Tetrahedron Vol. 43, No. 12, pp. 2831 to 2841, 1987
Printed in Great Britain.

0040-4020/87 $3.00+.00
Pergamon Journals Ltd.

GAS PHASE ALKYLATION OF DIHALOBENZENES BY FREE ISOPROPYL CATIONS

Bianca Aliprandi,* Fulvio Cacace and Simonetta Fornarini
University of Rome "La Sapienza" - P.le A.Moro 5, 00185 Rome, Italy

(*Received in UK* 30 *April* 1987)

Summary. The reactivity of selected dihalobenzenes toward free isopropyl cations has been studied in the gas phase by a combination of chemical ionization (CI) mass spectrometry with a radiolytic approach. In particular, the reactivity of m- and p-bromofluorobenzene and of m- and p-chlorofluorobenzene has been investigated in propane gas at 50-720 Torr and 37.5°C, measuring the substrate and positional selectivity of the alkylation, and compared with condensed-phase isopropylation under typical Friedel-Crafts conditions. The comparison has allowed detection of mechanistic peculiarities of the gas-phase reaction, traced to the participation of the halogen substituents, which enhances ortho orientation. A noteworthy feature of the gas-phase isopropylation of 4-bromofluorobenzene is the formation of 2-bromo-4-fluorocumene in significant yields, pointing to the occurrence of "ipso" attack at the bromine-bearing ring carbon.

INTRODUCTION

Recent experimental approaches allow aromatic substitution by charged electrophiles to be investigated in the gas phase, a reaction environment largely free of solvation, ion pairing and other complicating factors which affect ionic processes in condensed media. In particular, an integrated approach based on the combination of radiolytic,[1-2] or nuclear-decay[3] techniques with mass spectrometric methods has proved particularly effective, allowing the substrate and positional selectivity of a number of aromatic substitutions to be directly evaluated in the gas phase.[4-6] An interesting facet of aromatic alkylation by free carbenium ions, which points to a mechanistic peculiarity of the gas phase reaction, is the disproportionately high extent of ortho substitution, e.g. over 80% in the isopropylation of the halobenzenes.[7,8] It has been suggested that, in addition to direct attack, ring substitution proceeds via the formation of a preliminary adduct, characterized by the electrostatic interaction of the positively polarized H atoms of the carbenium ion with the n electrons of the halogen, which increases the local concentration of the electrophile at the ortho positions. Such behavior is consistent with that of aromatic substrates carrying substituents other than halogens, e.g. the hydroxyl, the methoxy[9] and the amino group,[10,11] which contain n-type electrons, as well as with that of substrates containing two adjacent π centers.[6]

In this paper we report the extension of the study to selected dihalobenzenes, with the aim of gathering additional evidence on the role of preliminary electrostatic adducts, and of estimating the relative ability of the different halogens in "chelating" the gaseous carbenium ions.

RESULTS

The reagent. Extensive mass spectrometric[12,13] and radiolytic[14,15] studies show that i-$C_3H_7^+$, formed directly, or via fast processes such as hydride transfer from C_3H_8 to fragment ions, e.g.

$C_2H_5^+$ and C_3H_5 , or isomerization of n-$C_3H_7^+$ cations, is by far the major species from the ionization of propane, its yield reaching a $G_{(+M)}$ value of ca.3 in the radiolysis of C_3H_8 in the pressure range of interest to this study.[16] Furthermore, the large excess of C_3H_8 ensures thermalyzation of any excited i-$C_3H_7^+$ ions by many unreactive collisions before a reactive encounter with the aromatic molecule can occurr.

Mass spectrometric evidence. The CI spectra of C_6H_4FX substrates (X=Cl, Br) recorded in C_3H_8 a 160°C at pressures ranging from 0.1 to 0.8 torr display the molecular ion M^+ and the protonated adduct $(M+H)^+$ as the major peaks. Interestingly, however, the isopropylated adduct $(M+C_3H_7)^+$ begins to be detectable above ca.0.5 torr, and its relative abundance, which depends on the specific substrate concerned, increases in all cases with the pressure. As a typical example, the abundance of the isopropylated adduct from m-bromofluorobenzene is about 20% of that of the $(M+H)^+$ adduct at 0.8 torr, the highest pressure investigated.

As a whole, the behavior of the dihalobenzenes is consistent with that of monohalobenzenes under CIMS conditions.[17] It should be noted, however, that while the CI results are of interest, demonstrating the formation of isopropylated ions even at the low pressures and high temperatures prevailing in the ion source, they provide no information on the nature of the adducts. The latter could reasonably be envisaged as ring-alkylated arenium ions, as well as halonium ions, or even as mere electrostatic complexes between isopropyl cations and dihalobenzene molecules.

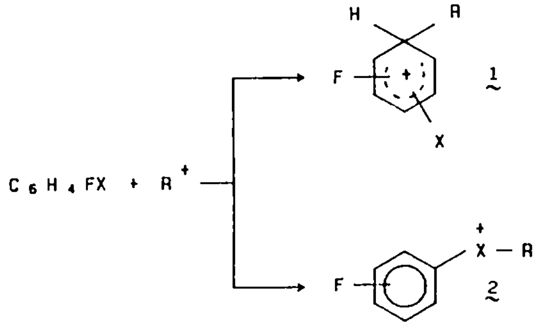
Radiolytic results. The composition of the irradiated systems, the nature and yields of the products, and the relative reactivity of the aromatic substrates are summarized in Table 1. The identity of the products has been established in all cases by GLC/MS. Their isomeric composition has positively been determined in the alkylation of m- and p-bromofluorobenzene and p-chlorobenzene using authentic samples as reference standards (see Experimental). The assignement of the isomeric products from m-chlorofluorobenzene is based on the elution order established for the corresponding products from m-bromofluorobenzene, and should be regarded as tentative. The ionic nature of the products is suggested by: i- the presence in the irradiated gas of a radical scavenger (O_2), at concentrations even higher than of the substrate. ii- the direct observation of charged alkylated adducts in the C_3H_8 CI mass spectra of the substrates investigated and, iii- the dramatic depression of the yields caused by addition to the gas of bases, such as NH_3, that intercept i-$C_3H_7^+$ via fast deprotonation processes. The $G_{(+M)}$ values which express in the Table 1 the absolute yields of the products must be regarded as crude estimates, owing to the recognized difficulties associated with accurate measurement of absolute radiation doses. Nevertheless, despite uncertainties estimated around 30%, comparison with the known $G_{(+M)}$ value of i-$C_3H_7^+$ ions from the radiolysis of C_3H_8 shows that alkylation of dihalobenzenes is indeed a major reaction channel, accounting for 50 to 60% of the isopropyl ions formed in the gas. These are remarkably high yields, if one considers that a fraction of the ions can undergo proton transfer to the aromatics, as shown by low-pressure CI mass spectral evidence,[18] and especially that the substrate undergoes competition with other nucleophiles, present as impurities, or formed from the radiolysis of the system.

The reactivity of the dihalobenzenes relative to that of PhH has been estimated indirectly, using as intermediate standards m- and p-difluorobenzene, whose k/k_{PhH} ratios had previously been reported.[8] The cumulative uncertainty of the ratios listed in the Table is estimated around ± 0.1.

Liquid-phase isopropylation. Direct comparison with condensed-phase reactivity has been sought by carrying out the $AlCl_3$ -catalyzed alkylation of m- and p-C_6H_4FBr by i-C_3H_7Cl in $MeNO_2$ at 25°C, i.e.under the same conditions adopted in a previous study on the isopropylation of monohalobenzenes.[19] m-Bromofluorobenzene gave 16% 2-fluoro-6-bromocumene, 28% 2-fluoro-4-bromocumene and 56% 2-bromo-4-fluorocumene without detectable formation of 3-fluoro-5-bromocumene. The absence of the latter is of interest, since it supports the view[19] that secondary isomerization processes are not significant under the conditions chosen. p-Bromofluorobenzene gave only 2-fluoro-5-bromocumene (64%) and 2-bromo-5-fluorocumene (36%), without detectable formation of 2-bromo-4-fluorocumene, produced in appreciable yields from the gas-phase isopropylation of the same substrate.

DISCUSSION

The alkylation process. Isopropyl ion, R^+, can add to the π- or n-type nucleophilic centers of dihalobenzenes, yielding respectively arenium and/or halonium ions, e.g.



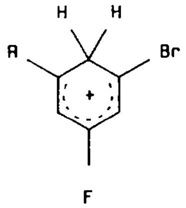
(1a)

(1b)

or behave as a Brønsted acid, yielding the corresponding protonated adducts

$$C_6H_4FX + R^+ \longrightarrow C_6H_5FX^+ + C_3H_6 \qquad (2)$$

Low-pressure CI mass spectral experiments have demonstrated the occurrence of both protonation and alkylation processes, the latter becoming increasingly significant as the source pressure was raised. The observation is consistent with the higher exothermicity of the isopropylation process, estimated in excess of 30 Kcal mol^{-1},[20] which contrasts with the mildly exothermic[18] character of the protonation. A larger fraction of the alkylated adducts 1 and 2 can be stabilized by collisional deactivation at higher pressures, a trend clearly apparent even in the limited range ($<$ 1 torr) accessible to CI mass spectrometers. Extrapolation to the substantially higher pressures and lower temperatures prevailing in the radiolytic experiments suggests that alkylation should become largerly predominant under these conditions, consistent with the high yields of isopropylated products, whose formation is traced to deprotonation of 1 by any suitable gaseous base.[21] A fraction of the primary ionic intermediates can isomerize before deprotonation, either via intermolecular processes, e.g.R^+ transfer from 1 to dihalobenzenes, or via intramolecular H, R, or halogen shifts. Except in the case of p-C_6H_4FBr, which deserves separate discussion (vide infra), there is little evidence for significant isomerization at 720 torr. This is suggested by the generally scarce effect of NH_3 on the relative reactivity and orientation pattern, despite the expected decrease of the isomerization extent caused by the reduced lifetime of ions 1 and 2. Furthermore, no 3-fluoro-5-halocumenes are formed from 3-halofluorobenzenes, showing that the primary arenium ions, formed under conditions of kinetic control, have not appreciably isomerized into the most stable structure 3



3

The situation is different at 50 torr, owing to the lower efficiency of collisional deactivation, which allows a fraction of the excited adducts from process (1) to isomerize, as suggested by the appreciable change of isomeric composition of products.

Selectivity of the gas-phase alkylation. The substrate selectivity of i-$C_3H_7^+$ is outlined by the k_S/k_{PhH} ratios of individual chlorofluorobenzenes and bromofluorobenzenes reported in Table 1, and by similar data concerning halobenzenes and difluorobenzenes, available as a result of earlier studies.[7,8] Concerning positional selectivity, Table 2 purports to compare the orientation observed in the gas-phase isopropylation of dihalobenzenes with that measured in solution. The summary of the situation seems to be that the selectivity of the gas-phase alkylation reflects the simultaneous operation of two distinct factors:

i- The ordinary effects of substituents on the reactivity of aromatic substrates toward electrophiles are clearly discernible, e.g. halogen substituents depress the reactivity of the substrate relative to PhH, their deactivating power increasing in the order F < Cl < Br, as shown by the following k_S/k_{PhH} ratios:

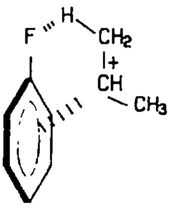
m-C_6H_4FX: 0.40 (X=F) > 0.33 (X=Cl) > 0.26 (X=Br)

p-C_6H_4FX: 0.40 (X=F) > 0.30 (X=Cl) > 0.24 (X=Br)[22]

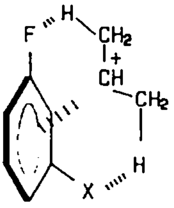
Furthermore, halogen substituents are invariably ortho/para directing, meta positions being strongly deactivated, to the point that no detectable alkylation occurs at ring positions meta to both halogen substituents.

ii - A strong bias for orientation ortho to groups, or atoms, carrying n-type electrons, which cannot be traced to ordinary substituents effects, characterizes isopropylation of gaseous dihalobenzenes, as noted in earlier gas-phase studies on different substrates. As an example, the reactivity of position 2 of 3-halofluorobenzenes, ortho to both halogens, largely exceeds in the gas-phase those of positions 4 and 6, despite their higher activation by the usual electronic effects, clearly discernible in condensed-phase isopropylation.

The present results provide further support to the view that the local concentration of the gaseous cation at the ortho positions is enhanced by its preliminary coordination with the n electrons of the halogen atom(s), leading to formation of electrostatic adducts, e.g.



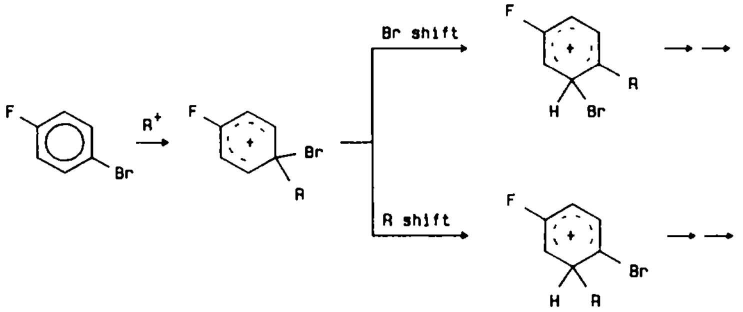
4



5

In the case of 3-halofluorobenzenes, the coordination can involve both halogen atoms, which is likely to further stabilize adduct 5, thus accounting for the high rate of alkylation at position 2 of these substrates. Comparison of the gas-phase orientation with that measured in solution, where coordination effects, if any, are expected to be far less significant, allows a rough estimate of the ability of the different halogens to bind positively polarized H atoms. As a whole, the set of data concerning halobenzenes and dihalobenzenes shows that F, Cl and Br substituents cause a comparable enhancement of ortho attack in passing from liquid-phase to gas-phase isopropylation, suggesting that their coordinating ability must be roughly equivalent, even though a closer comparison of F with Cl shows that the latter is somewhat more effective in certain substrates (PhX, p-C_6H_4FCl), consistent with independent evidence based on the stability of $X\cdots H^+$ bonds in α, ω-disubstituted alkanes.[23]

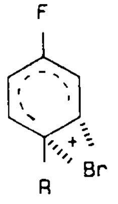
"Ipso" alkylation in p-bromofluorobenzene. Formation of significant amounts (22%) of 2-bromo-4-fluorocumene from isopropylation of 4-bromofluorobenzene is of interest, providing the first example of "ipso" attack on Br-bearing ring carbon by a gaseous carbenium ion



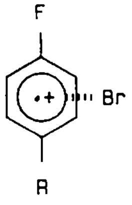
(3a)

(3b)

In fact, previous examples of "ipso" alkylation in the gas-phase were restricted to hexaalkylbenzenes,[24] while attack to ring positions bearing halogen atoms has previously been observed only in the protonation of bromoarenes by strong gaseous acids.[25] It should be noted that formation of 2-bromo-4-fluorocumene requires, in addition to "ipso" attack, successful competition of the 1 → 2 Br shift (3a) with the alternative R shift (3b). No products from "ipso" substitution are formed in the gas-phase isopropylation of 3-bromofluorobenzene and of the chlorofluorobenzenes, probably for different reasons. In fact, position 3 of 3-halofluorobenzenes, meta to F, is by far too deactivated, as shown by the remarkably low meta orientation in PhF, to allow "ipso" attack to occur at any appreciable extent. On the other hand, "ipso" attack is likely to be possible on the Cl-bearing atom of 4-chlorofluorobenze, as it is in the case of 4-bromofluorobenzene, since the position para to F is the most reactive toward electrophilic attack. However, in the subsequent step, migration of isopropyl (process 3b) is likely to be favored over migration of Cl (process 3a), which accounts for the failure to detect 2-chloro-4-fluorocumene among the products. As to the mechanism responsible for Br migration, it can involve either Br^+ ion, possibly via a cyclic bromonium intermediate, or the formation, and the subsequent collapse, of an aromatic



6



7

radical cation/bromine atom pair, as in the protonation-induced isomerization of gaseous bromoxylenes.[25] It is worth noting that no products whose formation requires "ipso" attack followed by Br shifts were formed from the reaction of 4-bromofluorobenzene with i-$C_3H_7Cl/AlCl_3$ in nitromethane at 25°C, perhaps on account of the steric bulk of the polarized $RX-AlX_3$ complex. However, the ability of halogen-bearing ring positions to undergo "ipso" attack by strong electrophiles, e.g.NO_2^+, is well documented in solution, and, interestingly, the "leaving ability" of the halogens increases in the order $F < Cl < Br < I$.[26]

EXPERIMENTAL

Materials and procedure. C_3H_8, O_2 and NH_3 were research-grade gases from Matheson Gas Products Inc., with a stated purity in excess of 99.99 mol %, and were used without further purification. The aromatic substrates were commercial samples, assayed by GLC on the same columns used for the analysis of the radiolytic products. The gaseous samples were prepared by introducing the desired amounts of reactants into carefully evacuated and outgassed 250-ml pyrex vessels, as described in previous reports.[1] The irradiations were carried out in a 220 Gammacell (Atomic Energy of Canada Ltd.) at a dose rate of $5.0 \cdot 10^3$ Gray h^{-1}, to a total dose of 10^4 Gray.

Analysis of the products. The irradiated ampoules were cooled to liquid nitrogen temperature, their content was dissolved into a suitable solvent (MeOH, EtOAc), and measured aliquots of the solution were analyzed by GLC using Perkin-Elmer Sigma 1 and Sigma 3 instruments fitted with FID and PID detectors. The identity of the products was established by comparison of their capacity factors with those of authentic samples and by GLC/MS, using a Hewlett-Packard 5982A quadrupole mass spectrometer. The yields of the products were calculated from the areas of the corresponding elution peaks, using the internal standard method and individual calibration factors.

The following chromatographic conditions were used, listed in the order given in Table 1:

1. A 1.8-m long, 1.4-mm i.d., glass column, packed with SP-2100 (3%) on 100-120 mesh Supelcoport, operated at 100°C.
2. A 30-m long, 0.25-mm i.d. silica capillary column, coated with SP-2100, operated at 80°C.
3. A 2.5-m long, 4-mm i.d. glass column, packed with SP-2100 (10%) and Bentone 38 (6%) on AW, DMCS-treated 80-100 mesh Chromosorb W, operated at 80°C.
4. Same column, operated isothermally for 4 minutes at 80°C, then programmed to 100°C at a gradient of 40°C min^{-1}.
5. Same column, operated isothermally for 11 minutes at 70°C, then programmed to 100°C at a gradient of 40°C min^{-1}.

Identification of isomeric fluorobromocumenes. Several isomeric fluorobromocumenes, required as reference standards for the gas chromatographic identification of the products from the isopropylation of fluorobromobenzenes, have been prepared and characterized by NMR spectroscopy. The required compounds were obtained by alkylating m-C_6H_4FBr with i-C_3H_7Cl in the presence of $AlCl_3$ in $MeNO_2$ at room temperature, and separated by GLC using a preparative column corresponding to analytical column 3, operated at 95-100°C. The various isomers, collected in separate glass traps and dissolved into $(CD_3)_2CO$, were analyzed by ^1H and ^{19}F NMR spectroscopy, using a Bruker WP 200 or a Varian XL 300 instrument, with the deuterium signal as the lock. The isomers were identified by the aromatic protons and fluorine absorption patterns, whose interpretation was tested against spectra calculated with a Laocoon-type program,[27] as shown by the example illustrated in Figure 1.

The ordering of the H and F atoms on the aromatic ring is established by the magnitude of the corresponding coupling constants. The meta relationship between the two halogens existing in the 3-bromofluorobenzene used as the starting material was maintained in the isopropylated products. A brief outline of the spectra is given below, with emphasis on aromatic protons, together with the assigned structures.

1-Bromo-3-fluoro-6-i-propylbenzene

1.26 ppm (6H,d), 3.36 (1H,m), 7.20 (H-4), 7.43 (H-2), 7.48 (H-5). $J_{2,F}$ 8.3 Hz, $J_{2,4}$ 2.8 Hz, $J_{F,4}$ 8.1 Hz, $J_{F,5}$ 6.2 Hz, $J_{4,5}$ 8.6 Hz.

1-Bromo-2-i-propyl-3-fluorobenzene

1.31 ppm (6H,dd), 3.54(1H,m), 7.12(H-4), 7.18(H-5), 7.43(H-6). $J_{F,4}$ 11.2 Hz, $J_{F,5}$ 6.0 Hz, $J_{F,6}$ 1.3 Hz, $J_{4,5}$ 8.2 Hz, $J_{4,6}$ 1.4 Hz, $J_{5,6}$ 7.9 Hz.

1-Bromo-3-fluoro-4-i-propylbenzene

1.21 ppm (6H,d), 3.16 (1H,m), 7.28-7.36 multiplet including an intense broad singlet (H-2, H-5, H-6). The ^{19}F spectrum is well resolved and gives $J_{2,F}$ 10.7 Hz, $J_{F,5}$ 7.0 Hz.

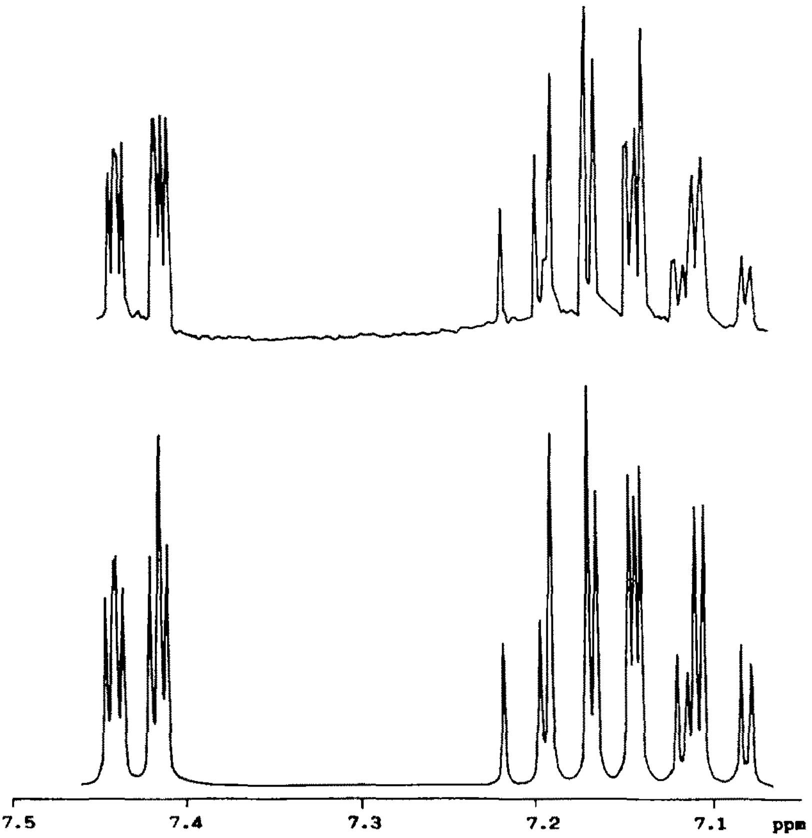
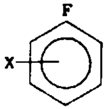
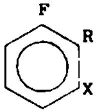
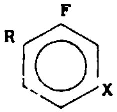
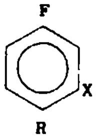
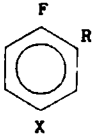
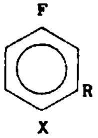


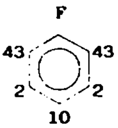
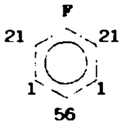
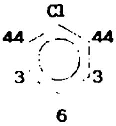
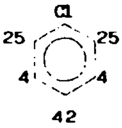
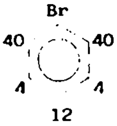
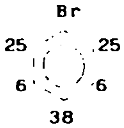
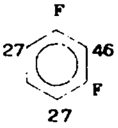
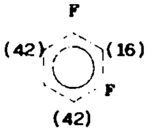
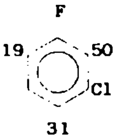
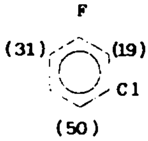
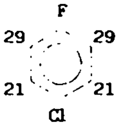
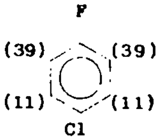
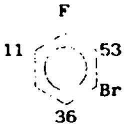
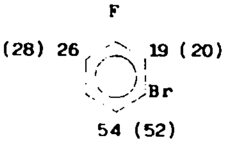
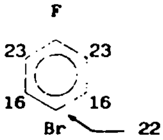
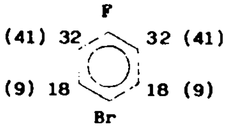
Figure 1. Experimental (upper trace) and calculated (lower trace) nmr spectrum of 1-bromo-2-i-propyl-3-fluorobenzene (see text).

TABLE 1. Alkylation of Fluorohalobenzenes by Gaseous $i\text{-}C_3H_7^+$ Ions.

System Composition[a] (torr)			Isomeric Composition[b] of Products (%)					$\frac{k_s}{k_{PhH}}$	Combined $G_{(+M)}$	GLC Separation[c]
	C_3H_8	NH_3								
X = m-Br	720		53	11	36			0.26[d]	1.5	2
	720	10	48	18	34				0.2	4
	50		28	28	44				1.9	4
X = m-Cl	720		50	19	31			0.33[d]	1.6	2
	720	10	45	20	35				0.2	4
	50		27	29	44				1.9	4
X = p-Br	720				22	45	33	0.34[d]	1.7	1,2,4
	720	10				e			ca. 0.2	1,2
	50				24	45	31		1.9	1,2
X = p-Cl	720					57	43	0.30[d]	1.0	3
	720	10				57	43		0.07	3
	50					64	36		1.8	3

([a]) All systems contained C_6H_4XF (ca. 1 torr) and O_2 (5 - 10 torr) as a radical scavenger. ([b]) R = $i\text{-}C_3H_7$, X = Cl or Br. Standard deviation of the data ±5% relative. ([c]) See Experimental. ([d]) Estimated indirectly, see text. ([e]) See Experimental.

TABLE 2. Comparison of Gas-Phase and Liquid-Phase Orientation.

Propane gas, 720 torr[a]	Ref.	MeNO$_2$, i-C$_3$H$_7$X/AlCl$_3$[b]	Ref.
	7		19
	7		19
	7		19
	8		c
	This work		c
	This work		c
	This work		This work, c
	This work		This work, c

---

([a]) Temperature was 28°C (ref.7), 30°C (ref.8) and 37.5°C (This work). ([b]) Temperature 25°C, X = Br (ref.19) and Cl (This work). ([c]) Values in parentheses are calculated from the partial rate factors desumed from the data of ref.19.

Chemical ionization mass spectrometry. The spectra were recorded using the quadrupole instrument operated in the CI mode, measuring the source pressure with a ionization manometer previously calibrated with a Bourdon gage inserted in the place of the direct introduction probe, or a ZAB-2F magnetic spectrometer from VG-Micromass Ltd., whose CI source was fitted with a MKS Baratron 221-A capacitance manometer. Typical operating conditions were: emission current 0.5 mA, electron energy 100 eV, source temperature 160°C, reactant gas pressure 0.2-0.8 torr.

Acknowledgment. This work has financially been supported by the Italian National Research Council (CNR) and by the Ministry of Pubblica Istruzione. The authors thank the Servizio NMR del CNR, Area della Ricerca di Roma (Montelibretti), and the Centro CNR sui Meccanismi di Reazione, Rome, for ^{1}H and ^{19}F NMR spectra.

REFERENCES

(1) F.Cacace, Radiat.Phys.Chem., 20, 99, (1982).

(2) M.Speranza, Gazz.Chim.Ital., 113, 37 (1983).

(3) F.Cacace and M.Speranza, in "Techniques for the Study of Gas-Phase Ion-Molecule Reactions" Techniques of Chemistry Series, J.M.Farrar and W.H.Saunders, Jr.Ed., Wiley, New York, 1987.

(4) M.Attinà and F.Cacace, J.Am.Chem.Soc., 108, 318 (1986).

(5) F.Cacace and G.Ciranni, J.Am.Chem.Soc., 108, 887 (1986).

(6) F.Cacace, G.de Petris, S.Fornarini, P.Giacomello, J.Am.Chem.Soc., 108, 7495.

(7) M.Attinà and P.Giacomello, J.Am.Chem.Soc., 101, 6040 (1979).

(8) M.Attinà, G.de Petris, P.Giacomello, Tetrahedron Lett., 23, 3525 (1982).

(9) M.Attinà, F.Cacace, G.Ciranni, P.Giacomello, J.Chem.Soc.Perkin Trans.2, 891 (1979).

(10) M.Attinà and F.Cacace, J.Am.Chem.Soc., 105, 1122 (1983).

(11) M.Attinà, F.Cacace, and G.de Petris, J.Am.Chem.Soc., 107, 1556 (1985).

(12) M.S.B. Munson, J.L.Franklin, and F.H.Field, J.Phys.Chem., 68, 3098 (1964).

(13) B.H.Solka, A.Y.-K.Lau, and A.G.Harrison, Can.J.Chem., 52, 1798 (1974).

(14) P.Ausloos and S.G.Lias, J.Chem.Phys., 36, 3163 (1962).

(15) P.Ausloos, in "Ion Molecule Reactions", J.L.Franklin Ed., Plenum Press, New York 1970.

(16) The $G_{(+M)}$ value, which represents the number of molecule formed per 100 eV absorbed by the system, expresses the absolute yield of a ionic product from the radiolysis. On the $G_{(+M)}$ value of i-$C_3H_7^+$ from C_3H_8, see S.G.Lias, R.E.Robbert, and P.Ausloos, J.Am.Chem.Soc., 92, 6430 (1970).

(17) A.G.Harrison "Chemical Ionization Mass Spectrometry", CRC Press, Boca Raton, Fa., 1983, p.102 and references therein.

(18) The gas-phase PA of bromo- and chlorofluorobenzenes is not available. However, from the PA of isomeric difluorobenzenes, 207-208 Kcal mol^{-1}, and a comparison of the PA of PhF, PhCl and PhBr, respectively 182.6, 181.7, and 182.4 Kcal mol^{-1}, proton transfer to the dihalobenzenes from i-$C_3H_7^+$ cannot be excluded. The PA of propene is 179.5 Kcal mol^{-1}. All values taken from S.G.Lias, J.F.Liebman, and R.D.Levin, J.Phys.and Chem.Ref.Data, 13, 695 (1984), and references therein.

(19) G.A.Olah, S.H.Flood, and M.E.Moffat, J.Am.Chem.Soc., 86, 1065 (1964).

(20) Lack of thermochemical data prevents specific calculations in the case of dihalobenzenes. However, taking PhF as a convenient model, its ring isopropylation (eq.1a) can be estimated to be exothermic by ca.35 Kcal mol^{-1}, by analogy with the calculation by R.S.Mason, D.K.Böhme, and K.R.Jennings, J.Chem.Soc.Faraday Trans.1, 78, 1943 (1982).

(21) Gaseous bases of sufficient strenght to ensure deprotonation of 1 are invariably present in the irradiated systems, being formed from the radiolysis of C_3H_8 containing O_2 as a radical scavenger. For instance, the PA of Me_2CO is 196.7 Kcal mol^{-1}, that of i-C_3H_7OH is 191.2 Kcal mol^{-1}, etc.

(22) Corrected for the contribution from "ipso" substitution which does not occur in the other substrates.

(23) D.H.Aue and M.T.Bowers, in "Gas Phase Ion Chemistry", M.T.Bowers Ed., Academic Press, New York 1979, V.2, p.19.

(24) M.Attinà, F.Cacace, G.de Petris, S.Fornarini, and P.Giacomello, J.Am.Chem.Soc., 107, 2297 (1985).

(25) F.Cacace, G.Ciranni, and A.Di Marzio, J.Chem.Soc.Perkin Trans.2, 1984, 775.

(26) K.Schofield "Aromatic Nitration", Cambridge University Press 1980, p.171-236, and references therein.

(27) S.Castellano and A.A.Bothner-by in "Computer Programs for Chemistry", D.F.De Tar Ed., Benjamin, New York 1978.