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THE ADDITION OF BROMOFLUOROCARBENE TO NORBORNENE[1]

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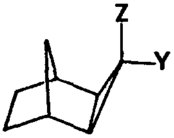
To date little has been reported of the generation and addition of bromofluorocarbene to olefins.[4] Accordingly we now report our preliminary results on the basic hydrolysis of dibromofluoromethane as a convenient source of bromofluorocarbene. As an extension of our previous work, norbornene was chosen to intercept the carbene.[5]

Dibromofluoromethane (0.16 M) was slowly added to a stirred slurry of potassium t-butoxide (0.23 M) and norbornene (0.38 M) in pentane (70 ml) at 0°.[6] After work-up, three products (I, II and III) were isolated by fractional distillation and thin layer chromatography. An average of five such additions gave a ratio of 1:3.2:4.1 for I:II:III. Compound I was found to be exo-2,3-dibromobicyclo[3.2.1]octene-2,[7] while the elemental analyses of compounds II and III showed them to be 1:1 adducts of norbornene and bromofluorocarbene.[8]

The absence of a band in the 1600 cm^{-1} region and the appearance of maxima at 3050 (shoulder) and 1012 cm^{-1} (strong) indicated the cyclopropane structure in II. The detailed nmr spectrum is described elsewhere,[9] but it will suffice to mention that comparison of the chemical shifts of the syn and anti C_8 protons with those found for anti-3-chloro-syn-3-fluoro- (IV)[10] and 3,3-dichloro-exo-tricyclo[3.2.1.0^{2,4}]octane (V)[11] establishes the exo fusion of the cyclopropane ring and the syn configuration of the 3-fluoro substituent in III (Table 1). In deuteriochloroform or carbon tetrachloride all the anti protons are shielded to about the same extent with respect to the C_7 protons of norbornane (δ = 1.21 ppm in CCl_4). On the other hand, all the syn protons are deshielded by the contiguous electronegative atom; chlorine being appreciably more effective than fluorine.

Structure III displayed a band at 1657 cm^{-1} and nmr signals characteristic of the bicyclo[3.2.1]octene skeleton with *exo* configuration of the allylic bromine atom.[12]

Compound II was surprisingly stable; heating to 110° for 4 hours was without effect. Treatment with an excess of three molecular equivalents of silver nitrate in aqueous acetone caused no change at 25°. However, after heating at reflux for 24 hours a 70% yield of *exo*-4-hydroxy-3-bromobicyclo[3.2.1]octene-2 (VI) was obtained.[7] There was no evidence for the formation of the fluoro-alcohol (VII).[8,13] These results demonstrate that a *syn* disposed substituent at C_3 in II is the only one which can qualify as a leaving group even in face of the apparent choice which favors the *anti* bromine atom. The rearranged product III undoubtedly arose spontaneously from the epimeric adduct VIII.[10]

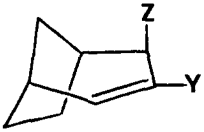


II Y = Br, Z = F

IV Y = Cl, Z =F

V Y = Z = Cl

VIII Y = F, Z = Br



I Y = Z = Br

III Y = F, Z = Br

VI Y = Br, Z = OH

VII Y = F, Z = OH

TABLE 1.

Chemical Shifts of the C_8 protons of Derivatives of *Exo*-Tricyclo[3.2.1.0^{2,4}]octane

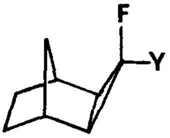
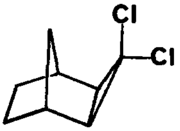
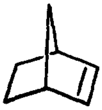
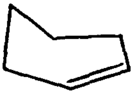
Compound		*syn*	*anti*	solvent	Ref. No.
	II Y = Br	- ppm	0.87 ppm	$CDCl_3$	-
		1.58	0.58	C_6D_6	-
	IV Y = Cl	1.52	0.85	$CDCl_3$	10
		1.55	0.83	CCl_4	10
	V	2.14	0.76	CCl_4	11

TABLE 2.

Z/E ratio for the Addition of CFCl and CFBr to Norbornene and Cyclohexene.

Compound	CFCl	CFBr	Ref. No.
	0.91 to 1	1.3 to 1	10
	1.2 - 1.5 to 1	1.4 - 1.7 to 1	4, 19

In addition to this validation of the Hoffman-Woodward rules,[14] the results raise two further items of theoretical interest. The first concerns the syn/anti or more precisely the Z/E stereoselectivity of the addition.[15] Table 2 shows that on passing from cyclohexene to norbornene the Z/E ratio for CFCl and CFBr drops. This trend can be attributed either to the suppression of the electrostatic attraction due to hyperconjugation or simply to a shift in the balance of attractive and repulsive dispersion forces.[5,16]

Lastly, the unexpected formation of the dibromo product I poses the question of its provenance. The source could be the presence as impurity of some undetected dibromocarbene precursor such as hexabromoacetone[17] or the dibromofluoromethide ion undergoing anomalous fission.[18]

Additions of bromofluorocarbene to other bridged bicyclic olefins should yield useful information on the importance of dispersion forces in the addition process as well as providing rigid molecules for the correlation of fluorine spin-spin coupling with structure. Such studies are in progress.

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References

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2. To whom enquiries may be addressed at the Ecole de Chimie, Boulevard des Philosophes, Geneva, Switzerland.
3. Recipient of a fellowship from the National Science Foundation, Washington, D.C., U. S. A.

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8. Compounds II, III and VII gave acceptable elemental analyses. Ratios were determined by n.m.r. spectroscopic examination of the reaction mixture before and after removal of solvent and unreacted olefin. In a typical experiment 6.2 g of adduct was obtained of which I accounted for 0.7 g, II 2.4 g and III 3.1 g.
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17. Dibromofluoromethane was obtained from R.A. Davis of Dow Chemical Co., Midland, Michigan. It was distilled and purified and its properties agreed well with those reported.[18] However, it contained 6% of *i*-propyl bromide as an impurity. Rigorous checks ensured the absence of bromoform.
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