.$^{-1}$.‡ The corresponding activation parameters fall in the same range as those obtained earlier on the related system (IX) → (X)[1] (Table). Experiments to differentiate between ground-state, electronic, or steric effects as the possible sources of the differences are underway.



SCHEME 2

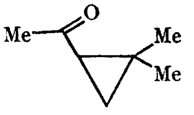
Similar differences exist between the monocyclic and the bicyclo[4,1,0]hept-2-ene forms of the analogous all-carbon systems.[8] Woodward and Hoffmann have given a molecular orbital description of the transition-state of sigmatropic shifts.[9] For shifts of order [1,5] they conclude that the migrating entity moves suprafacially from one end of the unsaturated system to the other. Accordingly *endo*-4-t-butoxy-*endo*-6-formylbicyclo[3,1,0]-hex-2-ene (XI)[10] was found unchanged even after prolonged heating to 140°.

TABLE

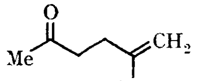
	ΔH‡ (kcal./mole)	ΔS‡ (e.u.)
(IX) → (X)	30	−10
(I) → (II)	24·7 ± 0·6	−15·7 ± 1·5

These findings extend further the synthetic value of (I) which has served as an entry into other bridged systems.[11] The formation of (VI) and (VII) shows that the 1,5-hydrogen migration reaction of compounds, such as (I), (II), and possibly (XII), can generate substituted cyclopentadienes under conditions which allow instantaneous reaction with an added dienophile. For certain substituents this opens a way to the synthesis of Diels–Alder adducts from substituted cyclopentadienes without the scrambling of substituents which is normally observed when the Diels–Alder reaction is carried out in a separate step.[12]

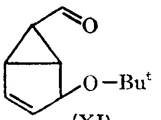
We are grateful to Miss W. H. E. M. Kronenburg for carrying out the n.m.r. work.



(IX)



(X)



(XI)

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‡ First-order disappearance of compound (I) is also observed in the gas phase. Rates are then about one half of those in solution.

[1] For pertinent literature see R. M. Roberts, R. G. Landolt, R. N. Greene, and E. W. Heyer, *J. Amer. Chem. Soc.*, 1967, **89**, 1404; also, J. K. Crandall and R. J. Watkins, *Tetrahedron Letters*, 1967, 1717.

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[12] S. McLean and P. Haynes, *Tetrahedron*, 1965, **21**, 2313.