REACTION OF FLUOROCHLOROCARBENE WITH CYCLOPENTADIENE, INDENE, AND THEIR ALKYL DERIVATIVES BY PHASE TRANSFER CATALYSIS

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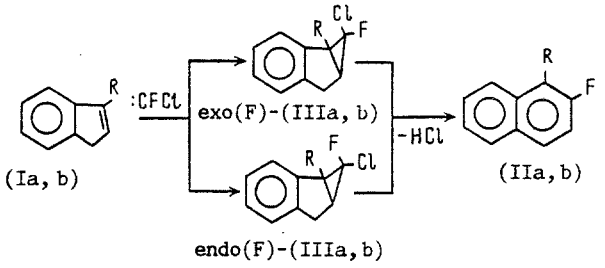
Fluorohalocarbene, generated from $CHCl_2F$ using phase transfer catalysis, reacts with indene, cyclopentadiene, and their alkyl derivatives to form 2-fluoronaphthalenes or fluorobenzenes in 9-60% yield. Reactions proceed through formation of unstable fluorochlorocyclopropanes, which rearrange selectively independently of their stereochemical configuration into the corresponding aromatic fluorides with elimination of HCl.

Fluorochlorocarbene (FCC), generated from $CHCl_2F$ by gas phase pyrolysis at 600°C, reacts with indene to form 2-fluoronaphthalene as the main product [1]. Cyclopentadiene (CPD) under these conditions reacts with FCC with formation of fluorobenzene [2]. The high temperature of the process excludes the possibility of observing the corresponding cyclopropane adducts postulated as intermediates.

In continuation of these investigations we studied the reaction of FCC with indene, cyclopentadiene, and their alkyl derivatives under conditions of phase transfer catalysis [3, 4].

It was shown that in the two-phase system CH_2Cl_2—aqueous KOH in the presence of catalytic amounts of triethylbenzylammonium chloride (TEBAC) reaction of $CHCl_2F$ with indene (Ia) at 0°C proceeds with formation of a mixture of approximately equal amounts of 2-fluoronaphthalene (IIa) and the two possible geometric isomers of 1-fluoro-1-chloro-1,1a,6,6a-tetrahydrocycloprop[a]indene, endo(F)-(IIIa), and exo(F)-(IIIa). By distillation of the mixture at 100°C compound (IIa) was obtained in 53% yield



R = H (Ia), Me (Ib).

Reaction of $CHCl_2F$ with 3-methylindene (Ib) under the same conditions leads to formation of 1-methyl-2-fluoronaphthalene (IIb) in 60% yield.

The structure of adducts (III) was established by PMR and ^{19}F NMR spectra. Assignment to geometric isomers was based on ^{19}F NMR spectra. For exo(F)-(IIIa) a triplet is observed with $\delta = -126.5$ ppm and $^3J_{F-H} = 15.5$ Hz and for endo(F)-(IIIa) a broad singlet upfield at $\delta = -161.3$. For (Ib) only endo(F)-(IIIb) was identified, which was displayed in the ^{19}F NMR spectrum in the form of a broad singlet with $\delta = -153.0$ ppm. The corresponding exo(F) isomer (IIIb) apparently is transformed completely into (IIb) under the reaction conditions.

The exo(F) adduct (IIIa) is thermally unstable and at room temperature after several hours is converted practically quantitatively into (IIa). Endo(F)-(IIIa, b) are more

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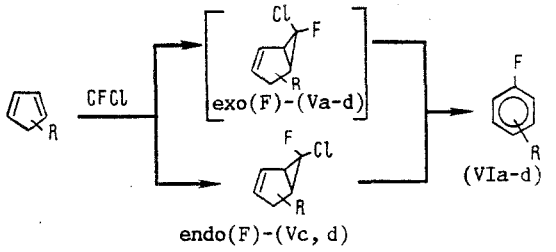
TABLE 1. Dependence of Isomeric Composition of Alkyl Fluorobenzenes $R-C_6H_4F$ (VI) (%) on Size of the Alkyl Substituent (R) in the Starting Alkyl Cyclopentadienes (IV)

R	2-R—C_6H_4F	3-R—C_6H_4F	4-R—C_6H_4F
Me	91	–	9
Et	81	4	15
i-Pr	58	10	32

stable, however, upon heating to 70-80°C they also rearrange with elimination of HCl, forming (IIa, b) in 80% yield. The decreased stability of fluorochlorocyclopropanes (IIIa, b) compared to the analogous gem-dichlorocyclopropane adducts, the rearrangement of which into 2-chloronaphthalene with HCl elimination requires heating to 100°C [5], is caused probably by the often noted [6] destabilizing influence of a cyclopropane-bound fluorine atom on the ring C—C bond opposite the halogen.

Rearrangements of dihalocyclopropanes are usually considered as symmetry controlled concerted processes with migration of the endo halogen atom [7]. This explains the formation of varying amounts of 2-bromo- and 2-chloronaphthalene upon reaction of the unsymmetric carbene CBrCl with indene [8]. In the case of exo(F)-(IIIa, b) the endo chlorine migrates and in endo(F)-(IIIa, b) the exo chlorine migrates with formation in both cases of aryl fluoride (IIa, b). The observed selectivity of aromatization of (III) into (II) primarily by elimination of HCl independently of the configuration of (III) is explained by the significantly different bond energies of C—Cl and C—F (40-50 kcal) [2]. The possibility of similar isomerization of gem-dihalocyclopropanes with concerted elimination of the exo halogen atom was postulated as a p-halogen migration based on the nodal properties of the molecular orbitals [9].

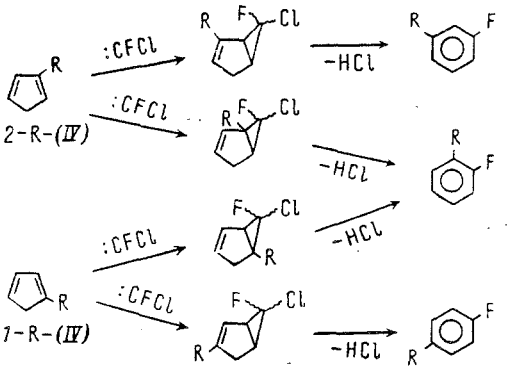
Reaction of FCC with CPD and its alkyl derivatives under the same conditions leads to the corresponding fluorobenzenes (VIa-d)



(IVa-d): R = H (IVa), Me (IVb), Et (IVc), *i*-Pr (IVd).

The reaction with CPD (IVa) proceeds with significant resinification and fluorobenzene is formed in small yield (9%). Use of alkyl substituted CPD (IVb-d) as acceptors of FCC increases the yield of (VIb-d) to 40-63%. In the reaction products of FCC with (VIb) were also found trace amounts (<1%) of two isomers of chlorotoluene (o:p = 95:5). Dienes (IVb-d) react as a thermodynamically equilibrated mixture of 1-R-(IVb-d) and 2-R-(IVb-d) in approximately equal amounts [10, 11]. Addition of FCC proceeds at the substituted and unsubstituted double bonds (IVb-d). As a result all three possible isomers are formed (IVb-d) (Table 1) (see scheme on following page).

From the data of Table 1 it follows that the selectivity of addition of FCC to the substituted bond of olefin (IVb-d) decreases with increased substituent size leading to a relative increase of fluorochlorocyclopropanation products at the unsubstituted double bond. In the reaction products of FCC with (IVc, d), together with fluoroaromatic compounds (VIc, d), we have found the cyclopropanes Et- and i-Pr- endo(F)-6,6-fluorochlorobicyclo[3.1.0]hex-2-ene (Vc, d). The four possible structural isomers endo(F)-(Vc, d) give the corresponding four signals in the ^{19}F NMR spectrum. The broadened singlet character of these signals and their location indicate the fluorine atom to be in the endo-position [12]. The PMR spectra also agree with the structure of (Vb, d).



Endo(F)-(Vb-d) are thermally unstable and at 40-50°C are transformed into (VIb, d) in 90% yield for (VIb) and 75% for (VId). Upon attempted chromatographic isolation of the adducts on silica gel, endo(F)-(Vb, d) also are converted into (VIb, d).

Thus, reaction of fluorochlorocarbene with (Ia, b) and (IVa-d) leads to formation of aromatic chlorides as main products as a result of rearrangement of the unstable intermediate fluorochlorocyclopropanes (IIIa, b) and (Va-d) independently of their stereochemical configuration with selective elimination of HCl.

EXPERIMENTAL

The GLC analysis was carried out on a LKhM-8MD instrument with a thermal conductivity detector, steel column 2000 × 3 mm with 5% silicone SE-30 on AW-HMDC, carrier gas helium. The PMR and ^{19}F NMR spectra were recorded on a Bruker WM-250 instrument for 5% solutions in $CDCl_3$. Mass spectra were obtained on a VC 7070E chromato-mass spectrometer with a OV-101 glass capillary column.

Starting compounds (Ib) and (IVb-d) were obtained by the method of [11]. Assignment of isomers (VIb-d) was made from the coincidence of their ^{19}F NMR spectral signals with those of the individual compounds. The isomer ratio was determined from the ratio of integral intensities of signals in the ^{19}F NMR spectra. Mass spectra of (IIa, b) and (VIa-d) show a molecular ion peak. PMR data are shown in ppm on the δ scale relative to TMS and ^{19}F NMR data in ppm on the δ scale relative to $CFCl_3$.

General method. To a mixture of 0.1 mole of olefin, 10 ml CH_2Cl_2, 7 ml (0.1 mole) of $CHCl_2F$, and 0.2 g TEBAC an aqueous solution of KOH (25 g KOH in 20 ml H_2O) was added. Stirring was continued for 3 h at 0°C. The mixture of organic products was separated from the aqueous phase and filtered through a thin layer of silica gel at room temperature and after analysis of ^{19}F NMR and PMR it was distilled to isolate the aromatic compounds.

2-Fluoronaphthalene (IIa): Yield 53%. PMR spectra: 8.0-7.1 m; ^{19}F NMR: −114.1.

1-Methyl-2-fluoronaphthalene (IIb): yield 61%. PMR spectra: 8.0-7.1 m (6H), 2.5 d (3H); ^{19}F NMR: −117.2.

1-Fluoro-1-chloro-1,1a,6,6a-tetrahydrocycloprop[a]indene (IIIa). PMR spectra: 7.7-7.0 m (4H), 3.2-2.9 m (3H), 2.4-2.1 m (1H); ^{19}F NMR spectra: −126.5 t [$^3J_{F-H}$ = 15.5 Hz, exo(F)-(IIIa)], −161.3 br. s [endo(F)-(IIIa)].

1-Fluoro-1-chloro-1,1a,6,6a-tetrahydro-1a-methylcycloprop[a]indene (IIIb). PMR spectrum: 7.25 m (4H), 3.2-3.0 m (2H), 2.05 m (1H), 1.6 d (3H). ^{19}F NMR spectrum: −153.0 br. s [endo(F)].

Ethyl-6,6-fluorochlorobicyclo[3.1.0]hexene (Vc). PMR spectra: 6.3-5.8 m (−CH=CH−), 5.6-5.5 m (−CH=CHEt−), 2.9-2.3 m, 1.6-1.5 m, 1.2-0.8 m ($-CH_3$); ^{19}F NMR spectra: −154.0 (F^1), −154.2 (F^2), −162.1 (F^3), −163.2 (F^4), ratio of signal intensities $F^1:F^2:F^3:F^4$ = 100:5:6:23.

Isopropyl-6,6-fluorochlorobicyclo[3.1.0]hexenes (Vd). PMR spectra: 6.0-5.75 m (−CH=CH−), 5.6-5.30 m (−CH=CH−Pr), 3.0-2.0 m, 1.65 m, 1.15-0.9 m [$-C(CH_3)_2$]; ^{19}F NMR: −150.2 (F^1), −150.4 (F^2), −162.3 (F^3), −163.0 (F^4), ratio of signal intensities $F^1:F^2:F^3:F^4$ = 55:3:15:39.

Fluorobenzene (VIa), yield 9%. PMR spectra: 7.2-6.8 m; ^{19}F NMR: −113.0.

Fluorotoluenes (VIb), yield 63%. PMR spectra: 7.1-6.7 m (4H), 2.3 s (3H); ^{19}F NMR: −117.5 (o-isomer), −118.1 (p-isomer), o:p isomer ratio = 91:9.

Ethylfluorobenzenes (VIc), yield 44%. PMR spectra: 7.1-6.7 m (4H), 2.6 q (2H), 1.5 t (3H, $^3J_{H-H}$ = 7 Hz); ^{19}F NMR: −113.2 (m), −117.2 (p), −118.7 (o). Ratio of m:p:o isomers = 4:15:81.

Isopropylfluorobenzenes (VId), yield 47%. PMR spectrum: 7.1-6.7 m (4H), 2.6 m (1H), 1.1 d (6H, $^3J_{H-H}$ = 7 Hz). ^{19}F NMR spectrum: −113.2 (m), −117.5 (p), −118.8 (o). Isomer ratio m:p:o = 10:32:58.

Chlorotoluenes (VIIb), yield 1%. o- and p-Isomers were identified from the identity of the signals in a chromato-mass spectrum with those of the individual substances. Isomer ratio o:p = 95:5.

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