

ADDITIONS OF FLUOROCARBENES TO NORBORNADIENE BY LINEAR CHELETROPIC REACTION

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If we accept the simplified description of a σ^2 carbene as consisting of the superposition of a carbocation and a carbanion¹, then in principle it should be able to undergo cyclo-addition with polyenes in two distinct ways. The ends of the polyene system can construct new sigma bonds by interaction with either the empty p_z -orbital or the filled sp^2 -orbital of the carbene (see Fig.)². Typically, butadiene would be expected to give cyclopropane derivatives with carbenes exhibiting electrophilic behaviour, whereas cyclopentenes should be obtained from a nucleophilic species^{3,4}. Up to the present time, only the first of these two possibilities is commonly realized⁵. Although several cases of 1,4 addition have been reported⁶, only one appears to be genuine, but even here the 1,4 product simply arises as a consequence of the competition between alternative courses of a two-step process arising from triplet carbene⁷.

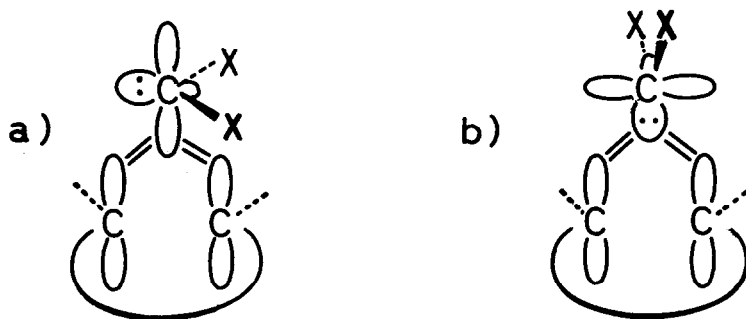


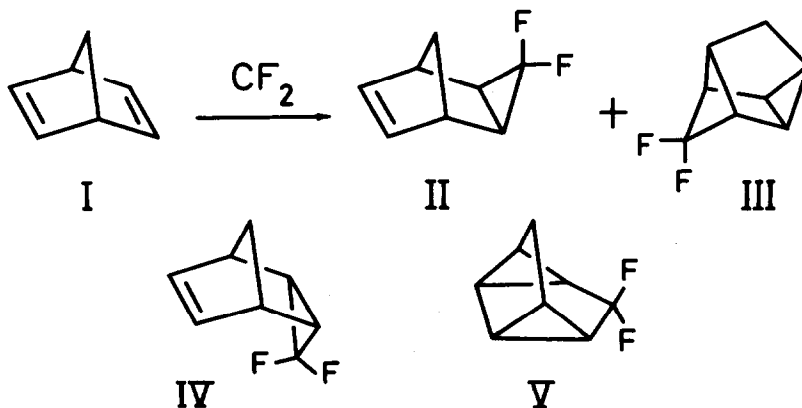
Figure. Transition states for addition of σ^2 carbenes to a polyene; a) engagement of the p_z -orbital (electrophilic attack) on non-linear approach and b) engagement of the sp^2 -orbital (nucleophilic attack) on linear approach.

With the appropriate choice of carbene and diene partners, it should be possible to create conditions favourable for the observation of concerted 1,4 cyclo-addition. The present paper describes reactions of difluoro and fluoro-chlorocarbenes with norbornadiene.

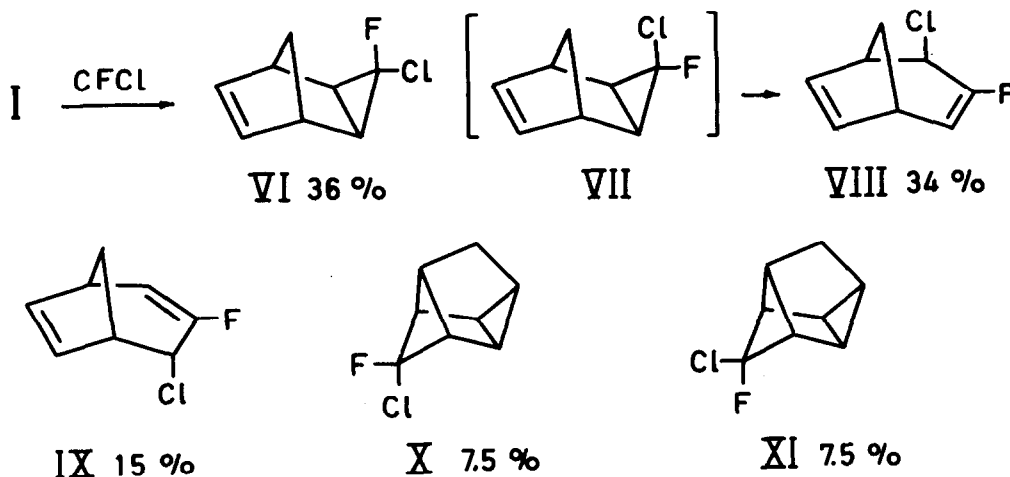
Difluorocarbene exists as a stable singlet in the ground state⁸ and is expected to be the stablest member of the dihalocarbene series by virtue of the overlap of its p_z -orbital with the lowest doubly occupied p-orbital on fluorine. Consequently its electrophilic character should be diminished, thereby potentially favouring the alternative addition process available to the filled sp^2 -orbital. Norbornadiene is a suitable diene as it is known to undergo the 2+2+2 or homoconjugate addition reaction⁹.

The reaction of norbornadiene (I) with trifluoromethyl(phenyl)mercury¹⁰ and sodium iodide at 80° for 8 hours gave two 1:1 adducts (II and III) in a ratio of 0.85 and a yield of 92%. Shorter reaction times did not affect the ratio nor was any evidence seen for the 1,2 endo-adduct IV. Structures II and III were established (and the alternative structure V for III ruled out) by consideration of their ¹H, ¹³C and ¹⁹F nmr spectra.

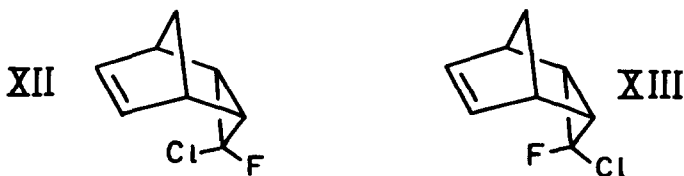
In a second experiment, I was heated with sodium dichlorofluoroacetate in diglyme at 140° for 12 hours¹¹. Five products (VI, VIII, IX, X, and XI) resulting from the 1:1 addition of fluorochlorocarbene were isolated by gas



chromatography in a yield of 25%. The structures of the rearranged adducts VIII and IX were elucidated by comparison of their nmr spectral data with that previously reported for the bicyclo[3.2.1]oct-2-en-4-yl series¹². Although isomers X and XI, present in equal amounts, were not separated, the tetracyclo[3.3.0.0^{2,8}.0^{3,6}]octane skeleton was easily identified from the nmr spectrum of the mixture.



The origin of VIII is undoubtedly the exo-syn adduct VII¹³. However, the provenance of the endo product IX is uncertain. If it arises from the endo-syn adduct XII, then the absence of its epimer XIII, which should be thermally stable like VI, is puzzling. Clearly, the eventual formation of X and XI from the homo-vinyl-cyclopropyl rearrangement of the presumed XIII has to be considered¹⁴. Nevertheless, the findings provide strong indications that these fluorocarbenes undergo linear cheletropic reaction with norbornadiene. Confirmation awaits the outcome of studies on the thermal stabilities of the actual adducts and their supposed precursors.



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