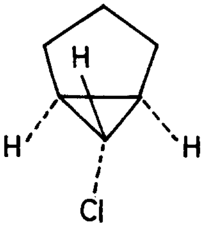
Tetrahedron Letters No.15, pp. 1379-1382, 1967. Pergamon Press Ltd. Printed in Great Britain.

EXO- AND ENDO-6-CHLOROBICYCLO[3.1.0]HEXANES

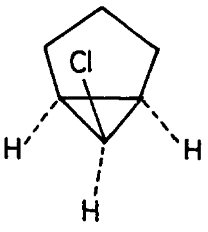
M. S. Baird and C. B. Reese

University Chemical Laboratory, Cambridge, England.

(Received 6 February 1967)



I



II

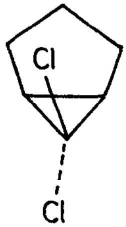
Reaction between cyclopentene and chlorocarbene (1) in ether solution at 20° gave exo- and endo-6-chlorobicyclo[3.1.0]hexanes (I and II, respectively), in ca. 35% combined yields. The more abundant isomer (ca. 75% of the mixture) was isolated by preparative g.l.c., and characterized as a chlorocarbene adduct of cyclopentene by elemental analysis* and mass spectrometry; it had the following n.m.r. spectrum (in CCl_4): τ 6.72, triplet ($J \sim 7$ c.p.s.), weight 1, assigned to H(6); τ 7.8-8.5, complex absorption, weight 8, assigned to all other protons. By virtue of the comparatively large coupling constant between H(6) and the other cyclopropyl protons (2), it was identified as the endo-isomer (II). The chemical shift and splitting of H(6) correspond closely with the data reported for H(7) of endo-7-chlorobicyclo[4.1.0]heptane (3).

The less abundant exo-6-chlorobicyclo[3.1.0]hexane (I) could not be

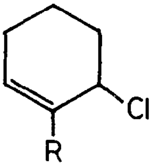
---

* Satisfactory analyses were obtained for all new compounds described.

separated completely from II by preparative g.l.c. However, it was obtained as a colourless liquid (b.p. 135°/760 mm; ca. 5% yield) by distilling the crude mixture of isomers from quinoline. It was characterized by elemental analysis and mass spectrometry, and had the following n.m.r. spectrum (in CCl_4): τ 7.38, triplet ($J \sim 1.5$ c.p.s.), weight 1, assigned to H(6); τ 8.0-8.5, complex absorption, weight 8, assigned to all other protons. The comparatively small splitting of H(6) is in accord with structure I (2,3).



III



IV

It is well known (4,5) that certain strained dihalocarbene adducts of cyclic olefins are subject to thermally induced ring expansion reactions. For example, when 6,6-dichlorobicyclo[3.1.0]hexane (III) was heated at 170°, a virtually quantitative yield of 2,3-dichlorocyclohexene (IV; R=Cl) was obtained in 1½ hr.** Endo-6-chlorobicyclo[3.1.0]hexane (II), in the same way, underwent quantitative rearrangement to 3-chlorocyclohexene (IV; R=H) in 4 hr. at 120°, whereas its exo-isomer (I) remained unchanged after it had been heated at 250° for 4 hr. The latter (I) decomposed slowly at 300° to give benzene as the major volatile product.

This difference in behaviour exhibited by exo- and endo-6-chlorobicyclo [3.1.0]hexanes towards the action of heat, provides clear experimental support for Woodward and Hoffmann's theoretical predictions (8) relating to reactions which proceed by the concerted rearrangement of cyclopropyl

---

** This result (6) corresponds closely to that reported earlier by Bergman (7).

to allyl cations. The required stereospecific disrotatory process can only occur in such strained ring systems when an *endo* carbon-halogen bond is broken.

Although it had been clearly demonstrated (9) that the solvolytic behaviour of cyclopropyl tosylates and chlorides was in accord with theory, the situation with regard to the thermally induced ring expansion reaction was previously less clear. Schweizer and Parham showed (10) that only one of the isomeric 2-oxa-7-chloronorcaranes rearranged in hot quinoline solution, and assumed that it was the *exo*-derivative. Jefford *et al*. recently examined the reaction between chlorocarbene and norbornene, and reported (11a) the formation of four isomeric products. These workers later revised their findings and concluded (11b) that chlorocarbene attacks norbornene exclusively on the less hindered side of its double-bond to give two tricyclic adducts. However, they were able to isolate only one of the latter, together with an isomeric unsaturated chloro-compound, which they regarded (11b) as the rearrangement product of the second adduct.

The study of the simpler system, described in this communication, has clarified the uncertainties in the previously published work: the isomeric 6-chlorobicyclo[3.1.0]hexanes were both stable enough to be isolated in a pure state, and then identified by n.m.r. spectroscopy. The investigation of the action of heat on the latter compounds (I and II) has established beyond doubt the stereochemistry of this synthetically useful ring expansion reaction.

Finally, it is noteworthy that the mass spectra of *exo*- and *endo*-6-chlorobicyclo[3.1.0]hexanes differ markedly. The spectrum of the *endo*-isomer (II) has a base peak at m/e = 79 (M - H_2Cl) and is virtually identical to that of 3-chlorocyclohexene (IV; R=H), whereas the spectrum of the *exo*-isomer (I) has a base peak at m/e = 67 (M - CH_2Cl).

Acknowledgement One of us (M.S.B.) thanks the Science Research Council for the award of a Research Studentship.

References

1. G. L. Closs and L. E. Closs, J. Am. Chem. Soc. 82, 5723 (1960).
2. H. M. Hutton and T. Schaefer, Canad. J. Chem. 40, 875 (1962); J. D. Graham and M. T. Rogers, J. Am. Chem. Soc. 84, 2249 (1962).
3. S. J. Cristol, R. M. Sequeira, and C. D. de Puy, ibid. 87, 4007 (1965).
4. W. E. Parham and E. E. Schweizer, Organic Reactions, 13, 55 (1963).
5. W. Kirmse, Carbene Chemistry, p. 145 et seq., Academic Press, New York, 1964.
6. D. G. Lindsay, Ph.D. Thesis, Cambridge University, 1965.
7. E. Bergman, J. Org. Chem. 28, 2210 (1963).
8. R. B. Woodward and R. Hoffmann, J. Am. Chem. Soc. 87, 395 (1965).
9. C. H. De Puy, L. G. Schnack, and J. W. Hausser, ibid. 88, 3343 (1966); P. von R. Schleyer, G. W. Van Dine, U. Schöllkopf, and J. Paust, ibid. 88, 2868 (1966).
10. E. E. Schweizer and W. E. Parham, ibid. 82, 4085 (1960).
11. (a) C. W. Jefford and R. Medary, Tetrahedron Letters, No. 19, 2069 (1966); (b) C. W. Jefford, E. Huang Yen, and R. Medary, ibid. No. 51, 6317 (1966).