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CHELETROPIC ADDITIONS OF DIFLUORO AND DICHLOROCARBENES TO HINDERED NORBORNADIENES

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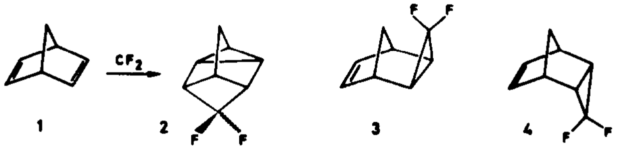
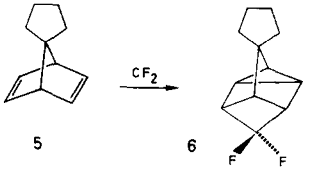
We have recently reported that linear homo-1,4 additions of fluorocarbenes to homodienes can be observed if the competing non-linear cyclopropanation reaction can be disfavoured by some special steric or entropy factor[1,2]. As a prototype of this reaction we studied the addition of difluorocarbene to norbornadiene (1). We demonstrated that the homo-1,4 adduct 2 arises directly and does not derive from rearrangements of the exo-1,2 (3) or the endo-1,2 adduct (4). This result taken together with a consideration of the exchange reaction for the two partners has constituted the basis of our argument for the concerted formation of 2 in an unprecedented cheletropic reaction[3,4].



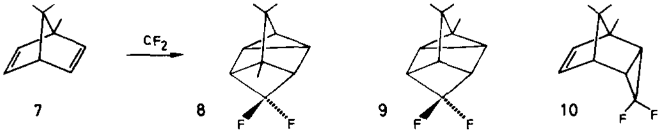
1 2 3 4

While in this instance the classic 1,2 addition is still dominant, it should be possible to favour homo-1,4 addition at the expense of cyclopropanation if a suitable choice of the diene partner is made. This we have done, and we present here our results obtained with norbornadiene derivatives substituted at C7 with moderately bulky groups. The thermolysis of phenyltrifluoromethylmercury and sodium iodide in benzene at 80°[6] in the presence of the spirocyclic norbornadiene 5[5] gave a single 1:1 adduct 6 in nearly quantitative yield (limits of detection of isomers of 6, about 3%), which we have established as the product of cheletropic reaction.

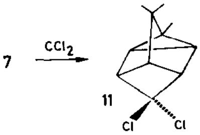


5 6

Another model diene which is strongly hindered on the exo side is bornadiene 7[7]. The reaction of 7 with difluorocarbene generated at 25° from triphenylbromodifluoromethylphosphonium bromide[8] gave predominantly adducts from cheletropic reaction. Apart from the endo cyclopropane adduct 10 which was formed to the extent of 4%, the rest of the mixture consisted of two isomeric homo-1,4 adducts. The more hindered adduct 8 having a methyl group disposed syn to the fluorine substituent was formed in preference to the anti-adduct 9 (61% vs. 35%). The total yield amounted to 42%. The distinction between 8 and 9 was made from the ^{19}F-NMR spectral analysis. The equatorial fluorine atom (F_x) of 8 is not only coupled with the contiguous methyl group (^5J = 3 Hz), but also displays the characteristically large double zigzag coupling (^5J = 7.5 Hz) with the hydrogen atom at position 8[3]. Both of these tell-tale heteronuclear couplings were absent in the case of 9 (Table 1).



7 8 9 10



7 11

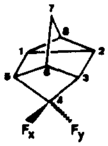
The discovery of these examples of cheletropic reactions resides partly in the "visibility" of the fluorine substituted adducts in the NMR which facilitated the identification and elucidation of their structures. However, one wonders if

Table 1. ^{19}F-NMR Chemical Shifts[a] in $CDCl_3$ and Characteristic Coupling Constants of Homo-1,4 Adducts[b].

Compound	δ F_x	δ F_y	$^2J_{FF}$	$^4J_{HF}$	$^5J_{HF}$
6	119.1	103.1	162.0 Hz	H-6, F_x 4.6 Hz	H-8, Fx 9.8 Hz
8	114.7	97.3	167.5		H-8, F_x 7.5 6-CH_3, F_x 3.0
9	120.2	101.7	163.5	H-6, F_x 4.5	

a) Expressed in δ [ppm] upfield from internal $FCCl_3$

b) See Scheme 1 for numbering convention.



Scheme 1

the fluorine substituent confers on the carbene in some undefined manner a preference for homo-1,4 addition. We believe that the answer ought to be no[4] and indeed we now find that dichlorocarbene can be induced to undergo homo-1,4 addition. Dichlorocarbene was generated at 50°[9] and was allowed to react with 7. In addition to small amounts of rearranged products, the cheletropic adduct 11 was found in 45% yield. The structure of 11 was unambiguously established from its mass, ^{13}C-NMR and ^{1}H spectra (cf. Table 2).

From these findings, it can be safely concluded that the cheletropic reaction is general for σ^2 carbenes. On the other hand, the extension of this reaction type to dienes not possessing the bicyclo[2.2.1]heptadiene skeleton remains to be explored. These matters are currently under investigation.

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Table 2. ^{1}H-NMR Chemical Shifts[a] in $CDCl_3$ of Homo-1,4 Adducts[b].

Compound	Proton 1	2	3	4	5	6	7	8	gem-CH_3	-CH_3
6	c)	c)	2.72	-	2.72	1.90	-	c)	-	-
8	1.48	1.48	2.44	-	2.44	-	-	1.64	0.78	1.12
9	1.35	1.35	2.72	-	2.70	1.85	-	-	0.81	1.06
10	-	2±0.3	-	2±0.3	2.64	5.76	5.95	-	0.90 +1.04	1.20
11	1.58	1.58	2.95	-	2.95	2.22	-	-	0.80	1.06

a) Expressed in δ [ppm] relative to internal TMS

b) See Scheme 1 for numbering convention

c) Complex spectrum between 1.2 and 1.8 ppm.

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