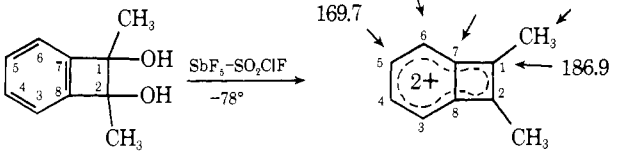
for the formation of the parent 1,2-benzocyclobutadiene dication **5**, and resulted only in the formation of unidentifiable polymeric products.[10] The 1,2-dimethylbenzocyclobutadiene dication **7**, however, could be prepared by careful addition of a suspension of *cis*- or *trans*-1,2-dimethylbenzocyclobutene-1,2-diols (**12** and **13**)[11] in SO_2ClF to a saturated solution of SbF_5 in SO_2ClF at dry ice–acetone bath temperature (ca. −78°). The resulting deep red solution of **7** is only stable below −30° and decomposes at higher temperatures.

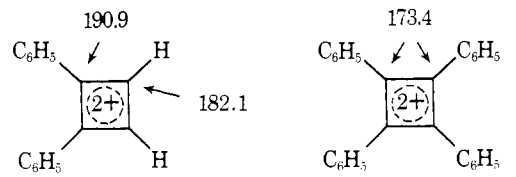


12, cis-
13, trans-

7

The 60-MHz proton NMR spectrum of **7** shows two equivalent methyl group absorption at δ 4.42 (singlet), and two broad deshielded two-proton aromatic resonances at δ 9.70 (overlaping with the hydronium ion peak) and at δ 10.08.[12] The natural abundance carbon-13 NMR spectrum obtained by Fourier transform technique (proton decoupled) consists of five carbon resonances at $\delta_{^{13}C}$ 27.9 (quartet, J_{C-H} = 136.8 Hz), 136.2 (doublet, J_{C-H} = 172.4 Hz), 169.7 (doublet, J_{C-H} = 182.8 Hz), 178.8 (singlet), and 186.9 (singlet). Carbon shift assignments are shown on structure **7**.[13]

Comparing the chemical shifts of cyclobutadiene ring carbons, $\delta_{^{13}C}$ 178.8 (C_7 and C_8) and 186.9 (C_1 and C_2), obtained for the 1,2-dimethylbenzocyclobutadiene dication **7** to those for the 1,2-diphenyl- (**14**, $\delta_{^{13}C}$ 182.1 and 190.9), tetraphenyl- (**15**, $\delta_{^{13}C}$ 173.4) and tetramethylcyclobutadiene (**16**, $\delta_{^{13}C}$ 209.7) dications[1] confirms that ion **7** is indeed also a fully delocalized 6π aromatic system, as are the compared cyclobutadiene dications.



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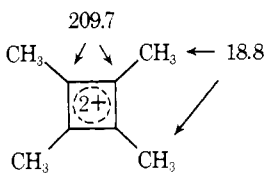

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(10) Ionization of secondary dialcohol or dihalide derivatives, **8**, **10**, and **11** apparently was complicated by complexation of SbF_5 with the benzo ring. On the other hand, ionization of tertiary alcohols **12** and **13** proceeded without difficulty.
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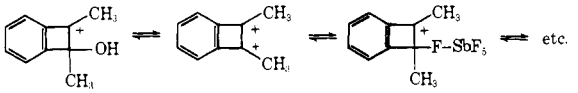
(12) ^1H and ^{13}C NMR shifts are given in parts per million from external (capillary) tetramethylsilane.
(13) The observation of symmetrical NMR spectra for the dication **7** with substantially deshielded proton and carbon shifts seems to eliminate the possibility of an equilibrium between a mono- and dication such as



In case of such an equilibrium much more shielded carbon shifts would be expected.

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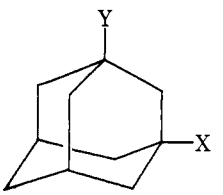
Fluorination at Saturated Carbon. 1. Direct Substitution of Adamantanes

Sir:

While investigating the fluorination of amides[1] we exposed *N*-trifluoroacetyladamantadine (**1a**) to CF_3OF. Surprisingly, the substrate underwent clean fluorination to 3-fluoro-*N*-trifluoroacetyladamantadine (**1b**). Adamantane itself with CF_3OF afforded 1-fluoroadamantane (**2b**). The substrates **4** and **5** afforded mixtures of fluorinated products which from fluorine NMR clearly bore secondary fluorine substituents.



1a, X = CF_3CONH; Y = H
1b, X = CF_3CONH; Y = F
2a, X = Y = H
2b, X = H; Y = F
3a, X = $OCOCF_3$; Y = H
3b, X = $OCOCF_3$; Y = F
3c, X = OH; Y = H
3d, X = OH; Y = F

Inasmuch as direct replacement of unactivated hydrogen atoms has appeared generally to be a consequence of a free radical reaction,[2] we sought to influence the initiation of this mild, selective, presumed radical fluorination. It is appropriate to note at this point that radical fluorinations with CF_3OF

Table I[a]

Solvent and/or additive	% composition of product 1a	1b	secondary and polyfluoro	Approx ratio 1b/other products
CH_2Cl_2	70	15	15	1
$CHCl_3$	66	31.5	2.5	13[b]
$CFCl_3$	30	46	24	2
$CFCl_3$ + 0.1 equiv of metadinitrobenzene	25	62	13	5
$CFCl_3$ + 0.1 equiv of nitrobenzene	25.5	69	5.5	12.5[b]
$CFCl_3$ + 0.1 equiv of $MeNO_2$	33.5	38.5	28	1.5
$CFCl_3$ + 0.1 equiv of 1,4-benzoquinone	22.5	71	6.5	11[b]
$CFCl_3$ + O_2 (slow stream)	20	73	7	11[b]
$CFCl_3$ + C_6Cl_6	34	28.5	37.5	0.6

[a] Adamantane (250 mg) in 30 ml of solvent at −25° was exposed to CF_3OF (2 mmol) and allowed to react under anaerobic conditions (unless otherwise stated) for 30 min. The product composition was determined by VPC. [b] Fully inhibited reactions.

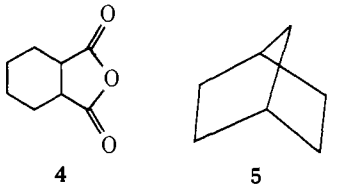
Table II[a]

Substrate	Reagent	Product	% Yield	Mp, °C
1a	CF_3OF	**1b**	65	68.5–69.5°
1a	F_2[8]	**1b**	83	
2a	CF_3OF	**2b**	75	
2a	F_2	**2b**	84	
3a	CF_3OF	**3b**	45	28–32°
3c	CF_3OF	**3d**	60[b]	182–185°

[a] The CF_3OF reactions were in the presence of 0.1 equiv of nitrobenzene or *m*-dinitrobenzene as inhibiter. No inhibiter was needed for F_2 reactions. [b] Contained 12% 3,5-difluoro-**3c**.

induced by extremely intense uv illumination have been reported[3] and that such reactions are substantially less regioselective than the reaction we had observed.

Adamantane with CF_3OF under tungsten illumination, or in the presence of benzoyl peroxide, or a combination thereof, resulted in a moderate enhancement of the reaction rate and a significant reduction of selectivity. Experiments with radical inhibitors, summarized in Table I, proved most illuminating. Effective "radical inhibitors" slowed the overall rate of fluorination moderately while remarkably enhancing selectivity. Solvents which might be expected to consume free radicals or divert radical chains showed a similar effect. Finally, the substrates **4** and **5** were essentially *inert to* CF_3OF in the



4 **5**

presence of radical inhibitors. Thus inhibition of a nonselective radical reaction clearly reveals a second, *highly selective* fluorination process. Products and yields resulting from treatment of various adamantyl derivatives with CF_3OF in the presence of radical inhibitors are summarized in Table II. The selective fluorination reaction which occurs in the presence of radical inhibitors was seen to have the following characteristics: (1) a marked polar effect on reaction rate [relative reactivity **2a** ≫ **1a** > **3a**], (2) a pronounced tendency toward monosubstitution (presumably a consequence of the above), and (3) high regioselectivity with substitution occurring almost exclusively at tertiary positions.

While these features are inconsistent with the known free radical halogenations of adamantanyl derivatives they are completely compatible with reported *electrophilic* halogenations of such substrates.[4] Such an electrophilic substitution at saturated carbon might be viewed as initiated by hydride abstraction leading to a classical tricoordinate carbocation or, in the light of more recent concepts advanced primarily by Olah et al.,[5] the reaction might be alternatively viewed as involving direct electrophilic attack on the electrons of the C–H σ bond leading to a species with a "nonclassical" three-center, two-electron bond and a formally pentacoordinate carbon. We favor the latter because fluorination reactions with CF_3OF which pass through the classical adamantyl "cation" lead, by capture of CF_3O^-, to substantial amounts of adamantyl trifluoromethyl ether, whereas this product does not arise in the direct fluorinations we report here. Such a mechanism would necessarily lead to retention of configuration.[6]

Our observation that CF_3OF could accomplish a direct electrophilic fluorination at saturated carbon led us to consider whether elemental fluorine itself might also accomplish such fluorination. In fact, certain reactions of elemental fluorine such as replacement of halogens and attack at carbon–carbon bonds of perfluoro hydrocarbons might be viewed more appropriately as electrophilic reactions rather than as radical reactions. In the event adamantane at low temperature with elemental fluorine[7] gave cleanly adamantyl fluoride. Similar fluorinations are summarized in Table II.[9] Exposure of a mixture of adamantane **2a** and the trifluoroacetate of adamantanol **3a** to elemental fluorine under the same conditions resulted, as expected, in nearly complete conversion of the adamantane into fluoroadamantane **2b** while virtually none of the trifluoroacetate **3a** was attacked. This demonstrates the expected sensitivity of the electrophilic fluorination to polar effects and, more significantly, that useful selectivity can be achieved even with so reactive a reagent as elemental fluorine. Indeed we find this remarkable new fluorination to be the most selective and controllable reaction of elemental fluorine with an organic substrate which we have encountered. Various applications of this reaction are described in the sequel.[6]

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(8) We thank A. J. Roszkiewicz for this experiment.
(9) All new compounds had the correct composition (established by microanalysis) and exhibited appropriate and unexceptional spectra.

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