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THE THERMAL STABILITY OF EXO AND ENDO TRICYCLO[3.2.1.0^{2,4}]OCT-6-ENES AND THEIR RELEVANCE TO THE CYCLO-ADDITION OF CYCLOPROPENES TO CYCLOPENTADIENE.

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As a general rule, cyclopropanes undergo cyclo-addition with cyclopentadiene (1) with various degrees of ease to give exclusively the endo adduct[1]. Exceptions are few, and a glaring one is that reported for 1,2-bis(trifluoromethyl)-3,3-difluorocyclopropene (2) (Fig. 1). Reaction with cyclopentadiene at -78° gave two 1:1 adducts in a ratio of 69 to 31. The major adduct was assigned the exo structure 3 and assumed to be the kinetic product since on gentle heating it progressively isomerized to the minor adduct of endo configuration 4[2]. Further heating of the purported endo isomer 4 at 200° resulted in its conversion to the tetracyclic isomer 5.

It is now evident from our experience with molecules of types 3 and 4, prepared by the carbene route[3], that the above configurational assignments are in error and should be reversed.

The generation of difluorocarbene at 20° in the presence of norbornadiene (6) gave rise to three 1:1 adducts[4]. The formation of the homo-1,4 adduct 7 constitutes a possible first example of the cheletropic addition of a carbene to a homo-conjugated diene[5]. However, what is important here is that it proved possible to separate the exo and endo adducts 8 and 9 by working carefully at low temperature and to examine their thermal behaviour.

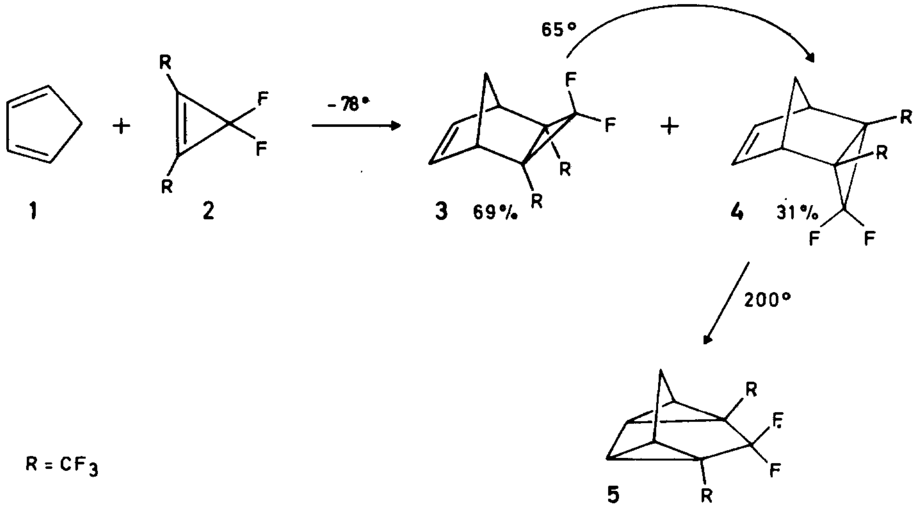
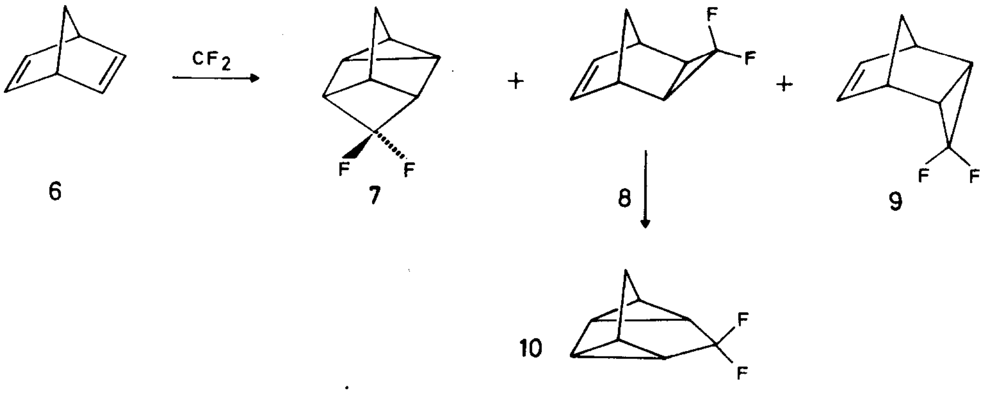
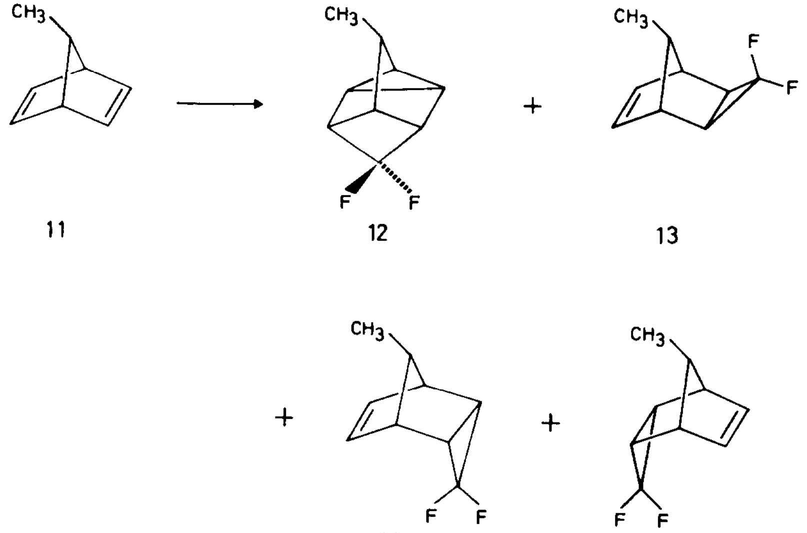


Fig. 1. Structures assigned to adducts obtained from cyclopentadiene and 1,2-bis-(trifluoromethyl)-3,3-difluorocyclopropene (ref. 2).



The crucial task of structure assignment is based on the analysis of the ^{19}F and ^{1}H NMR spectra and on comparison with the results obtained from 7-methylnorbornadiene (11)[6]. Once again, the addition of difluorocarbene at low temperature gives the mechanistically significant homo-1,4 adduct 12, a single 1,3 exo adduct 13, but two endo 1,2 adducts 14 and 15.



11 12 13

14 15

Apart from the conventional deductive spectral analysis, the clue which permitted identification of the endo fused cyclopropane structure is the long-range coupling, $^{5}J_{FH}$ = 8.5 Hz, which characterizes the double zig-zag arrangement of sigma bonds (Fig. 2). Only the endo structures 9 and 15, and significantly the purported "exo" structure 3 display this coupling. Where and when this zig-zag motif is absent, in the endo adduct 14 and the authentic exo adducts 8 and 13 and also in 4, then no such coupling is observed[7]. It is interesting to note in this respect that both the homo-1,4 adducts 7 and 12 possess the zig-zag feature and consequently display a coupling of 9.8 Hz between the single bridgehead proton and the appropriate apotropic fluorine atom.

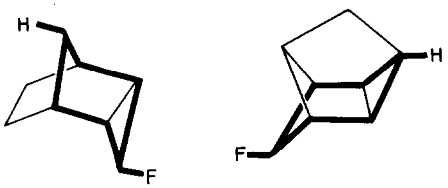


Fig. 2. Double zig-zag motif for ${}^{5}J_{HF}$ coupling.

Gentle heating (60 to 80°) of the *endo* adducts **9** and **14** converts them stereospecifically to the *exo* isomers **8** and **13** respectively. However, the *syn* disposed methyl group ensures that the *endo* adduct **15** remains stable to 120°. Further heating of the *exo* adduct **8** at 225° gives the tetracyclic isomer **10**.

The results clearly demonstrate that claims for *exo* addition of cyclopropene to cyclopentadiene and molecules of similar structure must be treated with caution[8].

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