Insertion of Fluoro Olefins into Carbon–Hydrogen Bonds to Yield 1:1 Adducts and Dehydrofluorination of the Adducts

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Tetrafluoroethylene and trifluoroethylene gave 1:1 adducts with isobutane under the influence of heat and in the absence of organic or inorganic initiators. Hexafluoropropene and chlorodifluoromethane gave $CF_2ClCF_2CHFCF_3$. Attempts to prepare 1:1 adducts between tetrafluoroethylene and chlorodifluoromethane resulted in cyclic dimerization of the tetrafluoroethylene. Dehydrofluorination of the adducts so obtained by means of solid potassium hydroxide afforded the corresponding fluoro olefins. NMR and mass spectral data are reported.

The investigation of radical additions to fluoro olefins other than tetrafluoroethylene and hexafluoropropene has been relatively little studied. Such investigations have mainly concerned reactions in which either a carbon–carbon bond or a carbon–hydrogen bond is formed together with a bond between carbon and a heteroatom.[1,2] Few reactions involving the simultaneous formation of both carbon–carbon and carbon–hydrogen bonds have been reported. These almost always involve the use of radical initiation catalysts such as *tert*-butyl peroxide, sodium peroxide, and azobisisobutyronitrile with the formation of predominantly telomeric products.[3–11] The reaction between fluoro olefins and alcohols has been investigated by Dedek and co-workers, who report the formation of 1:1 adducts between alcohols and chlorotrifluoroethylene under the influenee of γ irradiation (^{60}Co source).[12–15]

In the present work hexafluoropropene, tetrafluoroethylene, and trifluoroethylene have been found to insert into the carbon–hydrogen bonds of hydrocarbons such as chlorodifluoromethane and isobutane under the influence of heat alone (260–310 °C) to give good yields of 1:1 adducts (Scheme I). The conditions of thermal reactions are largely dependent upon the nature of the fluoro olefin employed. The operational temperatures and pressures are restricted because fluoro olefins can be dimerized individually to fluorinated cyclobutanes under the influence of heat. Hence tetrafluoroethylene reactions are generally confined to the temperature limits between 200 and 230 °C. Hexafluoropropene and trifluoroethylene reactions proceed favorably at temperatures in the range 260–320 °C.

Scheme I

$$RH + CF_2CFX \xrightarrow{\Delta} RCF_2CHFX + HCF_2CFRX$$

$$\begin{array}{ll} \text{I},\ R = CF_2Cl;\ X = CF_3 & \text{Ia},\ R = CF_2Cl;\ X = CF_3 \\ \text{II},\ R = Me_3C;\ X = F & \text{IIIa},\ R = Me_3C;\ X = H \\ \text{III},\ R = Me_3C;\ X = H & \\ \text{IV},\ R = CF_2Cl;\ X = F & \end{array}$$

Tetrafluoroethylene gave only a moderate conversion (20%) to 1,1,2,2-tetrafluoro-3,3-dimethylbutane (II) in the reaction with isobutane (ca. 1.5 atm) at 210 °C. Lower conversions (5–9%) to the structural isomers 1,1,2- and 1,2,2-trifluoro-3,3-dimethylbutane (III and IIIa) were obtained from a reaction between trifluoroethylene and isobutane even under higher reaction pressures (ca. 8 atm) and at temperatures in the range 210–280 °C. This lower reactivity of trifluoroethylene can be rationalized in terms of lower C–C π bond strengths of olefins containing vicinal fluorines.

The yields of III and IIIa were optimized (33%) by carrying out the reaction at elevated pressure (ca. 80 atm) at 280 °C. In this way minor quantities of some low-boiling liquid product and an appreciable quantity of high-boiling telomers were also obtained. The formation of telomers was partially inhibited when the mole ratio of hydrocarbon to fluoro olefin was increased from 3:1 to 6:1 (pressure ca. 134 atm), with a significant increase in the conversion to 1:1 adduct. Changing the mole ratios may not be the sole factor for the increased yield of the adducts, since the pressure is also much higher. Analysis by NMR and GLC showed the isomer ratios as 55:45 of III:IIIa.

The isomeric pair was separated from the reaction mixture by careful fractionation, and the two isomers were then separated by preparative GLC. The characteristic NMR spectra (^{1}H and ^{19}F) of compounds III, IIIa, and II are shown in Table I.

Chlorodifluoromethane reacted readily with hexafluoropropene at 275–280 °C under moderate pressures (ca. 8 atm) in the absence of any initiation catalyst, giving a relatively high yield of 1:1 adduct involving the carbon–hydrogen bond. The straight-chain adduct, 1-chloro-1,1,2,2,3,4,4,4-octafluorobutane (I), was separated from a complex reaction mixture by careful fractionation. The isomeric product (Ia) was obtained in only 2% yield.

When chlorodifluoromethane was heated at 210 °C in the presence of tetrafluoroethylene at pressures in the range 1–112 atm, no 1-chloro-1,1,2,2,3,3-hexafluoropropane (IV) was obtained. Cyclic dimerization of the olefin occurred at elevated pressures or temperatures.

Dehydrofluorination of Fluoro Hydrocarbons. Fluorocarbon olefins cannot be made directly from hydrocarbon olefins by treatment with fluorine or a reactive high-valency metal fluoride, since these methods lead to addition of fluorine across C=C bonds. Among the general methods reported for their preparation are dehydrofluorination reactions which are usually achieved thermally,[16] catalytically,[17–24] or by aqueous alkali elimination.[25,26] It seemed feasible to attempt HF elimination by the use of potassium hydroxide under anhydrous conditions. Thus a good yield (93%) of *cis*- and *trans*-1-chloroheptafluorobut-2-ene (Ib) was obtained when I was heated at 60–70 °C in vacuo in the presence of anhydrous, powdered potassium hydroxide (Scheme II). Heating above

Scheme II

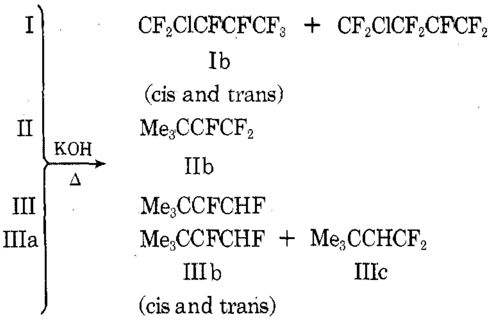

Table I. NMR Parameters of the 1:1 Adducts

	Chemical shifts,[a] ppm								Coupling constants, $J_{HF,FF_{gem}}$, Hz			
Compd	δCF_2	δCHF_2	δCHF	δCH_2F	δCF_3	δCHF_2	δCHF	δCH_2F	CHF_2	CHF	CH_2F	CF_2
$Me_3CCHFCHF_2$		50.0 (d)	130.2 (d)			0.98 (t)	2.69 (d)		50.8	46.2		
$Me_3CCF_2CH_2F$	42.2			160.4 (t)				2.25 (d)			47.7	
$Me_3CCF_2CHF_2$	46.4	54.2 (d)				0.81 (t)			53.4			
$CF_2ClCF_2CHFCF_3$	43.0, 51.0		136.2 (d)		−1.6		1.83 (d)			44.0		284.0

[a] ^{19}F, values to external trifluoroacetic acid; ^1H, positive values to high field of external benzene.

Table II. NMR Parameters of the Fluoro Olefins

	Chemical shifts,[a] ppm									Coupling constants, J, Hz					
Compd	δCF_a	δCF_b	δCF_x	δCF_2	δCF_3	δCH	δCMe_3[e]	J_{HF_a}	J_{HF_b}	$J_{F_aF_b}$	$J_{F_aF_x}$	$J_{F_bF_x}$	$J_{F_aF_y}$	$J_{F_bF_y}$	$J_{F_xF_y}$
Me_3CCF_b-CHF_a(cis)	−94.2[c]	−63.4[c]				−0.47[c]	−5.84	74.68	19.74	11.28					
Me_3CCH-CF_aF_b	−11.0[e]	−11.0[e]				−0.16	−5.84								
Me_3CCF_x-CF_aF_b	−27.8[c]	−43.2[c]	−99.8[c]				−5.14			85.0	45.0	110.0			
${}_yF_2CClCF_b$-$CF_aCF_{3_x}$	−61.0[f]	−68.0[f]		19.0[g]	11.0[h]					8.5	9.59	8.46	5.08	12.69	16.36
${}_yF_2CClCF_b$-$CF_aCF_{3_x}$(trans)	−76.8[f]	−83.0[f]		17.6[g]	7.0[h]					137.6	20.30	7.33	11.28	29.33	1.0

[a] ^{19}F values to external trifluoroacetic acid and ^1H to external benzene. [c] Doublet of doublets. [e] Complex. [f] Doublet of quartets of triplets. [g] Doublet of doublets of quartets. [h] Doublet of doublets of triplets.

70 °C resulted in the formation of undesirable side products. Optimum yield was obtained when a solid–gas phase, rather than solid–liquid phase, was maintained. There was little evidence for the formation of the isomeric olefin, 4-chloroheptafluorobut-1-ene (Ic). The isomeric ratio of Ib was found to be cis:trans, 44:56.

Dehydrofluorination of I with 80% aqueous potassium hydroxide gave only a low yield of the corresponding cis and trans olefins (Ib). The unreacted fluorobutane was difficult to extract from the reaction mixture.

The cis and trans isomers of Ib showed four regions of absorption in their ^{19}F NMR spectra which are presented in Table II.

A good yield (71%) of the isomeric olefins 1,2-difluoro-3,3-dimethylbut-1-ene (*cis-* and *trans*-IIIb) and 1,1-difluoro-3,3-dimethylbut-1-ene (IIIc) was obtained when a mixture of III and IIIa was treated similarly, with dry KOH at 80–85 °C. The major products were the cis isomer of IIIb and IIIc. The trans isomer of IIIb was obtained in small yield.

Above 95 °C considerable charring occurred which decreased the total yield of the fluoro olefins. An increased yield of the cis isomer of IIIb, at the expense of IIIc, was observed at temperatures above 85 °C.

The cis isomer of IIIb showed two regions of absorption in its ^{19}F NMR spectrum, whereas IIIc exhibited only a complex F_aF_b absorption (Table II). The mass spectrum of the cis isomer of IIIb showed significant ions at *m/e* 120 ($C_6H_{10}F_2^+$, 14.2%) and 105 ($C_5H_7F_2^+$, 100%). The most abundant ion at (P − 15) was due to allylic cleavage. This allylic cleavage was also observed in the mass spectra of IIIc and the trans isomer of IIIb.

1,1,2,2-Tetrafluoro-3,3-dimethylbutane (II) was more resistant toward dehydrofluorination than III and IIIa. Therefore a higher temperature and a longer reaction time were necessary. A low (21%) conversion to the corresponding olefin (IIb) together with a small amount of an unidentified product was obtained.

The ^{19}F NMR spectrum (Table II) of IIb showed three regions of absorption. The F_a absorption was broad, probably owing to "through space" coupling with the Me_3C group. Similarly the absorption peak due to the Me_3C group was complex owing to "through space" HF coupling. The mass spectrum of IIb exhibited the most abundant ion in (P − 15) due to allylic cleavage, which is accord with that of IIIc and IIIb. The mass spectrum of the minor reaction product showed *m/e* 120 ($C_6H_{10}F_2^+$, 15.2%) and 105 ($C_5H_7F_2^+$, 100%).

The dehydrofluorination reactions described reveal more about the general characteristics of this type of process for the preparation of fluoro olefins. The results indicate that the ease of dehydrofluorination is I > III ≃ IIIa > II. Compounds III and IIIa form 43% of the cis olefin whereas only 3% of the trans isomer is formed. Along these lines Buxton and Tatlow,[25] in their preparation of pentafluorocyclobutene from hexafluorocyclobutane, report that HF is eliminated preferentially from the two adjacent CHF groups, the flanking CF_2 groups being more resistant to removal of fluorine.

The new fluoro olefins which have been obtained are being currently investigated for their polymerizability.

Experimental Section

NMR spectra were recorded on Perkin-Elmer R10 or R20 spectrometers operating at 60 (^1H) or 56.46 MHz (^{19}F). In certain cases a Varian Associates HA-100 spectrometer operating at 100 (^1H) and 94.12 MHz (^{19}F) was employed. Mass spectra were obtained using an AEI MS 902 double-focusing instrument. Infrared spectra were recorded on Perkin-Elmer spectrophotometers (Models 137 and 257). Volatile samples (gases and liquids with adequate vapor pressures at room temperature) were examined in a gas cell (10-cm path length). A Pye 104 gas–liquid chromatograph was used for the analysis of liquids. Gaseous mixtures were analyzed on a Perkin-Elmer Model 451. Yields are calculated based on olefins consumed.

Preparation of 1,1,2-Trifluoro-3,3-dimethylbutane (III) and 1,2,2-Trifluoro-3,3-dimethylbutane (IIIa). A. Isobutane (19.2 g, 331 mmol) and trifluoroethylene (9.05 g, 110 mmol) were sealed in vacuo into a 250-ml Hastalloy-lined autoclave and heated with rocking at 280 °C for 96 h. The volatile product was transferred to a conventional vacuum system via an external trap cooled to −78 °C (dry ice–methanol) and distilled in vacuo through traps cooled successively to −23 (CCl_4 slush), −78, and −196 °C. The product which condensed at −196 °C was shown by ir spectroscopy and GLC (using a 2-m dinonyl phthalate column at 60 °C) to be isobutane (15.6 g, 269.5 mmol, 81.2% recovery).

The product which condensed at −78 °C was combined with the contents of the external trap (6.7 g) and fractionated up a Nester-Faust column to give a liquid mixture (0.81 g), bp 40–80 °C (unidentified), a mixture (5.2 g), bp 86–88 °C, of III (2.75 g, 19.6 mmol, 17.8% yield), and IIIa (2.5 g, 17.8 mmol, 15.2% yield), and a higher boiling liquid residue (0.41 g). The high boiling product which remained in the autoclave (5.0 g) was shown by NMR to be telomers and was not examined further.

B. Isobutane (37.9 g, 654 mmol) and trifluoroethylene (19.05 g, 110 mmol) were heated at 280 °C for 96 h in a 250-ml Hastalloy-lined autoclave to give isobutane (32.7 g, 564 mmol, 83.6% recovery), trifluoroethylene (trace amount by GLC), III (4.0 g, 28.5 mmol, 26% yield): NMR (Table I); mass spectrum *m/e* 140 (M^+).

Anal. Calcd for $C_6H_{11}F_3$: C, 51.42; H, 7.85. Found: C, 51.36; H, 7.90.

IIIa (3.2 g, 22.8 mmol, 21% yield): NMR (Table I); mass spectrum *m/e* 140 (M^+).

Anal. Calcd for $C_6H_{11}F_3$: C, 51.42; H, 7.85. Found: C, 51.39; H, 7.80.

A high-boiling autoclave residue (2.4 g, telomers) was also obtained.

Preparation of 1,1,2,2-Tetrafluoro-3,3-dimethylbutane (II). Tetrafluoroethylene (3.3 g, 33 mmol) and isobutane (5.7 g, 99 mmol) were sealed in vacuo into a 3.5-l. Pyrex bulb and heated at 210 °C for 96 h to give isobutane (4.8 g, 86.2 mmol, 84% recovery), tetrafluoroethylene (1.6 g, 16 mmol, 48% recovery), perfluorocyclobutane (0.39 g, 1.98 mmol, 12% yield), and II (1.04 g, 6.6 mmol, 60% yield): bp 83 °C; NMR (Table I); mass spectrum *m/e* 158 (M^+).

Anal. Calcd for $C_6H_{10}F_4$: C, 45.56; H, 6.32. Found: C, 45.60; H, 6.40.

Preparation of 1-Chloro-1,1,2,2,3,4,4,4-octafluorobutane (I). Hexafluoropropene (0.67 g, 4.5 mmol) and chlorodifluoromethane (1.16 g, 13.5 mmol) were sealed in vacuo into a 300-ml Pyrex ampule and heated at 280 °C for 4 days to give hexafluoropropene (0.20 g, 1.4 mmol, 30% recovery), chlorodifluoromethane (1.0 g, 11.7 mmol, 86% recovery), and I (0.32 g, 1.4 mmol, 58% yield): bp 44.5 °C; NMR (Table I); mass spectrum *m/e* 238, 236 (M^+).

Anal. Calcd for C_4HClF_8: C, 20.29; H, 0.42. Found: C, 20.32; H, 0.50.

About 2% of the isomer 1-chloro-1,1,2,3,3-pentafluoro-2-trifluoromethylpropane (Ia) was detected by NMR. Other complex mixtures (0.41 g) were also obtained.

Reaction between Tetrafluoroethylene and Chlorodifluoromethane. Tetrafluoroethylene (10 g, 100 mmol) and chlorodifluoromethane (54.5 g, 630 mmol) were sealed in vacuo into a 250-ml Hastalloy-lined autoclave and heated with rocking at 210 °C for 96 h. The volatile product was transferred to a conventional vacuum system and distilled in vacuo through traps cooled successively to −78, −95 (toluene slush), and −196 °C to give chlorodifluoromethane (quantitative recovery), perfluorocyclobutane (9.2 g, 46 mmol, 92% yield), and a liquid product (trace) which did not appear to be 1-chloro-1,1,2,2,3,3-hexafluoropropane (IV) by GLC–mass spectroscopy (2-m Phasesep at 100–170 °C). No C_2F_4 was recovered.

The above experiment was repeated several times, taking various mole ratios of hydrocarbon to olefin (varying pressures), and in all cases perfluorocyclobutane was obtained as the sole product.

Preparation of 1-Chloroheptafluorobut-2-ene (*cis*- and *trans*-Ib). A. A two-necked round-bottom flask was fitted with a gas inlet tube and a condenser surmounted by a cold-finger condenser and an external trap kept at −78 °C. I (1.1 g, 4.6 mmol) was bubbled in a stream of nitrogen through an excess of 80% (w/v) aqueous potassium hydroxide at about 80 °C contained in the flask. On completion of the addition, the cold finger was allowed to attain room temperature and the apparatus was purged with nitrogen. The organic product collected in the external trap was transferred to a conventional vacuum system. Analysis by ir and GLC (2-m Phasesep at 80–150 °C) confirmed the presence of the cis isomer of Ib (0.11 g, 0.51 mmol, 10% yield) and the trans isomer of Ib (0.12 g, 0.55 mmol, 11% yield). Only a trace amount of I was recovered.

B. I (0.61 g, 2.58 mmol) and anhydrous, powdered potassium hydroxide (6.4 g) were heated in vacuo (150-ml Pyrex ampule) at 60–70 °C for 30 min. It was imperative not to increase the temperature about 70 °C. The volatile product was then transferred to a vacuum system and shown by GLC (2-m Phasesep column at 80–150 °C) to contain I (0.03 g, 0.12 mmol, 4% recovery) and the cis isomer of Ib (0.25 g, 1.15 mmol, 40.9% yield): ir (vapor) 5.58 cm^{-1} (s) (C═C); NMR (Table II); mass spectrum *m/e* (rel intensity) 218 (M^+, 6.3), 216 (M^+, 20.6), 199 (M − F, 5.9), 197 (M − F, 18.9), 181 (M − Cl, 100), 149 (M − CF_3, 28.8), 147 (M − CF_3, 78.5), 131 (M − CF_2Cl, 96.7).

Anal. Calcd for C_4ClF_7: C, 22.22. Found: C, 22.3.

Trans isomer of Ib (0.32 g, 1.48 mmol, 52.1% yield): ir (vapor) 5.79 cm^{-1} (s) (C═C); NMR (Table II); mass spectrum *m/e* (rel intensity) 218 (M^+, 5.6), 216 (M^+, 17.6), 199 (M − F, 3.7), 197 (M − F, 12.2), 181 (M − Cl, 99.7), 149 (M − CF_3, 16.8), 147 (M − CF_3, 51.8), 131 (M − CF_2Cl, 100).

Anal. Calcd for C_4ClF_7: C, 22.22. Found: C, 22.3.

Preparation of 1,2-Difluoro-3,3-dimethylbut-1-ene (IIIb) and 1,1-Difluoro-3,3-dimethylbut-1-ene (IIIc). A mixture of III and IIIa (0.59 g, 4.2 mmol) and anhydrous, powdered potassium hydroxide (12 g) were heated in vacuo (100-ml Pyrex ampule) at 80–85 °C for 90 min. The volatile prouuct was transferred to a vacuum system. This process was repeated three times. The volatile product was then separated by preparative GLC (2-m Phasesep at 150 °C) and shown to contain starting materials III and IIIa (0.15 g, 1.07 mmol, 25% recovery) and IIIc (0.11 g, 0.91 mmol, 25.2% yield): ir (vapor) 3.35 (s) (C–H stretch), 5.75 cm^{-1} (s) (C═C); NMR (Table II); mass spectrum *m/e* (rel intensity) 120 (M^+, 20.5), 105 (M − CH_3, 100), 77 (M − C_3H_7, 31.5), 65 (M − C_4H_7, 19.8), 59 (M − C_3H_6F, 21), 57 (M − C_2HF_2, 6.7).

Anal. Calcd for $C_6H_{10}F_2$: C, 60.0; H, 8.3. Found: C, 60.0; H, 8.2.

Cis isomer of IIIb (0.19 g, 1.5 mmol, 43% yield): ir (vapor) 3.31 (s) (C–H stretch), 5.84 cm^{-1} (s) (C═C); NMR (Table II); mass spectrum *m/e* (rel intensity) 120 (M^+, 14.2), 105 (M − CH_3, 100), 77 (M − C_3H_7, 38.7), 59 (M − C_3H_6F, 9.8), 57 (M − C_2HF_2, 6.6).

Anal. Calcd for $C_6H_{10}F_2$: C, 60.0; H, 8.3. Found: C, 59.9; H, 8.4.

Trans isomer of IIIb (0.013 g, 0.1 mmol, ca. 3% yield): ir (vapor) 3.39 (s) (C–H stretch), 5.70 cm^{-1} (s) (C═C); mass spectrum *m/e* (rel intensity) 120 (M^+, 9.4), 105 (M − CH_3, 3.2), 77 (M − C_3H_7, 21.1), 59 (M − C_3H_6F, 4.2), 57 (M − C_2HF_2, 1.8), 43 (M − $C_4H_{10}F$, 100).

Preparation of 1,1,2-Trifluoro-3-3-dimethylbut-1-ene (IIb). II (1.0 g, 6.38 mmol) and anhydrous, powdered potassium hydroxide (6.55 g) were heated in vacuo at 155 °C for 20 h to give a liquid mixture (0.85 g) which was shown by GLC (using a 2-m Phasesep column at 160 °C or a 2-m dinonyl phthalate column at 60 °C) to contain II (0.62 g, 3.92 mmol, 62% recovery) and IIb (0.18 g, 1.3 mmol, 21% conversion, 54% yield): ir (vapor) 5.65 cm^{-1} (s) (C═C); NMR (Table II); mass spectrum *m/e* (Rel intensity) 138 (M^+, 16.0), 123 (M − CH_3, 100), 95 (M − C_2F, 26.1), 88 (M − CF_2, 10.5), 77 (M − C_3H_6F, 17.4), 73 (M − $C_2H_3F_2$, 23.7), 69 (M − CF_3, 10.4), 59 (M − $C_2H_5F_2$, 26.6), 57 (M − C_2F_3, 13.4), 39 (M − $C_3H_6F_3$, 12.0), 32 (M − $C_5H_8F_2$, 62.0).

Anal. Calcd for $C_6H_9F_3$: C, 52.17; H, 6.52. Found: C, 52.1; H, 6.6.

A product (ca. 0.05 g), mass spectrum *m/e* 120 (M^+), corresponding to $C_6H_{10}F_2$ was also obtained which was not further investigated.

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Registry No.—I, 53005-36-0; *cis*-Ib, 58384-33-1; *trans*-Ib, 58384-34-2; II, 354-75-6; IIb, 58384-35-3; III, 58384-36-4; IIIa, 58384-37-5; *cis*-IIIb, 58384-38-6; *trans*-IIIb, 58384-39-7; IIIc, 58384-40-0; isobutene, 75-28-5; trifluoroethylene, 359-11-5; tetrafluoroethylene, 116-14-3; hexafluoropropene, 116-15-4; chlorodifluoromethane, 75-45-6.

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Organometallic Chemistry. 12. Proton and Carbon-13 Nuclear Magnetic Resonance Study of Arenemercurinium Ions, the Intermediate Complexes of Aromatic Mercuration

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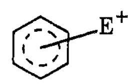
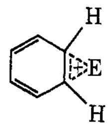
Arenemercurinium ion complexes were prepared and studied by proton and carbon-13 NMR spectroscopy. It is concluded that the complexes are involved in fast exchange.

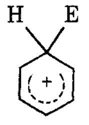
Electrophilic substitution reactions of aromatic compounds proceed via a mechanism involving intermediates of the types **1–3**.[2]



1
Mulliken outer π complex

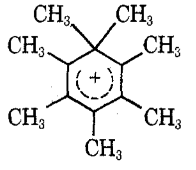


2
π complex (benzonium ion)



3
σ complex (benzenium ion)

Protonated arenes (arenium ions **3**) have been extensively studied,[3] but relatively little information is available regarding intermediates with other electrophiles. The heptamethyl **4** and heptaethylbenzenium ions are known from NMR studies,[4] and also from an x-ray crystallographic investigation of **4**.[5] Recently, direct observation of long-lived σ-complexes in



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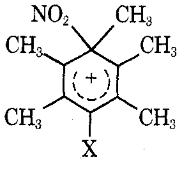

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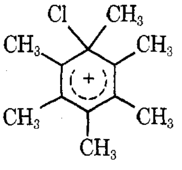

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nitration[6,7] (**5**) and chlorination[7] (**6**) of hexasubstituted benzenes was also reported.

Although the existence of π-bonded aronium ions **2** is suggested by chemical evidence, they have never been observed as reaction intermediates. We have reported the preparation of bridged π complexes of olefin–mercurinium ions and have investigated them by NMR spectroscopy.[8] We considered, therefore, that a similar study of arenemercurinium ions might yield information on intermediate π-bonded complexes. Previously π-bonded complexes (of type **1**) have been proposed for the mercurinium complexes of hexasubstituted benzenes from ^{1}H NMR studies,[9] while a σ complex was considered consistent with the complicated ^{1}H NMR spectrum obtained for the related pentamethylbenzenemercurinium ion.[9]

We now wish to report the results of our investigations by ^{1}H NMR and ^{13}C NMR spectroscopy of the intermediate complexes in aromatic mercurations.

Results and Discussion

Aromatics were mercurated using either mercuric trifluoroacetate or methylmercury acetate with excess fluorosulfuric acid in SO_2 solution.[9] ^{1}H NMR parameters of the intermediate arenemercurinium complexes so formed are summarized in Table I. In the ^{1}H NMR spectrum of monosubstituted benzenium ion complexes the ortho and meta protons show an AB-type quartet, the meta protons being further split by coupling with the para proton to give a doublet of doublets. Comparable spectra were obtained when *m*-methylanisole, 1,2,4-trimethoxybenzene, and pentamethylbenzene were mercurated. The observed spectra show some similarity to those obtained for monosubstituted ethylenearenium and benzenium ions (Table II).[10] Upon comparison, the ortho and meta protons of the mercurinium ion complexes are slightly shielded, the para proton more so, than the protons of the analogous arenium ions. However, the ^{1}H NMR spectra obtained from the mercurinium ion complexes of benzene, *m*-xylene, mesitylene, and 1,3,5-trimethoxybenzene are similar to those of the uncomplexed parent arenes except that the protons of the former show slight deshielding. No shifts characteristic of benzenium ions were observed.

Table III summarizes the ^{13}C NMR data for the arenemercurinium ion complexes investigated. For the arenemercurinium ions derived from monosubstituted benzenes, the ^{13}C NMR spectra show shifts characteristic of arenium ions. Upon complexation, ipso and ortho carbons become more deshielded, meta carbons are slightly deshielded, whereas shielding is observed for the para carbon. However, the shifts for the mercurinium complexes are not as large as for the corresponding ethylenearenium and arenium ions (Table II). On the other hand, unlike the corresponding arenium ions, the carbon-13 spectra of the mercurinium complexes of benzene, *m*-xylene, and mesitylene show symmetries related to their parent hydrocarbons, but not the arenium ions.

Based on the evidence of chemical shift data alone the possibility of the formation of σ complexes cannot be completely ruled out. The deshielding of the para proton and carbon in the monosubstituted complexes relative to the