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HOMO-1,4-ADDITION OF DICHLOROCARBENE AND DIBROMOCARBENE TO NORBORNADIENES

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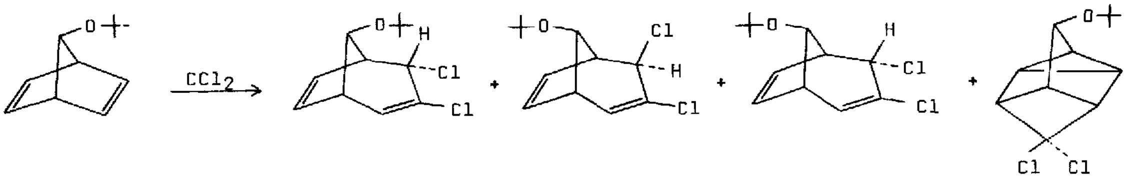
The homo-1,4-addition of difluorocarbene and of fluorochlorocarbene to norbornadiene (in competition with the commonly realized 1,2-addition) has been reported by Jefford and coworkers[1]. This behaviour - novel in singlet carbene chemistry and presumably a linear cheletropic reaction[2] - was attributed to the diminished electrophilic character of the fluorocarbenes. In the course of synthetic work we have discovered similar reactions of dichlorocarbene and dibromocarbene with 7-_t_-butoxynorbornadiene (I) and of dichlorocarbene with norbornadiene (X).

The reaction of I with dichlorocarbene, generated according to Makosza[3] as well as according to Doering and Hoffmann[4] gave the same mixture of four 1 : 1 adducts (II, III, IV and V) in total yields of 40% and 3 - 10%, respectively[5,6].



I II (38%) III (25%) IV (7%) V (30%)

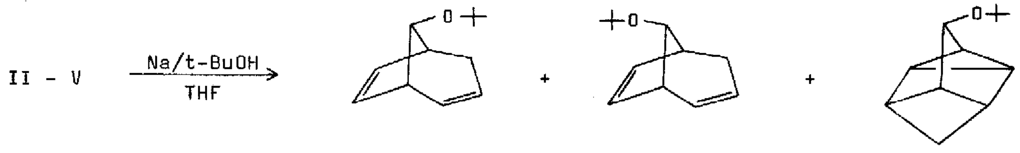
The NMR spectra of these products clearly establish the structures assigned. The principal differences between II, III and IV are due to the signals arising from the protons at C-4 and C-8 (Table 1):

Table 1 NMR characteristics (δ, ppm, $CDCl_3$) used in assignments of structures II - IV

Compound	Proton at C-4	Proton at C-8
II	4.75 (d), ($J_{4,5}$ = 5.0 Hz)	4.15 (t), [$J_{8,1(5)}$ = 4.4 Hz]
III	4.35 (d), ($J_{4,5}$ = 2.5 Hz)	4.35 (s)
IV	4.75 (d), ($J_{4,5}$ = 5.5 Hz)	3.95 (s)

The ^{1}H-NMR spectrum of V showed the following signals (δ, ppm, $CDCl_3$): 4.15 (s) (1H); 3.35 - 3.20 (m) (1H); 2.93 - 2.75 (m) (1H); 2.50 - 2.32 (m) (1H); 2.10 - 1.85 (m) (2H); 1.80 - 1.50 (m) (1H); 1.20 (s) (9H).

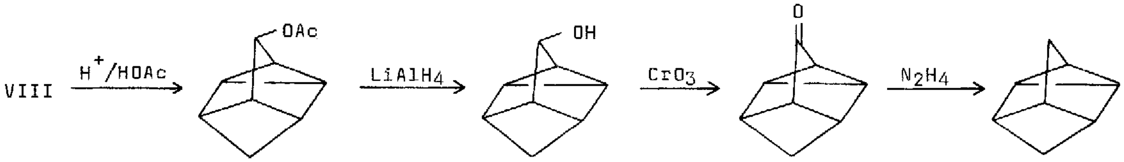
Further proof of structure was obtained by reduction (Na/THF/t-butanol) of II - V - as the original mixture as well as separately - to the known compound VI[7] and to VII and VIII (total yield from the original mixture: 55%; no rearrangements occur during this reduction).



VI (40%) VII (30%) VIII (30%)

Whereas VII was easily identified from the similarity of its NMR spectrum to the one of VI [C(8)-H: 4.08 (s)], VIII was identified by conversion into the known[8] hydrocarbon IX through the sequence of steps indicated in the scheme.

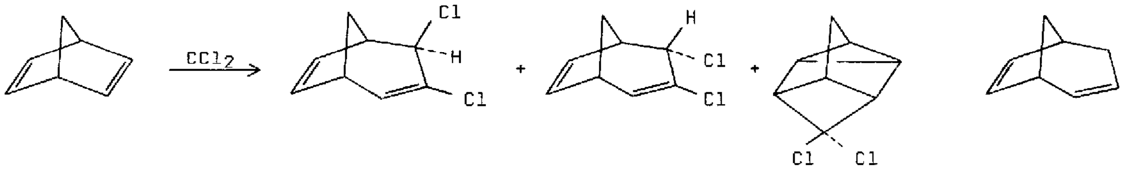
Scheme



IX

Homo-1,4-addition to I, albeit to a lesser degree, is also observed with dibromocarbene. Reduction (Na/THF/t-butanol) of the mixture of dibromides obtained in this case yielded VI, VII and VIII in a ratio of 5 : 2 : 1 and in an overall-yield of ca. 10%.

The results obtained with I prompted a reinvestigation of the reactions between dichlorocarbene and dibromocarbene and norbornadiene (X)[9,10,11].

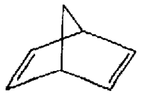
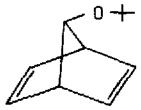


X XI (77%) XII (12%) XIII (11%) XIV

Using the Makosza-method three addition products (XI - XIII) were obtained from CCl_2 in about 50% yield[5]. The assignment of structure XII is based on the close similarity of its IR and mass-spectrum to those of the known[10,11] main-product XI and on the formation of XIV as the sole product of the (Na/THF/t-butanol)-reduction of the mixture of dichlorides. Since attempts to reduce XIII to IX led only to the disappearance of starting material the identification of XIII rests on its mass spectrum and its ^1H-NMR spectrum. The latter showed the following signals (δ, ppm, $CDCl_3$): 2.98 - 2.85 (m) (2H); 2.74 - 2.61 (m) (1H); 2.19 - 1.99 (m) (1H); 1.75 - 1.60 (m) (4H).

The course of the addition of CBr_2 to X was found to be in complete concordance with already published data[9]. No homo-1,4-addition product could be detected in this case. The results obtained with I and X and the various dihalocarbenes tested so far are summarized in Table 2.

Table 2 Homo-1,4-addition vs. 1,2-addition of dihalocarbenes to dienes I and X

Diene	Carbene	1,2-addition (%)	homo-1,4-addition (%)	Ref.
	CF_2	46	54	1
	CFCl	85	15	1
	CCl_2	89	11	This work
X	CBr_2	100	0	"
	CCl_2	70	30	"
I	CBr_2	88	12	"

Although our results show that homo-1,4-addition is not limited to the fluorocarbenes, it is evident from Table 2 that with I and X the nature of the halogens is of major importance in determining the partitioning between the 1,2- and the homo-1,4-addition mode, less homo-1,4-addition occurring with the heavier halogens. A more detailed comparison of the reactivities of I and X was possible through an intermolecular competition experiment with dichlorocarbene and the two diene partners I and X. Following the disappearance of the two dienes the ratio of the total rates was found:

$$(k^{I}_{1,2} + k^{I}_{1,4}) : (k^{X}_{1,2} + k^{X}_{1,4}) = 1 : 4.7$$

Combining this result with the product ratio obtained with each diene yields:

$$k^{I}_{1,2} : k^{X}_{1,2} = 1 : 5.5 \quad \text{and} \quad k^{I}_{1,4} : k^{X}_{1,4} = 1 : 1.6$$

The higher proportion of homo-1,4-addition observed in the case of I is therefore caused by the fact that deceleration of the addition by the 7-t-butoxy group is stronger for the 1,2-mode than for the homo-1,4-mode. Differing steric effects may provide a ready explanation[12,13].

Literature and footnotes

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5. Analytical and micropreparative glpc was carried out on a 1.5 m glass column containing 8% carbowax 1540 on 60-80 chromosorb W.
6. The fact that the same product ratio is obtained is further proof that in both procedures the same intermediate is involved.
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11. E. v. Dehmlow, Tetrahedron, 28, 175 (1972).
12. With I and X R.W. Hoffmann and K. Wetter have made observations, which are consistent with the results reported by us (private communication by Prof. Hoffmann).
13. Jefford and coworkers also have observed increased homo-1,4-addition of difluorocarbene as well as homo-1,4-addition of dichlorocarbene, when norbornadienes carrying alkyl groups at C-7 were used: C.W. Jefford, W.D. Graham and U. Burger, Tetrahedron Lett., in press.