Stereochemistry of an Intramolecular Friedel–Crafts Acylation

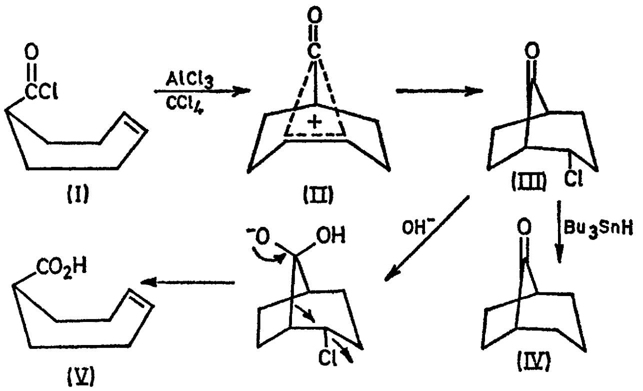
By Garry N. Fickes and Kenneth C. Kemp*
(*Department of Chemistry, University of Nevada, Reno, Nevada* 89507)

Summary In the presence of aluminium chloride cyclohept-4-ene-1-carbonyl chloride undergoes ready and stereospecific cyclization to 2-*endo*-chlorobicyclo[3,2,1]-octan-8-one.

Although Friedel–Crafts acylation of alkenes has been known for many years, little is known about the stereochemistry of the reaction.[1] We report the ready and completely stereospecific intramolecular acylation of the acid chloride (I).

Reaction of (I) with $AlCl_3$ (1 mol. equiv.) in CCl_4 at room temperature for 45 min gave the *endo*-chlorobicyclo-octanone (III) (74%; m.p. 36·5—38°) after work-up. G.l.c. analysis showed the absence of any *exo*-isomer. The mass spectrum showed a molecular ion at *m/e* 159.†

Chemical and spectral data support the assigned structure (III). The basic ring structure of (III) is confirmed by its reduction (Bu_3SnH) to the known[2] bicyclo-octanone (IV). The *endo*-configuration of chlorine was established by the behaviour of (III) towards refluxing methanolic KOH, which afforded the acid (V);[3] no bicyclo[3,2,1]hept-2-en-8-one was formed. Ring fragmentation rather than elimination shows the C–Cl bond is *trans* coplanar with the C(1)–C(8) bond. This ring scission is identical to that of 2-*endo*-chlorobicyclo[3,3,1]nonan-9-one.[4] The i.r. [ν(C=O) 1750 cm^{-1}] and n.m.r. spectra [δ 4·25 (m, total band width 25Hz, 1H, C-2 *exo*-proton)] are consistent with the assigned structure.



Unlike *cis*-cyclo-oct-4-ene-1-carbonyl chloride[4] and 3-(cyclohex-3-en-1-yl)propionyl chloride[5] which cyclize to mixtures of stereoisomers, (I) undergoes a stereospecific *trans*-addition to give only the *endo*-isomer in excellent

---

† Satisfactory analytical data were obtained for the tosylhydrazone.

yield. This specificity strongly suggests the intervention of the nonclassically stabilized intermediate (II). Apparently, the constraint imposed on this system results in favourable interaction between the incipient acylium ion and the olefinic π bond.

We acknowledge financial support from the Petroleum Research Fund of the American Chemical Society and the Research Advisory Board, University of Nevada.

(*Received*, 4*th December* 1972; *Com.* 2002.)

---

[1] J. K. Groves, *Chem. Soc. Rev.*, 1972, **1**, 73; G. A. Olah, 'Friedel–Crafts and Related Reactions, vol I, Wiley, New York, 1963, pp. 129—133.

[2] C. S. Foote and R. B. Woodward, *Tetrahedron*, 1964, **20**, 687.

[3] G. Stork and H. K. Landesman, *J. Amer. Chem. Soc.*, 1956, **78**, 5129.

[4] W. F. Erman and H. C. Kretschmar, *J. Org. Chem.*, 1968, **33**, 1545.

[5] E. N. Marvell, R. S. Knutson, T. McEwen, D. Sturmer, W. Federici, and K. Salisbury, *J. Org. Chem.*, 1970, **35**, 391.