

144. Sigmatropic Rearrangements Accompanying the Addition of Dichlorocarbene to Norbornadiene¹⁾

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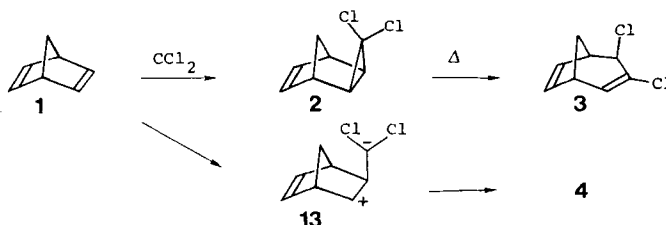
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Summary

A new product arising from the reaction of dichlorocarbene with norbornadiene, *6endo*-(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 norbornadiene¹⁾ (**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 norbornadiene is 8,9,10-trinorborna-2,5-diene.

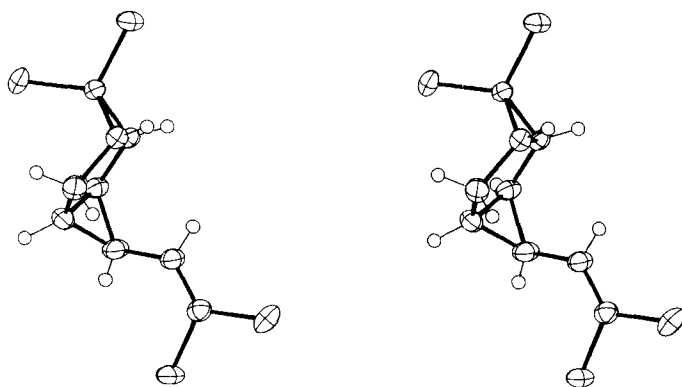
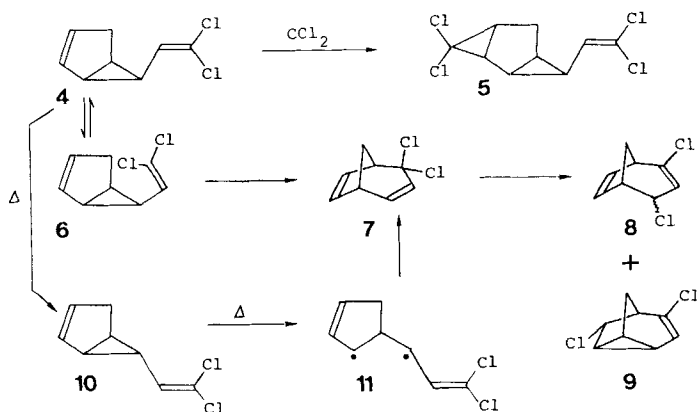


Fig. 1. ORTEP stereoscopic view of the molecular structure of compound 5

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).

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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. Veeckind & F. Bickelhaupt, Recl. Trav. Chim. Pays-Bas 88, 767 (1969); W. Adam, O. De Lucchi & D. Scheutzw, 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.