

- [12] *D. H. Ball, F. A. Carey, I. L. Klundt & L. Long*, Carbohydrate Research **10**, 121 (1969).
 [13] *A. D. Ezekiel, W. G. Overend & N. R. Williams*, Tetrahedron Letters **1969**, 1635.
 [14] *J. S. Brimacombe & D. A. Ching*, Carbohydrate Research **8**, 82 (1968).
 [15] *J. D. Stevens & H. G. Fletcher*, J. org. Chemistry **33**, 1799 (1968).
 [16] *J. Prokop & D. H. Murray*, J. pharmaceut. Sci. **54**, 359 (1965).
 [17] *F. A. Carey, D. H. Ball & L. Long*, Carbohydrate Research, **3**, 205 (1966).
 [18] *K. Biemann & J. A. McCloskey*, J. Amer. chem. Soc. **84**, 2005 (1962).
 [19] *S. Hanessian, D. C. De Jongh & J. A. McCloskey*, Biochim. biophys. Acta **117**, 480 (1966);
J. J. Dolhun & J. L. Wiebers, Organic Mass Spectroscopy **3**, 669 (1970).
 [20] *C. D. Jardetsky*, J. Amer. chem. Soc. **82**, 229 (1960).
 [21] *M. Karplus*, J. chem. Physics **30**, 11 (1959).
 [22] *R. J. Abraham, L. D. Hall, L. Hough & K. A. McLauchlan*, J. chem. Soc. **1962**, 3699.
 [23] *B. J. Blackburn, A. A. Gray, I. C. P. Smith & F. E. Hruska*, Canad. J. Chemistry **48**, 2866 (1970).
 [24] *F. E. Hruska, A. A. Gray & I. C. P. Smith*, J. Amer. chem. Soc. **92**, 4088 (1970).
 [25] *J. M. J. Tronchet & J. Tronchet*, Résultats non publiés.
 [26] *A. Bloch, M. J. Robins & J. R. McCarthy*, J. medicin. Chemistry **10**, 908 (1967).
 [27] *H. T. Shigeura & S. D. Sampson*, Nature **215**, 419 (1967).
 [28] *C. H. Gray & E. L. Tatum*, Proc. natl. Acad. Sci. U.S. **30**, 404 (1944).
 [29] *L. J. Hanka & M. R. Burch*, Antibiotics & Chemotherapy **10**, 484 (1960).
 [30] *J. A. Souza & A. L. Bluhm*, J. org. Chemistry **25**, 108 (1960).
 [31] *M. W. Bullock, J. J. Hand & E. L. R. Stokstad*, J. org. Chemistry **22**, 568 (1957); *J. Davoll & B. A. Lowy*, J. Amer. chem. Soc. **73**, 1650 (1951).
 [32] *C. P. J. Glaudemans & H. G. Fletcher*, J. org. Chemistry **28**, 3004 (1963).

153. The Synthesis of 7,7-Difluoronorbornene

Preliminary Communication¹⁾

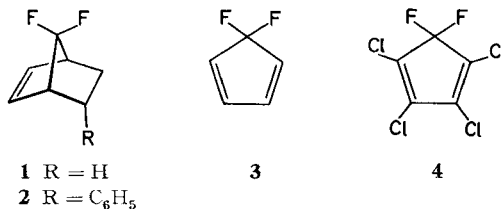
by **C. W. Jefford** and **W. Broeckx**

Département de Chimie Organique, Université de Genève, 1211 Genève 4

(25. V. 71)

Summary. The synthesis of 7,7-difluoronorborn-2-ene and its *endo*-5-phenyl derivative is described.

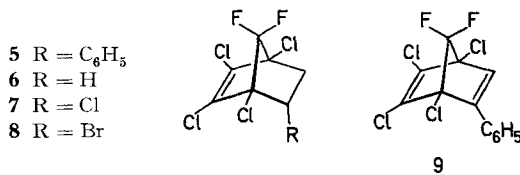
7,7-Difluoronorbornene (**1**) and its derivatives should be excellent candidates for mechanistic studies, especially so in view of the versatility of the norbornene skeleton [1] and the particular spectroscopic visibility of the substituent fluorine [2]. We report here an effective method for the synthesis of **1** and its *endo*-5-phenyl derivative **2**.



The obvious approach to the synthesis of **1** and its derivatives is by the (4 + 2) cyclo-addition of 5,5-difluorocyclopentadiene (**3**) to olefins. Unfortunately, compound

¹⁾ A detailed article will be submitted later to *Helv.*

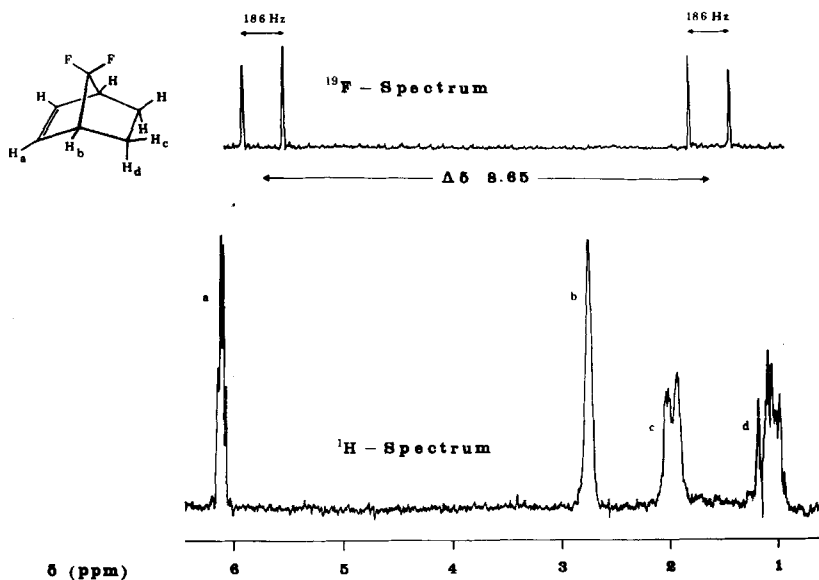
3 is not known [3]. However the tetrachloro derivative **4** is easily available [4] and its cyclo-addition affords a route to the desired derivatives of **1** provided that the chlorine atoms can be removed without disturbing the fluorines. By extension of a well-established procedure [5] some chlorinated 7,7-difluoronorbornenes (**5-9**) were prepared as candidates for trial experiments of selective reduction.



The dehalogenation of bridged bicyclic halogen compounds by dissolving metals is an old reaction although the precise mechanism is not known [6]. In our case a solution of lithium or sodium in a mixture of *t*-butanol and tetrahydrofuran (THF) was chosen as being the most promising reducing agent as it works well for the reductive dechlorination of isodrin, aldrin and related compounds such as 7,7-dimethoxy-1,2,3,4-tetrachloronorborn-2-ene [7] [8]. Moreover, it shows some discrimination in the reduction of *gem*-fluorochlorocyclopropanes [9].

Heating a solution of **5** (29 g = 0.084 mol), sodium (20 g; 0.87 g-atoms) in *t*-butanol (20 ml) and THF (140 ml) gave *endo*-2-phenyl-7,7-difluoronorborn-5-ene (**2**) (5.10 g, 72% yield) as a colourless liquid, b.p. 110°/12 Torr, $n_D^{22.5} = 1.5240$. No other product was formed.

Similar treatment of **6** (1.44 g) gave 7,7-difluoronorborn-2-ene (**1**) as an extremely volatile colourless solid (200 mg) which had to be immediately stored in a closed

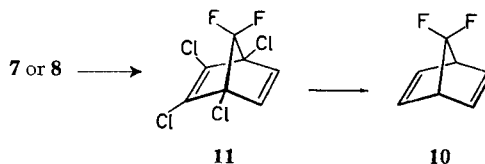


¹H-NMR-Spectrum of 7,7-difluoronorborn-2-ene in CCl₄ at 100 MHz with internal (CH₃)₄Si (bottom) and the ¹⁹F-AB-Quartet at 94.1 MHz (top)

bottle. Although the yield is small, this is undoubtedly due to loss during isolation, as gas-chromatography showed the reaction to be complete with **1** being the only product formed.

The structures of **1** and **2** were confirmed by their NMR. spectra. The proton and fluorine spectra of **1** are shown in the figure.

In an attempt to prepare 7,7-difluoronorbornadiene (**10**), both the *endo* chloro and bromo derivatives **7** and **8** were submitted to similar reduction; however, a mixture of



three products was found, from which only **1** could be isolated (30% yield) and characterized.

It is possible that **1** could have arisen by reductive removal of all five halogens on the six-membered ring. On the other hand, elimination could have initially occurred to give **11** which then gives **10** with subsequent formation of **1**. This second possibility cannot be excluded as pure **11** (prepared by treatment of **7** or **8** with potassium *t*-butoxide in dimethyl sulfoxide) gave on reduction the same products as those obtained directly from **7** and **8**. Similarly the reductive dechlorination of the phenyl-tetrachlorodiene **9** gave the norbornene **2** in 40% yield together with six other uncharacterized products.

It can be concluded that although the *gem*-difluoro grouping easily survives the conditions of the *Winstein-Gassman* procedure, the second double bond of norbornadiene does not. Other methods for obtaining **10** by reduction are being studied. The chemical and physical properties of these new fluorinated norbornenes will be described elsewhere.

Compounds **5–9** and **2** gave acceptable elemental microanalytical values. The NMR. spectra of **1** and **2** were determined on a *VARIAN* model XL-100 spectrometer.

We are indebted to the *Swiss National Fund for Scientific Research* for an equipment grant (No. 5202.2). We thank Dr. *U. Burger* of our department for the proton and fluorine NMR. spectra.

BIBLIOGRAPHY

- [1] *G. E. Gream*, *Pure appl. Chemistry* **16**, 25 (1966); *G. D. Sargent*, *Quart. Rev.* **20**, 301 (1966).
- [2] *C. W. Jefford*, *D. T. Hill*, *L. Ghosez*, *S. Toppet* & *K. C. Ramey*, *J. Amer. chem. Soc.* **91**, 1532 (1969); *C. W. Jefford*, *D. T. Hill* & *K. C. Ramey*, *Helv.* **53**, 1194 (1970).
- [3] *J. Sauer*, *Angew. Chem.* **78**, 233 (1966).
- [4] *E. T. McBee*, *D. K. Smith* & *H. E. Ungnade*, *J. Amer. chem. Soc.* **77**, 387 (1955); *E. Forche*, in *Houben-Weyl, 'Methoden der Organischen Chemie'*, Band V/3 p. 270, Thieme, Stuttgart 1962.
- [5] *K. L. Williamson* & *J. C. Fenstermaker*, *J. Amer. chem. Soc.* **90**, 342 (1968).
- [6] *R. C. Fort, Jr.* & *P. von R. Schleyer*, *Adv. alicycl. Chemistry* **1**, 283 (1966).
- [7] *P. Bruck*, *D. Thompson* & *S. Winstein*, *Chemistry & Ind.* **1960**, 405.
- [8] *P. G. Gassman* & *J. L. Marshall*, *Org. Syn.* **48**, 68 (1968); *P. G. Gassman*, *D. H. Aue* & *D. S. Patton*, *J. Amer. chem. Soc.* **90**, 7271 (1968).
- [9] *M. Schlosser* & *G. Heinz*, *Angew. Chem., Int. Ed.* **6**, 629 (1967).