144. Sigmatropic Rearrangements Accompanying the Addition of Dichlorocarbene to Norbornadiene[1])

by **Charles W. Jefford, Gérald Bernardinelli, Jean-Claude Rossier** and **Jacques A. Zuber**
Département de Chimie Organique, Université de Genève, CH-1211 Genève 4

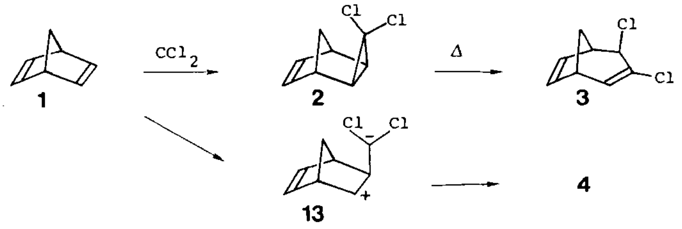
(17.V.82)

Summary

A new product arising from the reaction of dichlorocarbene with norbornadiene, 6*endo*-(2,2-dichlorovinyl)-*cis*-bicyclo[3.1.0]hex-2-ene, is described. It does not arise from the normal *exo*-1,2-adduct, but possibly originates by sigmatropic rearrangement of an initially formed zwitterionic intermediate.

Nearly all additions of singlet halocarbenes to mono-olefins occur in a single concerted step. The result is a cyclopropane adduct which retains the configuration of the original substituents [1]. However, a few exceptions have been noted where the products have been rationalized by two-step processes [2]. We now report an exception where a sigmatropic rearrangement apparently occurs during the addition of dichlorocarbene to norbornadiene[1]) (**1**), a reaction which, despite much study, still reveals novel facets of reactivity [3].

When dichlorocarbene generated by the action of potassium *t*-butoxide on chloroform in ether is allowed to react with **1** in excess, several additions take place [4]. The most important is 1,2-addition which gives the *exo*-adduct **2**. The normal fate of **2** is rapid rearrangement [5] to 3,4-*exo*-dichlorobicyclo[3.2.1]octa-2,6-diene (**3**). However, we have now discovered that another simple addition must have occurred, because a second rearrangement product **4** is formed, albeit in small yield (8–11%). It was isolated and identified by its further reaction with dichlorocarbene. The structure of the single ensuing adduct **5** was unambiguously



---

[1]) The IUPAC name of norbornadien is 8,9,10-trinorborna-2,5-dien.

0018-019X/82/5/1467-03$01.00/0

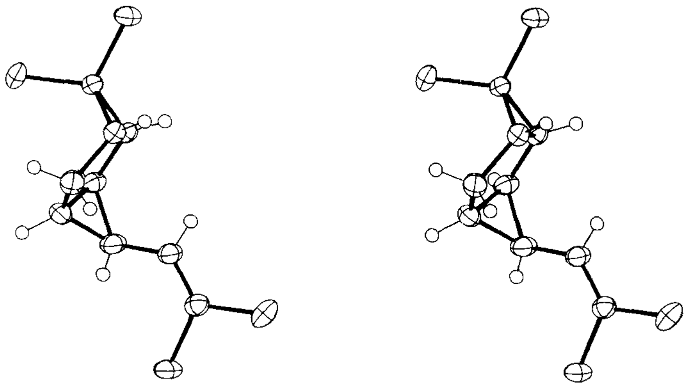
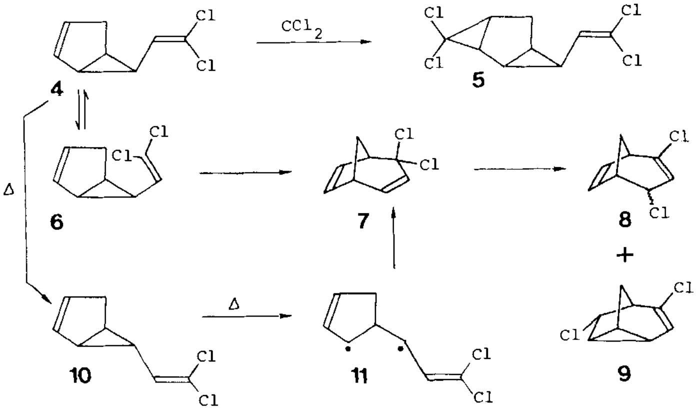


Fig. 1. *ORTEP stereoscopic view of the molecular structure of compound* **5**

identified by single crystal X-ray analysis [6]. Apart from the pair of *trans*-disposed cyclopropane rings, the chief features are the *endo*-configuration of the vinyl group with respect to the parent *cis*-fused bicyclo[3.1.0]hexene fragment and its extended conformation *(Fig. 1)*. This geometry may be extrapolated to the mono adduct **4**, which undoubtedly accounts for its existence. If the more hindered conformation **6** were adopted, *Cope* rearrangement to 4,4-dichlorobicyclo[3.2.1]octa-2,6-diene (**7**) would be the expected outcome. In fact, similar molecules, but lacking bulky geminal substituents on the vinyl group, undergo instantaneous rearrangement to the bicyclo[3.2.1]octa-2,6-diene skeleton [7]. Nonetheless, strong heating of **4** (150–170°) gives initially the presumed 4,4-dichlorobicyclo[3.2.1]octa-2,6-diene (**7**), which is converted entirely into its rearrangement products **8** and **9**. However, at lower temperatures, namely 120°, the first-formed product is the *exo*-isomer **10** which on further heating to 150–170° gives products **8** and **9**. The *endo*- and *exo*-isomers **4** and **10**, respectively, are easily distinguished by the values of the vicinal coupling constants of the cyclopropane H-atoms.



Both isomerization processes may arise by homolytic rupture of the cyclopropane ring. Both the passage of **4** to **10** and the ultimate conversion of **10** to products **8** and **9** undoubtedly involves the double allylic radical **11** [8]. Closure can occur in two senses either to equilibrate **4** and **10** or to give the final product **7**, which is presumably the most stable thermodynamically.

The last question concerns the origin of **4**. It is unlikely that the *exo*-cyclopropane product **2** would spontaneously generate **4** on account of its ready ionization to give **3**. Although oxa- and azacyclopropane analogues of **2** readily rearrange at room temperature to the corresponding hetero atom substituted skeleton **3** [9], the *exo*-tricyclo[3.2.1.$0^{2,4}$]octane requires elevated temperatures to bring about rearrangement [10]. In order to verify this conclusion, one equivalent of dichlorocarbene was allowed to add to **1** at 0°. The *exo*-adduct **2** was carefully isolated. Thermal isomerization of pure **2** at 20° was monitored by NMR. spectroscopy and GC. Conversion to **3** was quantitative with no trace of **4** being detected. On the other hand, initial mixtures obtained from the reaction of dichlorocarbene with norbornadiene at temperatures below –10° always contained **2** as main product, small amounts of **4**, but no trace of **3**. Consequently, we believe that 1,2-addition is preceded by a zwitterionic species such as **2** which branches to **2** and **4**[2].

We thank the *Fonds national suisse de la recherche scientifique* for support of this work.

REFERENCES

[1] *W. Kirmse*, 'Carbene Chemistry', 2nd ed., Academic Press, New York, N.Y. 1971; *idem*, 'Carbenes', Vol. I and II, ed. M. Jones, jr. and R.A. Moss, J. Wiley, New York, N.Y. 1973 and 1975.

[2] *N.C. Yang & T.A. Marolewski*, J. Am. Chem. Soc. *90*, 5644 (1968); *J.B. Lambert, K. Kobayashi & P.H. Mueller*, Tetrahedron Lett. *1978*, 4253; *M. Jones, jr., P.P. Gaspar & J.B. Lambert*, ibid. *1978*, 4257.

[3] *C.W. Jefford, J.C. Rossier & J.A. Zuber*, Angew. Chem. *1982*, in press.

[4] *C.W. Jefford, V. de los Heros & U. Burger*, Tetrahedron Lett. *1976*, 703; *C.W. Jefford, J.C. Rossier & J.A. Zuber*, unpublished work.

[5] *C.W. Jefford, J. Mareda, J.C.E. Gehret, T. Kabengele, W.D. Graham & U. Burger*, J. Am. Chem. Soc. *98*, 2585 (1976).

[6] *G. Bernardinelli, J.A. Zuber & R. Gerdil*, to be published.

[7] *C. Cupas, W.E. Watts & P.v.R. Schleyer*, Tetrahedron Lett. *1964*, 2503; *J.M. Brown*, J. Chem. Soc., Chem. Commun. *1965*, 226; *G.W. Klumpp, J.W.F.K. Barnick, A.H. Veefkind & F. Bickelhaupt*, Recl. Trav. Chim. Pays-Bas *88*, 767 (1969); *W. Adam, O. De Lucchi & D. Scheutzow*, J. Org. Chem. *46*, 4130 (1981).

[8] *J.E. Baldwin & K.E. Gilbert*, J. Am. Chem. Soc. *98*, 8283 (1976).

[9] *J. Meinwald, S.S. Labana & M.S. Chadha*, J. Am. Chem. Soc. *85*, 582 (1963); *A.C. Oehlschlager & L.H. Zalkow*, J. Org. Chem. *1965*, 4205.

[10] *R.B. Kinnel & P.K. Freeman*, Tetrahedron Lett. *1973*, 4803; *V. de los Heros*, Thesis No. 1942 (1979), Geneva.

---

[2] Alternatively, the *endo*-counterpart of **13** could also form and lead to product **4**. We will expatiate on this matter in the full paper.