cycloheptyl peroxide because of insufficient volatility to give the required radical flux. Both d_0 and d_2 dicyclopentyl and dicyclohexyl peroxides were analyzed. In the case of **9** ($n = 4$), the major radicals trapped by TCNQ were $nC_4H_9\cdot$ and H· with virtually no C_1, C_2, C_3, or C_5 alkyl radicals.[15] Radical **9** ($n = 5$) likewise gave mostly n-$C_5H_{11}\cdot$ and H· radicals with only minor amounts of C_1, C_2, C_3, C_4, or C_6 radicals. When the starting material was **9** ($n = 5$), an oxygen-containing carbon-centered radical, isomeric with the ω-formylpentyl radical **4** ($n = 5$), was observed with an intensity equal to about 10% that of n-$C_5H_{11}\cdot$. No significant amount of the corresponding radical was observed starting with **9** ($n = 4$). A possible explanation is that the trapped oxygen-containing radical when $n = 5$ was the stabilized α-formyl radical **5** ($n = 5$) formed by intramolecular H-atom transfer of radical **4** ($n = 5$). Formation of **5** ($n = 5$) proceeds via a favorable 6-membered transition state. Formation of homologous **5** from **4** with $n = 4$ would require a much less favorable 5-membered transition state and was not observed. The energetics of gas phase intramolecular H atom transfer processes requiring 5- and 6-membered transition states have recently been discussed.[14c] Significantly faster rearrangements involving 6-membered transition states have been noted for both thermally and chemically activated radicals.

With **9**-d_2 as starting material, ($n = 4$), n-butyl radicals were trapped by TCNQ and contained at least 86% monodeuteration.[16] Collision Induced Decomposition (CID) analysis of the trapped n-butyl radicals showed loss of $C_3H_6D\cdot$ fragments consistent with a location of D in the methyl group of **8** ($n = 4$, R = D). Likewise, **9**-d_2 ($n = 5$) gave rise to n-pentyl radicals containing at least 95% monodeuteration. CID analysis of the TCNQ-trapped n-pentyl radicals showed the presence of both 2-pentyl and 1-pentyl radicals, in agreement with results obtained previously for pentyl radicals generated from n-hexylamine.[14b] The isomeric pentyl-d radicals contained D enrichment in the propyl and butyl portions. Precise analysis of the positions of D in the 1- and 2-pentyl radicals was not possible because of the degree of peak overlap of peaks differing by only one mass unit. The high level of deuterium enrichment found in n-butyl and isomeric pentyl radicals, generated from **4**-d with $n = 4$ and 5, indicates that gas phase intramolecular H-atom transfer of ω-formyl radicals proceeding through both 6- and 7-member transition states is quite favorable.

Experimental Section

Undeuterated and α,α′-dideuterated dicycloalkyl peroxides were prepared by reaction of KO_2 and the appropriate cycloalkyl methanesulfonate esters as recently reported.[9] Characterization of each of the dicycloalkyl peroxides was based on attainment of correct m/e values by GC/MS analysis and by analysis of the major ketone (**3**) and alcohol (**2**) thermolysis products by LC, GC, and GC/MS.[9]

The percentages of deuterium enrichment in the peroxide-d_2 were established by GC/MS analyses. The complete regiospecificity of α,α′ deuterium incorporation was based on GC/MS analyses of starting cycloalkyl-α-d methanesulfonate esters and precursor cycloalkanols-α-d used for syntheses.

Gas chromatography was carried out using a Varian Model 3700 instrument equipped with a flame ionization detector and a 25-M Carbowax 20M glass capillary column. GC/MS analyses were performed using a Varian Model 3700 gas chromatograph coupled to a VG Micromass Model 16F mass spectrometer. Vapor phase MS analyses were done using a VG ZAB-2F mass spectrometer.

Solution-Phase Thermolysis of α,α′-Dideuteriodicyclohexyl Peroxide [9-d_2 ($n = 5$)] in Dodecane. A solution containing **9**-d_2 (0.058 g, 0.29 mmol) dissolved in 1.87 mL of dodecane was placed into a 10-mL glass tube equipped with a Teflon (Du Pont) fluorocarbon resin stopcock and was purged of air by bubbling with N_2 for 15 min. Analysis of the solution by GC/MS gave a parent peak of m/e 200 (calcd m/e for $C_{12}H_{10}D_2$ 200). The N_2-purged tube was sealed and was heated at 160 °C for 1 h. A GC/MS analysis of the product solution for low-boiling hydrocarbons revealed a major peak for pentane and a trace peak for butane. Comparison of peak intensities for $C_5H_{11}D$ (m/e 73) and C_5H_{12} (m/e 72) showed a ratio of 40/100, corresponding to 29% $C_5H_{11}D$/71% C_5H_{12} after correction of the $C_5H_{11}D$ peak intensity for 1.1% natural abundance ^{13}C.

Vapor-Phase Thermolysis of α,α′-Dideuteriodicyclohexyl Peroxide 9-d_2. A 10-μL sample of neat **9**-d_2 ($n = 5$) was injected into a 15-mL glass reservoir held at 110 °C from which it could escape through a glass capillary into the ion source of the mass spectrometer, which was maintained at 200 °C. A pressure of about 10^{-4} torr of TCNQ and about 0.3 torr of N_2 were also present in the ion source. The mass spectrum showed major ions corresponding to trapped $C_3H_7\cdot$, $C_5H_{10}D\cdot$, $C_5H_{11}\cdot$, and $C_6H_{10}DO\cdot$ with relative intensities of 24:100:10:14. The calculated ratio of $C_5H_{10}D\cdot/C_5H_{11}\cdot$ was 10:1.

Acknowledgment. We wish to thank W. B. Arters, T. S. Winant, R. G. McKay, and A. G. Bolinski for skilled experimental assistance.

Registry No. 1 ($n = 4$; R = H), 53578-06-6; 1 ($n = 5$; R = H), 3384-35-8; 1 ($n = 6$; R = H), 78939-49-8; 9 ($n = 4$; R = H), 55999-66-1; 9 ($n = 5$; R = H), 1758-61-8; 9 ($n = 6$; R = H), 86148-71-2; $\cdot(CH_2)_4CHO$, 78939-50-1; $\cdot(CH_2)_5CHO$, 59282-49-4; $\cdot(CH_2)_6CHO$, 78939-51-2; H, 1333-74-0.

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[15] Carbon-centered radicals were trapped with TCNQ and were characterized, free of neutral organic byproducts.

[16] Some loss of deuterium enrichment in ω-formyl radicals from H–D exchange with H_2O on heated glass and metal surfaces is expected.

Aerosol Direct Fluorination Syntheses: Alkyl Halides, Neopentyl Chloride and Bromide, Free Radicals vs. Carbocations

James L. Adcock,* William D. Evans, and Lilly Heller-Grossman

Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996

Received April 13, 1983

Aerosol direct fluorination of neopentyl chloride produces perfluoroneopentyl chloride in 74% yields. Analogous fluorination of neopentyl bromide produces perfluoroisopentane in 63% yield. Data are presented that support a carbocation rearrangement in the fluorination of neopentyl bromide. The carbocations are presumed to arise from disproportionation of neopentylbromine fluorides.

The direct fluorination of alkyl halides to perfluoroalkyl halides would provide a method of obtaining specific fluorocarbons in which the site for further reaction has been preselected prior to fluorination. the fluorination of chloroalkanes by metathesis using HF, F^-, or SbF_3 does not provide for prior selection of residual halogens although

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specific fluorocarbon halides may be obtained as products.[1] Several investigators have shown the feasibility of maintaining carbon–chlorine bonds during cobalt trifluoride fluorinations[2] and during electrochemical fluorinations.[3] There has to our knowledge, however, been only one published report of an elemental direct fluorination of an alkyl halide to a perfluoroalkyl halide.[4] In this paper we demonstrate the facility of maintaining a primary chlorine substituent during aerosol direct fluorinations. The stability of this chlorine substituent to both elemental and photochemically generated atomic fluorine at 20 °C is exceptional. The stability of bromine substituents is, however, very low and they tend to be oxidized by elemental fluorine at temperatures as low as −60 °C. Generation of carbocations is indicated in the fluorinations of alkyl bromides but not in the fluorinations of alkyl chlorides.

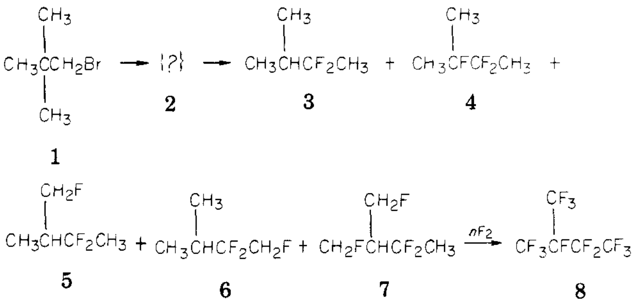
Results and Discussion

The aerosol direct fluorination process has been described in detail elsewhere.[5] Two major elements of the process involve contact of elemental fluorine with a finely divided particulate reactant aerosol over a gradual temperature and fluorine concentration gradient followed by "photochemical finishing" of the highly fluorinated product by ultraviolet irradiation of the effluent under ambient fluorine concentration conditions at ca. 20 °C. The two steps may be separated for analytical purposes simply by making control runs with the mercury lamp off. The reactant aerosol is formed by adsorption/condensation of hydrocarbon onto a sodium fluoride preaerosol.

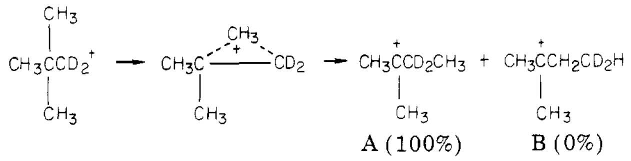
Initially two prototype molecules for probing the feasibility of the alkyl halide reactions were chosen because of their sensitivity to mechanistic reaction paths and their expected, near-ideal, reactor-process behavior. The first candidate, neopentyl chloride, was prepared by the method of Wiley et al. from neopentyl alcohol.[6] It was shown to be uncontaminated with isopentyl chloride by gas chromatography and by proton nuclear magnetic resonance. The aerosol fluorination of this molecule was uneventful and produced product in 79.6% purity (GLC assay) direct from the reactor trap. Isolated yields of pure perfluoroneopentyl chloride were 74% of theoretical. The remaining 20% of the material in the product trap was composed of approximately 20% *F*-isobutane, 20% *F*-isobutyl chloride, 40% *F*-pivaloyl fluoride, and the remainder numerous very small peaks with retention times greater than that of *F*-neopentyl chloride.

The second candidate, neopentyl bromide, was produced also by the method of Wiley et al.[6] and was shown to be free of isopentyl bromide by gas chromatography and proton NMR. The aerosol fluorination of neopentyl bromide was carried out under conditions similar to those for the chloride. The product consisted of 80% *F*-isopentane, 10% *F*-isobutane, elemental bromine, and lesser products.

Scheme I



Scheme II



The most significant result of the neopentyl bromide fluorinations is the near total rearrangement of the neopentyl moiety to the isopentyl. Such rearrangements must certainly occur early in the fluorination because low fluorine, control runs without photochemical finishing (reaction 2 → 5, Table I) produce exclusively rearranged products or unreacted starting material. Reactions 2–5 represent stepwise reductions in neopentyl bromide to fluorine mole ratios from approximately 1:12 to 1:1. Product distributions for neopentyl bromide reactions 1–5 are also given in Table I.

The major product isolated at 1:1 stoichiometry (reaction 5) is 2-methyl-2-butene (**9**). As the fluorine to neopentyl bromide ratio is increased (reaction 4), 2-methyl-2-butene (**9**) disappears and 2,3-difluoro-2-methylbutane (**10**) becomes the prevalent product. However "abnormal" products having the geminal difluoromethylene group are collectively of near-equal prevalence. These abnormal products increase as the relative amount of fluorine increases (reactions 3 and 2) and the amount of 2,3-difluoro-2-methylbutane actually decreases in reaction 2. Compounds having this geminal difluoro substitution (**3–5**, Table I) are classified "abnormal" because none are the statistically probable products expected from fluorine attack on the products (**9** and **10**) prevalent at the lowest stoichiometries.

The facility with which neopentyl cations rearrange to isopentyl cations is a well-known phenomenon.[7] It is also known that neopentyl radicals do not show a pronounced tendency to rearrange.[8] This leads to the inescapable conclusion that the fluorination of neopentyl bromide must produce intermediate carbocations, although highly polar species or carbene type intermediates cannot be totally eliminated. Furthermore these carbocations and their precursor intermediate(s), {?} (**2**), Scheme I, must account for the "abnormal" fluorine products (**3–7**) containing the difluoromethylene group (Scheme I). The nature of these intermediates are not known, but their behavior bears a striking resemblence to the rearrangements of the neopentyl cation observed by Skell et al. (Scheme II).[7] Skell et al. observed that all derived products of the rear-

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[1] (a) Henne, A. L.; Trott, P. *J. Am. Chem. Soc.* **1947**, *69*, 1820. (b) McBee, E. T.; Wiseman, P. A.; Bachman, G. B., *Ind. Eng. Chem.* **1947**, *39*, 415. (c) Henne, A. L.; Newby, T. H., *J. Am. Chem. Soc.* **1948**, *70*, 130. (d) Henne, A. L.; Ruh, R. P., *Ibid.* **1947**, *69*, 279.

[2] (a) Bagnall, R. D.; Bell, W.; Pearson, K. *J. Fluorine Chem.* **1977**, *9*, 359–375. (b) Banks, R. E.; Haszeldine, R. N.; Walton, *J. Chem. Soc.* **1963**, 5581.

[3] Fox, H. M.; Ruehler, F. N.; Childs, W. V. *J. Electrochem. Soc.* **1971**, *118*, 1246–9. (b) Ashe, B. H.; Childs, W. V. U.S. Patent 3 720 597, 1973. (c) Abe, T.; Nagase, S. *J. Fluorine Chem.* **1979**, *13*, 519–530.

[4] Schmeisser, M.; Ehlers, K. P.; Sartori, P. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 627.

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[6] Wiley, G. A.; Herskowitz, R. L.; Rein, B. M.; Chung, B. C. *J. Am. Chem. Soc.* **1964**, *86*, 964.

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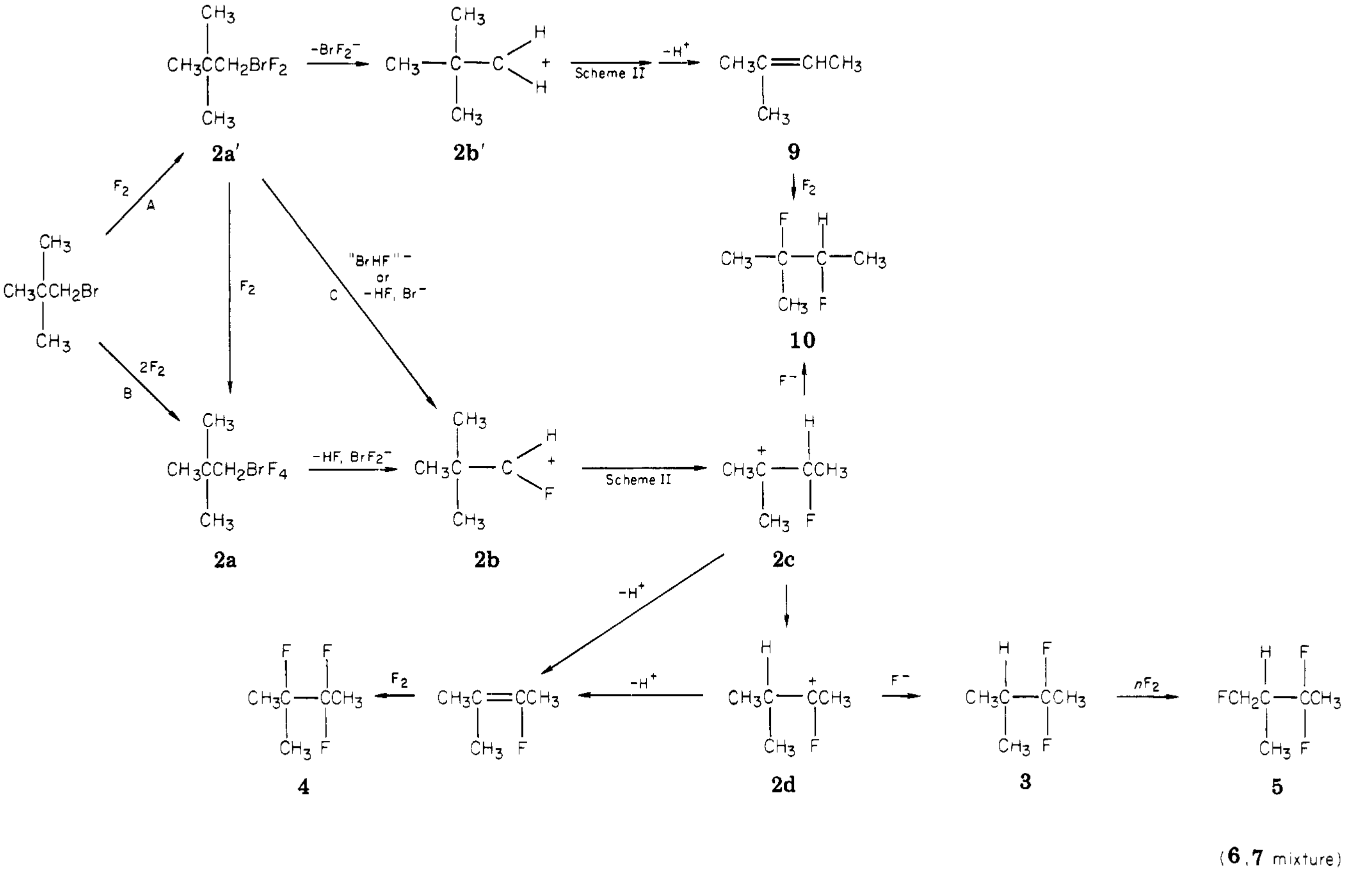
Table I. Results of Aerosol Fluorinations of Neopentyl Bromide

no.	name	prod. distrib[b] for rctn no. (F/hydrocarbon mole ratio): 1[a] (105)	2 (12)	3 (4)	4 (2.5)	5 (1)
1	neopentyl bromide[c]			15	28	50
3	3,3-difluoro-2-methylbutane		18	14	6	
4	2,3,3-trifluoro-2-methylbutane		10	2	4	
5	1,3,3-trifluoro-2-methylbutane		18	6	2	
6	3,3,4-trifluoro-2-methylbutane	*e*	16	5	5	
7	1,3,3-trifluoro-2-(fluoromethyl)butane					
8	*F*-isopentane	80				
9	2-methyl-2-butene					30
10	2,3-difluoro-2-methylbutane		11	20	20	
	F-isobutane	10				
	residual peaks[d]	10	27	38	35	20

[a] Photochemical stage operative here only. [b] Area percent of total injection by peak integration of the thermal conductivity gas chromatogram. [c] Unreacted starting material. [d] Small peaks in gas chromatogram. [e] Inseparable mixture, tentative identification by ^{19}F and ^{1}H NMR.

Scheme III



rangement were consistent with the deuterium label in the 3-position, i.e., exclusively derived from A. A protonated cyclopropane derivative was thus discounted because it could cleave either of two ways, producing *tert*-amyl derivatives consistent with the deuterium label in the 4-position (derived from B) also, which was not observed. Karabatsos et al. observed this rearrangement of neopentyl cations using a ^{13}C label and obtained the same result.[10]

One hypothetical scheme (Scheme III) that not only provides a reasoned approach to *all* of the products produced but also addresses the product shift as the fluorine stoichiometry is increased, is in effect two schemes. The basic postulate supported by reaction 5 (Table I) is that fluorine attacks only the bromine and that depending on the stoichiometry either (or both) an alkylbromine difluoride (**2a′**) or an alkylbromine tetrafluoride (**2a**) is formed. Conceivably **2a′** may disproportionate, giving the known interhalogen anion, BrF_2^- and the carbocation **2b′**, which through Scheme II produces the *tert*-amyl cation A and, by loss of a proton, 2-methyl-2-butene (**9**), the largest single product in reaction 5. As the fluorine to alkyl bromide ratio is increased, significant amounts of the alkylbromine tetrafluoride (**2a**) are produced, leading to formation of the fluorinated carbocation **2b**, which through Scheme II produces the fluorinated *tert*-amyl cation **2c**. The major product in reaction 4, 2,3-difluoro-2-methylbutane, may be produced by fluorine addition to **9** or by fluoride ion trapping of **2c**. Both routes A and B are probably operating. As the fluorine/alkyl bromide ratio

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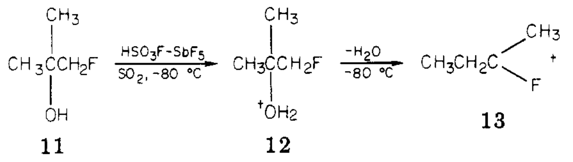
(9) Skell, P. S.; Starer, I.; Krapcho, A. P. *J. Am. Chem. Soc.* **1960**, *82*, 5257–8.

(10) Karabatsos, G. J.; Graham, J. D. *J. Am. Chem. Soc.* **1960**, *82*, 5250–1.

Scheme IV



is increased further (reactions 3 and 2), the proportion of route A is diminished over route B since the other products produced by route B alone (**3**–**5**) are increasing, while that product (**10**) produced by route(s) A (and B) is diminishing. It is also likely that the β-fluorinated *tert*-amyl cation **2c** contributes less to product **10** than expected because of its ready rearrangement (1,2 hydride shift) to the α-fluorinated secondary butyl cation **2d**. The σ-inductive destabilization of **2c** by the β-fluorine coupled to the resonance (π-donor) stabilization of **2d** by the α-fluorine inverts the usual primary < secondary < tertiary carbocation stabilization.[11] Fluoride ion trapping of **2d** leads to 3,3-difluoro-2-methylbutane (**3**), which by statistically directed, radical-chain, direct fluorination leads to product **5**, 1,3,3-trifluoro-2-methylbutane, and to the tentatively identified 3,3,4-trifluoro-2-methylbutane (**6**) and 1,3,3-trifluoro-2-(fluoromethyl)butane (**7**) and, ultimately, to *F*-isopentane (**8**). Together products **3**, **5**, and the **6**, **7** mixture make up 52% of the total products in reaction 2 with product **4**, 2,3,3-trifluoro–2–methylbutane, produced by proton abstraction from **2c** and/or **2d** followed by fluorine addition to the olefin produced, making up an additional 10% of the total.

Support for this hypothesis is provided by Olah and Bollinger in which the protonation studies of 1-fluoro-2-methyl-2-propanol in "magic acid", $HSO_3F–SbF_5/SO_2$, at −80 °C produced the results shown in Scheme IV.[11] The only carbocation detected in this system was **13** although the chloro analogue produced the chloro-*tert*-butyl cation. Carbocation **13** requires, in effect, two hydride shifts and one methide shift to occur for it to be produced from a transient fluoro-*tert*-butyl cation, which was not detected by Olah and Bollinger.[11] The only unsubstantiated or unsupported parts of our hypothesis (Scheme III) is the formation of **2a** and **2a′** and their "disproportionation" to **2b** and **2b′**, respectively. The formation of perfluoroalkylbromine tetrafluorides, however, is documented.[12] Although a potential route C from **2a′** to **2b** is shown in Scheme III, our evidence does not support or require it, although it cannot be eliminated a priori. It is also problematical whether **2a′** will have sufficient lifetime to interact with a second mole of fluorine to form **2a** or whether 2 mol of fluorine must act in concert as implied by route B Scheme III. Whatever the mechanism, insufficient data exist to more than simply pose the question. The solution of this problem might be obtained through matrix isolation studies. It is, however, clear that fundamental differences in the mode of fluorine attack on alkyl chlorides and bromides exist and that the consequences will likely involve "carbocation" type rearrangements of the organic substituent.

Experimental Section

The basic aerosol fluorinator design and a basic description of the process are presented elsewhere.[5] Workup of products following removal of hydrogen fluoride and possibly fractional collection at ambient pressures using in-line cold traps consisted of vacuum-line fractionation; infrared assay of fractions; gas chromatographic separation of components, using either a 7 m × $^3/_8$ in. 13% Fluorosilicone QF-1 (Analabs) stationary phase on 60–80-mesh, acid-washed Chromosorb P column conditioned at 225 °C (12 h) or a 4 m × $^3/_8$ in. 10% SE-52 phenylmethylsilicone rubber on acid-washed, 60-80-mesh Chromosorb P column conditioned at 250 °C (12 h). Following gas chromatographic separation (Bendix Model 2300 subambient multicontroller), all products of significance were collected, transferred to the vacuum line, assayed, and characterized by vapor-phase infrared spectrophotometry (PE1330), electron-impact (70 eV) and chemical-ionization (CH_4 plasma) mass spectrometry (Hewlett-Packard GC/MS, 5710A GC, 5980 A MS, 5934A computer), and ^1H and ^{19}F nuclear magnetic resonance (JEOL FX90Q, omniprobe) in $CDCl_3$ with 1% $CFCl_3$ internal standard. Elemental analyses where necessary were performed by Schwartzkopf Microanalytical Laboratories, Woodside, NY. Detailed reaction parameters and compound characterizations are available as supplementary material.

Aerosol Fluorination of Neopentyl Chloride. 1-Chloro-2,2-dimethylpropane was prepared by the method of Wiley et al. from neopentyl alcohol.[6] Its vapor pressure at −10 °C is such that a flow of 85 mL/m of helium through ~50 mL of the material contained in a sparge tube evaporator produces a throughput of 0.38 g/h (3.6 mmol/h). Details of the aerosol fluorination parameters are available as supplementary material. For a 3-h photochemical finished run, 2.659 g of crude product was collected, which when vacuum-line fractionated [−131 °C (2.56 g), −196 °C (0.09 g discarded)] and gas chromatographically purified on the SE-52 column (15 °C/5 m; 10 °C/m to 75 °C; 50 °C/m to 150 °C/7 m) produced 2.03 g of *F*-neopentyl chloride (79.6% of the crude material collected, 74% yield based on calculated throughput). Characterization by ^{19}F NMR gave ϕ_{CF_3} −64.18 (t, 9), ϕ_{CF_2Cl} −52.29 (dectet, 2, J = 10.7 Hz). Anal. Calcd for $C_5F_{11}Cl$: C, 19.72; F, 68.63. Found: C, 19.67; F, 68.60. Detailed IR and MS (CI, EI) data are available as supplementary material.

Aerosol Fluorination of Neopentyl Bromide. 1-Bromo-2,2-dimethylpropane was prepared by the method of Wiley et al. from neopentyl alcohol.[6] Its vapor pressure at −10 °C is such that a flow of 25 mL/m of helium through ~20 mL of the material contained in a sparge tube evaporator produces a throughput of 1.4 mmol/h. Details of the aerosol fluorination parameters are available as supplementary material. Five fluorination runs were carried out, differing mainly in the photochemical finishing (i.e., runs 2–5, UV lamp off) and the fluorine to hydrocarbon stoichiometry (Table I). All products were vacuum-line fractionated (−131 °C, −196 °C discarded) and the −131 °C trap separated gas chromatographically on the SE-52 column (10 °C/4 m; 2 °C/m up to 55 °C/1 m; 50 °C/m to 125 °C/10 m).

The photochemically finished, 2-h run (reaction 1) produced 0.629 g of crude product after removal of elemental bromine with the following product distribution: 80% *F*-isopentane (62.5% yield), 10% *F*-isobutane, and 10% other unidentified lesser products. *F*-isopentane collected displayed spectra identical with the infrared and ^{19}F NMR spectra published.[13,14] Detailed mass spectra, infrared, and ^{19}F NMR are available as supplementary material.

The runs without the ultraviolet lamp (reactions 2–5, Table I) produced similar quantities of crude product containing elemental bromine with the product distributions listed. Characterizations of intermediate products are available as supplementary material. 3,3-Difluoro-2-methylbutane (**3**)[15] and 2,3-difluoro-2-methylbutane (**10**)[16] are known compounds. 2,3,3-Trifluoro-2-methylbutane (**4**) and 1,3,3-trifluoro-2-methylbutane (**5**) have not been previously characterized.

Acknowledgment. This work was supported in part by the Office of Naval Research whose support is gratefully

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J. Org. Chem. 1983, 48, 4957-4962 4957

acknowledged.

Registry No. **1**, 630-17-1; **3**, 51891-58-8; **4**, 87517-38-2; **5**, 87517-39-3; **6**, 87517-40-6; **7**, 87517-41-7; **8**, 594-91-2; **9**, 513-35-9; **10**, 53731-25-2; neopentyl chloride, 753-89-9; perfluoroneopentyl chloride, 87136-72-9; *F*-isobutane, 354-92-7; *F*-isobutyl chloride, 10537-60-7; *F*-pivaloyl fluoride, 1813-18-9.

Supplementary Material Available: Detailed reaction parameters and compound characterizations (7 pages). Ordering information is given on any current masthead page.

Preparation and Characterization of Some Pentaarylethyls

William B. Smith* and Michael C. Harris

Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129

Received June 6, 1983

The reaction of triphenylmethylsodium with dichlorodiphenylmethane does not give pentaphenylethyl as previously reported, but when the anion reacts with 9,9-dichlorofluorene, it does form the reported 9-tritylfluorenyl radical which has been characterized by ESR spectroscopy. The radical is better prepared by oxidation of the anion of 9-tritylfluorene. The 9-tritylfluorenyl radical reacts with traces of oxygen to give triphenylmethyl and fluorenone. With light it forms triphenylmethyl and fluorenylidene. The latter was established by photolyzing 9-diazofluorene in the presence of triphenylmethyl with the generation of 9-tritylfluorenyl. Small yields of the persistent pentakis(*p*-*tert*-butylphenyl)ethyl radical have been prepared, and it is probable that pentaphenylethyl has also.

Pentaphenylethyl was reported as a stable radical isolated as a solid in 1922 by Schlenk and Mark,[1] who formed it by reacting ether solutions of dichlorodiphenylmethane with triphenylmethyl- (trityl) sodium or by the reaction of the disodium adduct of tetraphenylethylene with triphenylmethyl chloride. Since electron spin resonance spectroscopy (ESR) did not exist at the time, they characterized ether solutions of the radical by their reactivity with oxygen and with chlorine, forming a presumed pentaphenylethyl chloride which was reported to give back the radical when treated with copper bronze and also to be hydrolyzed to pentaphenylethyl alcohol. In a subsequent paper,[2] they also reported the isolation of the 9-tritylfluorenyl radical as a purple solid obtained from the reaction of tritylsodium with 9,9-dichlorofluorene.

In 1935, Dorfman[3] reported that numerous attempts to prepare pentaphenylethyl by the dichlorodiphenylmethane route were unsuccessful. He did find the path through tetraphenylethylene satisfactory and determined the electron affinity of the radical by measuring the amount of sodium taken up from a standard sample of sodium amalgam. Similar measurements were made on the purple 9-tritylfluorenyl.

While no reference to pentaphenylethyl per se was made, Gregg and Mayo[4] found the chain-transfer constant in styrene polymerization to be three orders of magnitude larger for pentaphenylethane than for triphenylmethane. Such chain-transfer phenomena involving benzyl-type hydrocarbons are usually discussed in terms of the relative strength of the C–H bonds being broken and might be interpreted in this case as implying an unusually large stabilization for the pentaphenylethyl radical.

Recently, we have studied the photochemical bromination of pentaphenylethane at room temperature.[5] The only products are a quantitative yield of trityl bromide and dibromodiphenylmethane. The pentaphenylethyl radical was proposed as a transient species here, the resultant pentaphenylethyl bromide decomposing to the trityl radical and the bromodiphenylmethyl radical.

The postulation of pentaphenylethyl as a substance of unusual persistence of course begs the question. The diphenylmethyl radical is not persistent, but rather dimerizes to tetraphenylethane. The introduction of steric hinderance in the form of *o*-methyl groups alters the dimerization from ethane formation to the formation of a methylenecyclohexadiene.[6] The same has recently been found true for the 1,1-diphenyl-2,2-dimethylpropyl radical.[7] This mode of dimerization appears to be equally accessible to the pentaphenylethyl radical. Phenyl bridging in radical reactions has never found experimental support unlike the formation of phenonium ions in carbocation processes. A bridged phenyl radical appears to be at best a transition state during phenyl migration.

Experimental Section

All ESR spectra were obtained on a Varian Model E 102A instrument with a 9.5-GHz microwave bridge using a modulation frequency of 100 kHz. Proton and carbon NMR spectra were obtained on Varian EM-390 and JEOL FX-60 instruments, respectively. Unless otherwise noted all NMRs were obtained in deuteriochloroform with tetramethylsilane as an internal standard. Routine mass spectra were obtained on a Finnigan OWA-1020 GC-MS-DS operating after a Perkin-Elmer Sigma-3 gas chromatograph. High-resolution mass spectra were kindly provided by Dr. David Russell of Texas A&M University.

Reactions carried out in the absence of oxygen were conducted in a standard glovebag purged with prepurified nitrogen or argon. Such reactions were frequently carried out in standard Schlenk ware after similar purging.

Reaction of Tritylsodium with Dichlorodiphenylmethane. Tritylsodium was generated by shaking 2.0 g (7.2 mmol) of trityl chloride in 75 mL of ether with sodium amalgam (ca. 2.5%) formed from 0.7 g (30 mmol) of sodium and 2 mL of mercury. After 15 h the dark red solution was filtered under nitrogen, and a solution composed of 0.85 g (3.6 mmol) of dichlorodiphenylmethane in 25 mL of ether was added in small protions. When ca. 2.7 mmol of the dichloro compound had been added, the dark red initial color altered to light red. An ESR analysis of the solution at this

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