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CHELETROPIC REACTIONS OF DICHLORO- AND DIBROMOCARBENES WITH NORBORNADIENE

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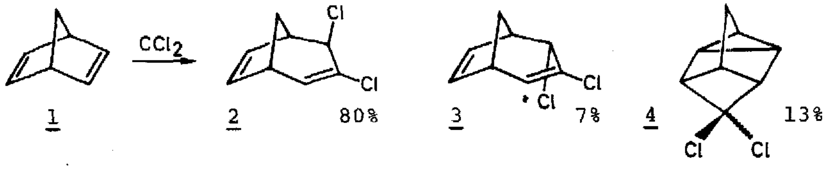
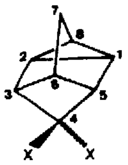
We have recently discovered that difluoro- and fluorochlorocarbene both undergo substantial homo-1,4 addition to norbornadiene as well as giving the conventional *exo* and *endo* 1,2 adducts[1]. This unprecedented observation, a clear example of a linear cheletropic reaction with a σ^2 carbene, is due to the geometric particularity of the norbornadiene skeleton which allows *endo* homo-1,4 addition to compete favorably with the normal course of cyclopropanation. When the *exo* side is blocked, as exemplified by bornadiene, then difluorocarbene is diverted exclusively to the *endo* side. Although we originally thought that difluorocarbene might constitute a special case, it transpired that even dichlorocarbene could be induced to furnish homo-1,4 adducts in some 45% yield with bornadiene[2]. This illuminating finding leads us to question those reports in the literature which state that various carbenes[3] including dichloro-[4] and dibromocarbenes[5] apparently only give 1,2 adducts with norbornadiene. We now report on a re-examination of the behavior of the last two named carbenes with norbornadiene (1).

The addition of dichlorocarbene, generated by the phase-transfer method[6], gave three 1:1 adducts in an overall yield of 80%. They were separated by gas-liquid chromatography[7], and identified by NMR spectroscopy. In addition to the usual rearrangement products (2 and 3) deriving from *exo* and *endo* 1,2 addition, the homo-1,4 adduct 4 was isolated in appreciable quantity. It was easily characterized by comparison of its ^{1}H and ^{13}C resonance spectra with those of the difluoro analogue[1]. In both cases, the tetracyclic skeleton is unambiguously identified by the six distinct ^{13}C signals (Fig.).

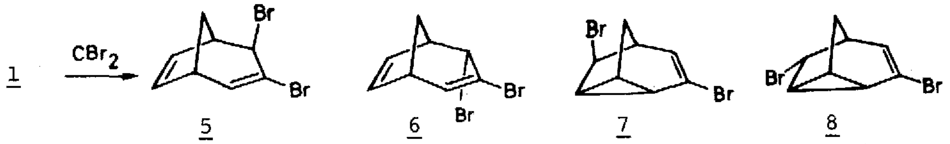




	X=F	X=Cl
C1, C2	12.91	18.95
C8	25.61	30.65
C7	31.77	34.38
C6	33.81	40.62
C3, C5	49.19	58.20
C4	128.20	91.69

Fig. ^{13}C resonances of 4,4-difluoro and dichlorotetracyclo$[3.3.0.0.^{2,8}0.^{3,6}]$octane. Values expressed in ppm downfield from tetramethylsilane in CDCl$_3$ as solvent.

The behaviour of dibromocarbene turned out to be remarkably different. Careful analysis of the product mixtures obtained by generating dibromocarbene in two different ways[8,9] revealed the presence of four rearranged adducts formed in a yield of 80-90%, but no homo-1,4 adduct. Products were separated by thin-layer chromatography using neutral silica gel and *n*-hexane as eluant. Three of the structures (5, 6, and 7) were the same as those previously reported[5] and the fourth one, a new isomer (8), was characterized from its proton NMR spectrum[10].



	5	6	7	8
Method a (ref. 8)	36.3%	26.0%	24.7%	13.0%
b (ref. 9)	51.0	21.9	19.5	7.6

In summary, we note that along the series, difluoro-, fluorochloro-, dichloro-, and dibromocarbene, the *exo/endo* selectivity ratios for norbornadiene increase somewhat (1.2, 1.8, 4.0, 2.0), but the selectivity ratio for 1,2 versus homo-1,4 addition jumps dramatically with the bulkiest carbene reagent (0.85, 6.0, 6.7, ∞). These findings reveal that steric accessibility in *both* partners is a *sine qua non* for homo-1,4 addition, otherwise the spatially less demanding 1,2 addition mode will predominate[11].

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7) Chromatography was effected on a 3M. column of 20% FFAP on Chromosorb W at 120°.

8) The method of Moore et al. was followed at 20° (ref. 5).

9) The method of Joshi et al. was used at 60° (ref. 6)

10) Proton coupling constants for derivatives of bicyclo[3.2.1]octene are well characterized (C.W. Jefford & K.C. Ramey, Tetrahedron, 24, 2927 (1968); C.W. Jefford, J. Gunsher, & K.C. Ramey, J. Amer. Chem. Soc., 87, 4384 (1965).

11) These ratios are rough in that the experimental conditions are not uniform and that some equilibration may have taken place, nevertheless they serve to indicate trends.

12) See accompanying letter by P.M. Kwantes and G.W. Klumpp.