

THE REACTION OF DIFLUOROCARBENE WITH QUADRICYCLANE<sup>1</sup>

Ulf Misslitz and Maitland Jones, Jr.\*

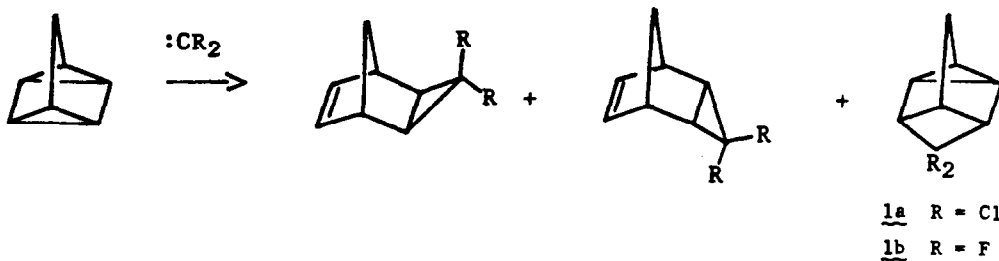
Department of Chemistry, Princeton University  
Princeton, New Jersey 08544

Armin de Meijere

Institut für Organische Chemie und Biochemie  
Universität Hamburg  
Federal Republic of Germany

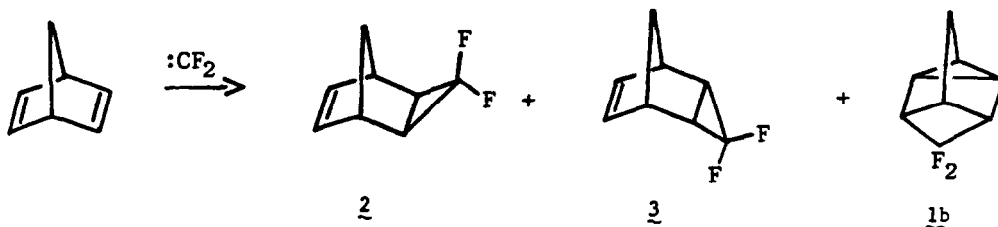
**Summary:** The reaction of quadricyclane with difluorocarbene to give endo-6-(2,2-difluoro-vinyl)bicyclo[3.1.0]hex-2-ene (4) along with previously reported minor products is described and compared with earlier work.

CARBENES are renowned for their ability to react with carbon-hydrogen  $\sigma$  and carbon-carbon  $\pi$  bonds, yet examples of their reaction with carbon-carbon  $\sigma$  bonds are rare. However, we have twice reported the reaction of carbenes with pairs of carbon-carbon single bonds.<sup>2,3</sup> In the course of the second report<sup>3</sup> we remarked on the difference between our results on the reaction of dichlorocarbene and quadricyclane with those reported earlier.<sup>4</sup> We were unable to resolve the discrepancy which centered on the formation



of large amounts of 1a in Geneva but not in Princeton. In the course of an investigation of the reactions of difluorocarbene with compounds containing strained  $\sigma$  bonds we reinvestigated the reactions of difluorocarbene with norbornadiene and quadricyclane. We were able to reproduce the reported results in the former case<sup>5,6</sup> but not in the latter,<sup>4</sup> as we were unable to isolate appropriate amounts of 1b from quadricyclane. Here we describe the hitherto unreported major product of the reaction and suggest a resolution of the disparate results with quadricyclane.<sup>2,3,4</sup>

Generation of difluorocarbene in norbornadiene by the method of Burton<sup>7</sup> led to the product mixture shown below and in table 1 (overall yield: 33%). Crude reaction mixtures were examined by <sup>1</sup>H and <sup>19</sup>F NMR spectroscopy<sup>8</sup> and individual compounds identified by examination of collected samples and/or independent synthesis. The composition of new compounds was determined by elemental or high resolution mass spectral analysis. The

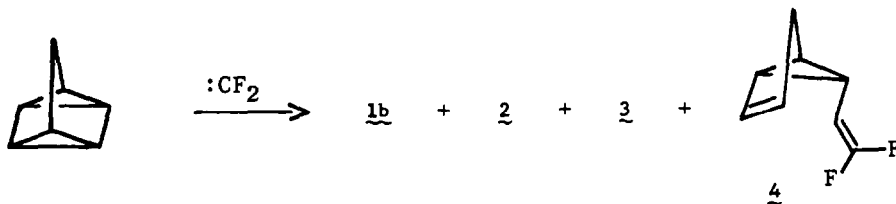


relative amounts of the products (1b, 2, 3) compare favorably with those reported previously<sup>5,6</sup> (table 1). It is important to note that no difficulty was found in detecting or isolating 1b.

**Table 1.** Reaction of Norbornadiene with Difluorocarbene

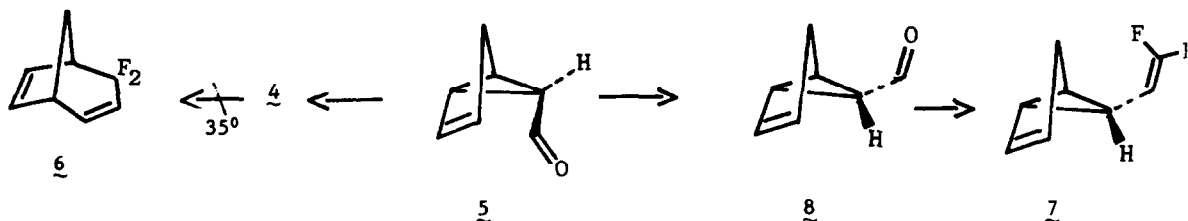
Reference	1b	2	3
This work	31.4	65.6	3.0
Reference 5	34	55-62	4-11

By contrast, generation of difluorocarbene in quadricyclane did not reproduce previously reported data<sup>4</sup> (table 2). The reported relative yields of 1b could not be duplicated and a new major product, endo-6-(2,2-difluorovinyl)bicyclo[3.1.0]hex-2-ene **4** was found along with a number of secondary minor products derived from **4** and difluorocarbene (overall yield: 3%). The structure of **4** was secured by its synthesis by a difluoro



methylenation reaction<sup>9</sup> on bicyclo[3.1.0]hex-2-en-6-endo-carboxaldehyde **5**.<sup>10</sup> As we were startled by the stability of **4** towards rearrangement to

4,4-difluorobicyclo[3.2.1]oct-2,6-diene **6**,<sup>11</sup> we generated **7**, the exo epimer of **4** from the exo aldehyde **8**.<sup>13</sup> The <sup>1</sup>H NMR spectrum of the endo aldehyde showed the expected equilibrium with the bicyclo[3.2.1] valence tautomer<sup>10</sup> whereas the exo aldehyde was



static. Thus our assignment of stereochemistry to **4** and **7** is secure. Although a dichloro relative of **4** was isolated by Jefford and his coworkers from a reaction of dichlorocarbene and norbornadiene,<sup>14</sup> the formation of **4** from quadricyclane is unprecedented.<sup>15</sup>

**Table 2.** Reaction of Quadricyclane with Difluorocarbene

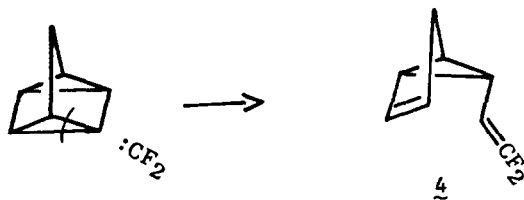
Reference	1b	2	3	4	diadducts (from 4)
This work	2.7	12.2	-	60.1	25.3
1b + 2 = 100% <sup>a</sup>	18	82			
Reference 4	28	70	2		

(a) This allows direct comparison with ref. 4 in which compound **4** was not detected.

Two questions remain. First, what is the origin of the discrepancy in results concerning the formation of **1**?<sup>16</sup> Second, what is the mechanism of the formation of **4**?

Quadricyclane is most difficult to obtain completely free of norbornadiene. The best we have achieved is 99.75% purity. This results in a 2.7% relative yield of **1b**, and a much larger relative yield if **4** and diadducts are ignored. Thus the previous reports<sup>4</sup> may be the result of reaction with quadricyclane containing ca. 5% norbornadiene.

The question of mechanism is difficult at the moment. It is becoming fashionable to posit stepwise reactions of singlet carbenes,<sup>14,18</sup> and such a mechanism can be crafted for the formation of **4**. But **4** is also potentially the product of a concerted reaction of difluorocarbene with the bicyclo[2.1.0] system contained within quadricyclane. Precedent for such a mechanism exists in the reactions of carbenes with bicyclobutanes.<sup>3</sup>



## REFERENCES AND NOTES

- (1) Support from the National Science Foundation through Grant CHE-8118345 is gratefully acknowledged. We also thank the Studienstiftung des deutschen Volkes for a Fellowship for UM.
- (2) M. L. Tetef and M. Jones, Jr., Tetrahedron Lett., **25**, 161 (1984).
- (3) J. E. Jackson, G. B. Mock, M. L. Tetef, G-x. Zheng and M. Jones, Jr., Tetrahedron, **41**, 1453 (1985).
- (4) C. W. Jefford, J.-C. E. Gehret and V. de los Heros, Bull. Soc. Chim. Belg., **88**, 973 (1979).
- (5) C. W. Jefford, J. Mareda, J.-C. E. Gehret, nT. Kabengele, W. D. Graham and U. Burger, J. Am. Chem. Soc., **98**, 2585 (1976).
- (6) For a discussion see also: P. M. Kwantes, Dissertation, Vrije Universiteit, Amsterdam, 1979.
- (7) D. J. Burton and D. G. Naeae, J. Am. Chem. Soc., **95**, 8467 (1973).
- (8) We thank Dr. R. W. Creekmore and R. Fischer of the FMC Company and M. W. Baum of Princeton for most generous help in determining the  $^{19}\text{F}$  NMR spectra.
- (9) M. Obayashi, E. Ito, K. Matsui and K. Kondo, Tetrahedron Lett., **23**, 2323 (1982).
- (10) M. Rey and A. S. Dreiding, Helv. Chim. Acta, **48**, 1985 (1965).
- (11) For a discussion of the thermal rearrangement of the parent hydrocarbon which isomerizes at 33° C see J. J. Gajewski, "Hydrocarbon Thermal Isomerizations," Academic Press, New York, 1981, p 258 ff. At ca. 125° C, **4** does isomerize to **6**, U. Misslitz, unpublished work.
- (12) J. M. Brown, Chem. Commun., 226 (1965).
- (13) D. L. Garin, J. Chem. Soc., Chem. Commun., 403 (1973). N. W. Alcock, J. M. Brown, J. A. Conneely and D. H. Williamson, J. Chem. Soc., Perkin Trans. II, 962 (1979).
- (14) C. W. Jefford, G. Bernardinelli, J.-C. Rossien and J. A. Zuber, Helv. Chim. Acta, **65**, 1467 (1982).
- (15) For reactions of the parent bicyclo[2.1.0]pentane see the accompanying paper.
- (16) The problem is actually even more serious. Although the Geneva group is now in agreement with the results reported here for :CF<sub>2</sub> there is still disagreement concerning the reaction with :CCl<sub>2</sub>. The original claim of 57% **1a** has been reduced to 12% but is still in contrast to the upper limit of "traces" as reported by us in ref. 3. In addition, a substantial amount of the dichloro analogue of **4** is now reported<sup>17</sup> to be formed in this reaction. We stand by our earlier results.<sup>3</sup>
- (17) We thank Prof. C. W. Jefford for the most opportune communication of a preprint. Be alert for C. W. Jefford, J. Roussilhe and M. Papadopoulos, In Press.
- (18) E. V. Dehmlow and R. Kramer, Angew. Chem. Internat. Ed. Engl., **23**, 706 (1984).

(Received in USA 2 August 1985)