Aromatic Substitution in the Gas Phase. Alkylation of Xylenes and Toluene by i-$C_3H_7^+$ Ions

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Abstract: Isopropyl cations, obtained in the dilute gas state from the γ radiolysis of propane, have been allowed to react with individual xylene isomers, both neat and in competition with toluene, in the pressure range 20–720 Torr, and in the presence of variable concentrations of a gaseous base (NH_3). The mechanism of the substitution, and of subsequent isomerization and dealkylation processes are discussed, and the *substrate* and *positional* selectivity, together with the *intrinsic* steric requirements of the free, unsolvated i-$C_3H_7^+$ ion, are evaluated. Comparison of the gas-phase alkylation by i-$C_3H_7^+$ and t-$C_4H_9^+$ with related reactions occurring in solution reveals no basic mechanistic differences, the gas-phase reactivity of free cations representing the limit more or less closely approached in solution by poorly solvated alkylating agents, of incipient cationic nature.

In the first papers of this series the application of a specifically designed radiolytic technique to the study of aromatic substitution by alkyl cations in the diluted gas state has been reported.[1-4] In particular, investigation of the gas-phase *tert*-butylation of benzene, toluene, and the xylenes has provided direct information on the *intrinsic* reactivity, selectivity, and steric requirements of the t-$C_4H_9^+$ cation.

We now report the extension of the study to the gas-phase alkylation of xylenes, both neat and in competition with toluene, by i-$C_3H_7^+$ ions from the radiolysis of propane. The investigation has been primarily undertaken to bring to a sharper focus the correlation between reactivity and selectivity of gaseous cations by comparing the known behavior of t-$C_4H_9^+$ with that of a considerably stronger, yet closely related reagent, such as i-$C_3H_7^+$, toward the same aromatic substrates. Furthermore, the choice of xylenes could hopefully prove suitable, as in the case of *tert*-butylation, for the direct evaluation of the *intrinsic* steric requirements of the isopropyl cation, that can be hardly deduced from the rather scattered data of solution chemistry studies.[5]

Experimental Section

Materials. Toluene and the xylenes were gas chromatographic standards from C. Erba Co. A GLC analysis revealed an impurities content below 0.2 mol % and the absence of detectable isopropylated products. Cymenes and isopropylxylenes used as chromatographic standards were commercial products, or were prepared according to established procedures,[6,7] identified by NMR and IR spectroscopy, and purified by preparative GLC using a 5-m Carbowax 20M column operated at 170 °C for isopropylxylenes and at 140 °C for cymenes.

C_3H_8, O_2, and N_2 were research grade gases from Matheson Co., with a stated purity of 99.99 mol %, and were used without further purification.

Procedure. The experimental technique used for the preparation of the samples and their irradiation has been described previously.[4] The radiation dose was 2.9 MRad, delivered at the rate of 0.55 MRad $hour^{-1}$, for all samples, at a temperature of 24°.

A few runs, carried out at a dose of 10 Mrad, revealed no significant differences in the relative k values and in the isomeric composition of products. The analysis of products was carried out by injecting measured aliquots of the irradiated gas samples into a C. Erba Model 2400 T or a Hewlett Packard Model 5700A gas chromatograph equipped with FID units.

The following columns were used in the temperature range from 120 to 140 °C: 4-m and 8-m Apiezon "L", and 4-m UCON-LB 550 on acid-washed Chromosorb W, using N_2 as the carrier gas. The products were identified by comparison of their retention volumes with those of authentic samples, and their yields determined from the area of the correspondent elution peaks, using appropriate calibration factors.

Results

Isopropylation has been found to occur for all substrates, and to represent a significant reaction channel of the radiolytic i-$C_3H_7^+$ ions. Overall G values for the formation of isopropylated arenes depend on the composition of the gaseous system, since the aromatic substrate faces competition for the i-$C_3H_7^+$ ion by other nucleophiles deliberately added to the system (e.g. NH_3), initially present as impurities in the C_3H_8 gas, or formed from its radiolysis. Accordingly, G values increase with the substrate concentration and decrease with the concentration of nucleophiles from the radiolysis, determined by the amount of energy absorbed by the gas, which in turn depends on the C_3H_8 pressure and the radiation dose. Typical values measured at 720 Torr at a dose of 2.9 Mrad with a xylene pressure of 1.0 Torr and in the absence of added bases range from 0.36 to 0.47. Addition of NH_3 causes a sharp decrease of the G value, which drops to ca. 0.1 in the presence of 10 Torr of the base. The isomeric composition of products from the isopropylation of neat xylenes is given in Table I, while the competition of individual xylenes with toluene and the isomeric composition of products at different C_3H_8 pressures and NH_3 concentrations are illustrated in Table II. No other products were identified, except for traces of n-propylated arenes (vide infra). From Tables I and II it is apparent that isopropylation of xylenes leads to the formation of all possible isomers, with a remarkably low degree of *positional* selectivity. Thus, referring to 720-Torr experiments, the rate of substitution at positions 3 and 4 of o-xylene is nearly the same, while m-xylene undergoes predominant substitution at positions 4 (ca. 60%) and 2 (ca. 25%) with a somewhat lower (ca. 15%) substitution at position 5. No products of methyl shifts could be detected, and isopropylation of p-xylene yields exclusively the expected 1,4-dimethyl-2-isopropylbenzene. At 720 Torr the composition of products from toluene and the xylenes, and the value of the apparent $k_{xylene}/k_{toluene}$ ratios, which are close to unity for all isomers, are not appreciably affected by NH_3, even at relatively high concentrations.

The pressure dependence of the alkylation process is considerably different for toluene and xylenes. In agreement with previous findings,[1,8] the proportion of meta isomer from toluene is found to monotonically increase with the decrease of pressure, prevalently at the expense of the ortho isomer.

Addition of NH_3 has little effect on the composition of the products at all pressures. On the other hand, decreasing the pressure does not appreciably affect the alkylation of xylenes, except at the lowest pressures investigated, i.e., in the range from 20 to 50 Torr, where the $k_{xylene}/k_{toluene}$ ratios undergo a significant decrease for all isomers and the composition of

Table I. Alkylated Products from the Gas-Phase Attack of i-$C_3H_7^+$ on Xylenes

System composition, Torr				Isomeric composition of products,[a] %		
C_3H_8	O_2	NH_3	Xylene			
720	10		ortho: 1.26	1,2,*3*: 54.5	1,2,*4*: 45.5	
720	10	10	ortho: 1.25	1,2,*3*: 52.2	1,2,*4*: 47.8	
720	10		meta: 1.24	1,3,*5*: 14.6	1,3,*4*: 58.7	1,*2*,3: 26.7
720	7	10	meta: 1.03	1,3,*5*: 17.2	1,3,*4*: 59.4	1,*2*,3: 23.4
720	10		para: 1.30	1,*2*,4: 100.0		

[a] Position of the isopropyl groups italicized. Standard deviation of data ca. 5%.

Table II. Competition of Toluene and Individual Xylenes for the i-$C_3H_7^+$ Ion

System composition, Torr					$k_{xylene}/k_{toluene}$	Products composition,[a] %					
						Isopropyl xylenes			Cymenes		
C_3H_8	O_2	NH_3	Toluene	Xylene					*o*-	*m*-	*p*-
720	10		1.55	ortho: 1.31	0.9	1,2,*4*: 41.8	1,2,*3*: 58.2		46.7	30.0	23.3
720	10	5	0.25	2.78	1.0	48.0	52.0		45.8	30.3	23.9
720	7	23	1.57	1.36	1.0	48.2	51.8		43.1	31.1	25.8
100	2		1.13	1.06	1.0	38.9	61.1		37.8	37.6	24.6
50	2		0.34	0.93	0.6	42.7	57.3		25.7	50.8	23.5
50	2	2	0.34	0.31	1.0	66.2	33.8		24.3	48.3	27.0
20	2		0.56	0.48	0.4	29.1	70.9		16.7	67.0	16.3
720	10	5	1.55	meta: 0.14	0.9	1,3,*5*: 17.0	1,3,*4*: 60.9	1,*2*,3: 22.1	43.9	30.0	26.1
720	7	23	1.46	1.27	1.0	15.6	60.7	23.7	42.9	30.6	26.5
100	2		1.49	1.38	0.9	20.4	59.4	20.2	34.9	40.3	24.8
50	2		0.83	0.60	0.6	33.4	50.5	16.1	27.4	49.9	22.7
50	2	2	0.40	0.55	1.0	30.8	61.4	7.8	22.6	53.2	24.2
20	2		0.72	0.51	0.5	54.3	37.3	8.4	16.4	66.5	17.1
720	7	13	2.00	para: 1.60	0.9	1,*2*,4: 100.0			42.2	31.8	26.1

[a] Position of the isopropyl group italicized. Standard deviation of data ca. 5%.

products also changes considerably.

Assuming a constant reactivity of toluene within the whole range of pressures, the reactivity of positions 3, and especially 4, of *o*-xylene appears to decline at low pressure. Addition of NH_3 brings the k ratio back to unity, as in the high-pressure alkylation; however, the isomeric composition is shifted in favor of 1,2-dimethyl-4-isopropylbenzene.

Taking into account both the k ratios and the isomeric composition of products, the reactivity of position 5 of *m*-xylene appears to increase in the low-pressure alkylation at the expense of positions 4 and especially 2, whose combined decline accounts for the decrease of the $k_{m\text{-xylene}}/k_{\text{toluene}}$ ratio. Addition of NH_3 makes the overall low-pressure reactivity of *m*-xylene equal to that of toluene, as at 720 Torr; however, with a different composition of products, a higher proportion of 1,3-dimethyl-5-isopropylbenzene is obtained at the expense of the 1,3-dimethyl-2-isopropylbenzene isomer.

Discussion

Nature and Properties of the Alkylating Reagent. Gaseous i-$C_3H_7^+$ is formed from the radiolysis of C_3H_8 either directly or via hydride ion abstraction of fragment ions, e.g., $C_2H_5^+$ and $C_3H_5^+$, from the alkane. Extensive studies on the radiolysis and the related ionic chemistry of gaseous C_3H_8 indicate that, in the pressure range of interest to the present work, i-$C_3H_7^+$ represents by far the most significant ionic species, and is formed with a G value of the order of 3.[9-13] In particular, isomerization of n-$C_3H_7^+$ to the secondary structure, suggested by radiolytic[14] and mass spectrometric[15] studies, is consistent with our finding that n-propylated arenes represent only minor products whose yields amount to only a few percent of those of isopropylated arenes.[16]

The presence of an effective scavenger (O_2) ensures that thermal radicals do not contribute to the formation of the observed products, while the ionic nature of the alkylation process is confirmed by the sharp decrease of the absolute yields caused by increasing concentrations of NH_3, an effective interceptor of the i-$C_3H_7^+$ reagent. Use of an excess of C_3H_8 over the arenes can be reasonably expected to deactivate excited i-$C_3H_7^+$ from the radiolysis, owing to the large number of unreactive collisions with the alkane molecules undergone by the alkyl cation before attacking the aromatic substrate.

Theoretical[17] and mass spectrometric[18] investigations show that i-$C_3H_7^+$ is a relatively stable gaseous cation, whose $\Delta H_f{}^\circ$ value (190-192 kcal mol^{-1}) is intermediate between those of n-$C_3H_7^+$ (208 kcal mol^{-1}) and of t-$C_4H_9^+$ (167 kcal mol^{-1}). However, in contrast with the behavior of the latter reagent, the reactivity of i-$C_3H_7^+$ toward toluene and the xylenes is not limited by energetic constraints to the condensation channel

$$i\text{-}C_3H_7^+ + ArH \rightarrow [i\text{-}C_3H_7\text{-}ArH]^+ \quad (1)$$

since, in addition, protonation

$$i\text{-}C_3H_7^+ + ArH \rightarrow [ArH_2]^+ + C_3H_6 \quad (2)$$

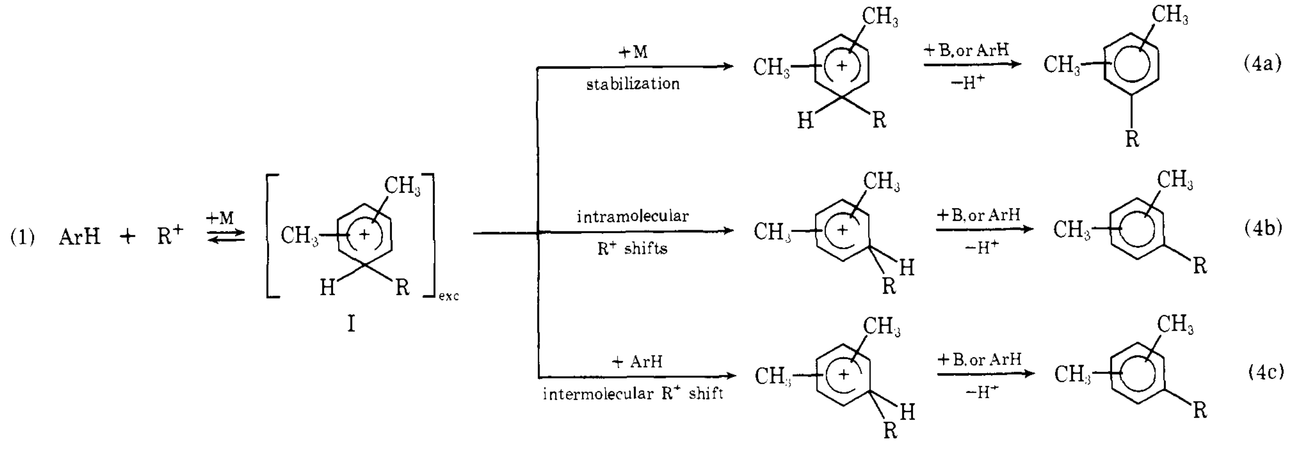
and hydride ion abstraction from the side chain

$$i\text{-}C_3H_7^+ + ArCH_3 \rightarrow [ArCH_2]^+ + C_3H_8 \quad (3)$$

are energetically allowed.[19] Since the final products from reactions 2 and 3 cannot be detected with the analytical techniques employed in the present investigation, it must be explicitly pointed out, when comparing the i-$C_3H_7^+$ attack to different arenes, that the selectivity measured in this work *concerns exclusively the alkylation channel,* rather than the overall electrophilic reactivity of the cation, and that variations of the *substrate* selectivity associated with changes of the reaction environment may also reflect alterations of the *relative* efficiency of processes 1-3, in addition to changes in the *absolute* rate of process 1.

The Alkylation and Isomerization Processes. The present results, and the available mass spectrometric evidence, suggest

Scheme I



the general reaction scheme outlined in Scheme I. Isopropylation of the xylenes is a considerably exothermic process, whose $\Delta H°$ value can be estimated between −37 and −42 kcal mol^{-1} for the different isomers,[20] and requires conceivably third-body stabilization.[21] Nevertheless, condensation of i-$C_3H_7^+$ with arenes has been observed by CI mass spectrometry even in CH_4 at 1 Torr,[21] and should become increasingly more efficient as the C_3H_8 pressure is raised from 20 to 720 Torr. The reversible nature of the attack is suggested, inter alia, by the facile dealkylation of comparably[22] excited arenium ions from the protonation of isopropylbenzenes by CH_5^+ and $C_2H_5^+$ ions in CI experiments.[21]

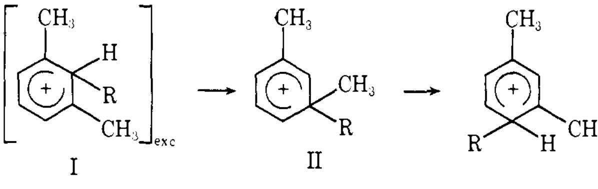
Several reaction channels are available to the excited arenium ions from reaction 1. Apart from reversible dealkylation, a direct route to products is represented by collisional stabilization of the arenium ions, followed by loss of a proton to a gaseous base (NH_3, or another molecule of substrate), as illustrated in eq 4a. The constancy of the apparent reactivity of xylenes with respect to toluene, and of the isomeric composition of products, together with the lack of significant effects of NH_3 in the pressure range from 720 down to ca. 50 Torr, suggests that the stabilization–deprotonation route is indeed the predominant pathway, except at the lowest pressures. The appreciable decrease of the $k_{\text{xylene}}/k_{\text{toluene}}$ ratios measured at the lowest pressures investigated can be rationalized taking into account the reduced efficiency of collisional stabilization, which allows a larger fraction of the excited arenium ions from reaction 1 to undergo decomposition, or, for that matter, isomerization (vide infra). In fact, fragmentation processes can be reasonably expected to affect to a larger extent the arenium ions from the more exothermic[21] i-$C_3H_7^+$ attack to the xylenes with respect to those from toluene.

Furthermore, owing to their high proton affinity that in the absence of NH_3 makes dimethylisopropylbenzenes the strongest bases contained in the gas,[23] deprotonation of certain arenium ions from the alkylation of the xylenes can represent an endothermic, and therefore comparatively slow process, that allows a longer lifetime, and a more extensive decomposition, of the charged intermediates. On the other hand, the excited arenium ions from alkylation of toluene can be rapidly quenched via fast, exothermic proton transfer to other bases contained in the gas, including, in the first place, the xylenes used in the competition experiments.

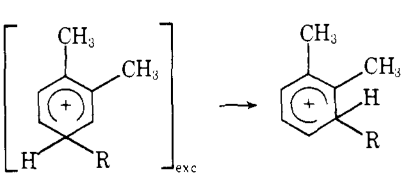
These considerations explain the decline of the apparent reactivity of the xylenes with respect to toluene, measured at the lowest pressures, and are consistent with the opposite influence exercised by a few mole percent of NH_3 in the gas. Indeed, ammonia ensures fast, exothermic deprotonation of *all* arenium ions, irrespective of the different strengths of their conjugate bases, thus leveling the lifetime and the extent of decomposition of the alkylated cations from both toluene and the xylenes.

Concerning isomerization, only isopropyl group shifts affect the composition of the products, while the intramolecular proton shifts that are likely to occur to a comparatively high rate within the excited arenium ions[24] are not directly relevant to the present discussion, and are not illustrated in Scheme I. No methyl group shifts could be detected in the isopropylation of the xylenes, irrespective of the isomer considered, even at the lowest pressures investigated.

The isomerization of the gaseous arenium ions excited by the exothermicity of eq 1 can involve either *intramolecular* proton and isopropyl group shifts (eq 4b) or *intermolecular* isopropyl group transfer (eq 4c), in analogy with the conclusions discussed in detail in earlier papers.[1-4] Nevertheless the data on the isopropylation of the xylenes reveal, in this connection, an interesting feature whose detection was prevented in previous investigations by the nature of the substrates employed, benzene and toluene,[1-3] or by the large steric requirements of the gaseous electrophile, the t-$C_4H_9^+$ cation.[2,4] The effect of decreasing the C_3H_8 pressure on the yields of 1,3-dimethyl-2-isopropylbenzene from m-xylene is *not* any smaller than for other products where the isopropyl substituent is not framed between two methyl groups, e.g. 1,2-dimethyl-4-isopropylbenzene from o-xylene. This observation appears hardly consistent with any isomerization pathway involving *exclusively* intramolecular 1,2 alkyl shifts. In fact, intramolecular migration of the isopropyl group within the first-formed arenium ion (I) necessarily requires the formation of the ipso-alkylated intermediate II (eq 5), singularly unfavorable on energetic grounds.[23] As a consequence, isomerization of I via intramolecular 1,2-alkyl shifts should be at any given pressure, and for comparable excitation levels much slower than, for instance, the process shown in eq 6. The data concerning isopropylation of o- and m-xylene show that this is not



(5)



(6)

Table III. Energetics and Substrate Selectivity of the Gas-Phase Isopropylation and *tert*-Butylation of Arenes

Reagent	$\Delta H_f°$, kcal mol^{-1}	$\Delta H°$, kcal mol^{-1}			Relative reactivity	
		Benzene[a]	Toluene[a]	Xylenes[b]	k_T/k_B	k_X/k_T
i-$C_3H_7^+$	192	−29	−36	−37 to −42	0.63–0.87[c]	0.9–1.0
t-$C_4H_9^+$	169	≥0	−10	−15 to −20	55[d]	1.9–2.2[e]

[a] From the data of ref 20. [b] Values depending on the specific isomer considered, the lowest exothermicity referring to para, the highest to the meta isomer. [c] Reference 8. [d] Reference 2. [e] The lower value refers to *m*-xylene, the higher one to *o*-xylene, while the para isomer does not react appreciably with t-$C_4H_9^+$.

the case, suggesting, at least for the latter substrate, intervention of some other isomerization mechanism in addition to intramolecular 1,2-isopropyl shifts. The lack of any detectable methyl group migrations in the alkylations of the xylenes, even at the lowest pressures, indicates that the relative rate of competing isomerization processes is quite sensitive, even for free arenium ions in the diluted gas state, to differences of the correspondent activation energies which represent only a modest fraction of the available excitation energy.[25]

Correlation of Reactivity and Selectivity of i-$C_3H_7^+$ and t-$C_4H_9^+$. Owing to the multiplicity of reaction channels in the gas-phase attack of i-$C_3H_7^+$ to arenes, and to the occurrence of secondary dealkylation and/or isomerization, using the experimental k ratios and isomeric composition of products as a basis for comparing reactivity and selectivity of gaseous alkyl cations is open to question. Nevertheless, restricting comparison to the alkylation processes and referring exclusively to the results obtained at the highest alkane and base pressure, i.e., under conditions where effective deactivation and deprotonation reduce, if not eliminate, secondary processes, a comparison of i-$C_3H_7^+$ and t-$C_4H_9^+$ behavior is possible and underlines several typical features of the gas-phase aromatic substitution.

The energetics and the *substrate* selectivity of the two gaseous reagents are illustrated in Table III. The isopropyl cation is characterized by the lack of appreciable selectivity, reacting with arenes at rates which depend on the number of free ring positions irrespective of their activation, i.e., in the order benzene > toluene > xylenes. On the other hand, t-$C_4H_9^+$, whose attack is less exothermic by ca. 20 kcal mol^{-1}, follows the normal reactivity order benzene < toluene < xylenes. The k_T/k_B ratio for t-$C_4H_9^+$ is unusually large for gas-phase aromatic substitutions and is therefore traced to the endothermic, or thermoneutral, character of the t-$C_4H_9^+$ condensation with C_6H_6.[2] The rate of *tert*-butylation is also higher, as expected, for *o*- and *m*-xylene than for toluene. The high "steric" substrate selectivity of the bulky t-$C_4H_9^+$ cation, which is totally unreactive toward *p*-xylene, should be noted.

Concerning *positional* selectivity, and referring to alkylation of toluene, t-$C_4H_9^+$ is characterized by a para:½ meta ratio of ca. 35, far exceeding the low (1.6) ratio of i-$C_3H_7^+$. It is worth mentioning, however, that in contrast with its lack of substrate discrimination, the isopropyl cation exhibits a measurable, if modest degree of positional selectivity, a typical feature of all charged electrophiles in the gas-phase aromatic substitutions.

From the present work, the *intrinsic* steric requirements of i-$C_3H_7^+$ in the diluted gas state, i.e., in the absence of solvation and ion pairing, appear barely detectable. In particular, in contrast with the lack of *tert*-butylation, the rate of isopropylation in the position 2 of *m*-xylene, ortho to both methyl groups, is only 0.8 times that in each of the two comparably activated positions 4. In the isopropylation of toluene, the ½ ortho:para ratio is unity, indicating that individual ortho and para positions react exactly at the same rate, again in sharp contrast with failure of t-$C_4H_9^+$ to attack ortho positions of toluene.

Comparison with Solution Chemistry Results. From a general standpoint, while the present results reveal no fundamental mechanistic diversity of the gas-phase ionic alkylation with respect to comparable processes occurring in solution, they suggest that the gas-phase reactivity of bona fide free and unsolvated alkyl cations represent a limit, more or less closely approached in solution by exceedingly strong and poorly solvated alkylating species.

This point is illustrated, in connection with substrate selectivity, by the gradual decline of the k_T/k_B ratio measured in isopropylation as the incipient ionic character of the reagent increases and its solvation decreases. Thus, a k_T/k_B value of 1.98 is observed with C_3H_6–$AlCl_3$ in nitromethane,[5] passing to 1.78 with C_3H_6–$GaCl_3$ in the same solvent,[5] to 1.76 with i-$C_3H_7NH_2$–HNO_2 in aromatics,[26] to 1.41 with i-C_3H_7Br–$AlCl_3$ in liquid SO_2,[5] and to 0.70 with i-C_3H_7F–BF_3 in *n*-hexane.[27] Furthermore, the combination of a measurable positional selectivity with the complete lack of substrate selectivity, mentioned above as a typical feature of gas-phase ionic alkylation, is also observed in the liquid-phase reactions with incipient, poorly solvated carbonium ions.

Finally, the steric requirements of isopropylation, measured in solution under conditions of decreasing bulk, and especially solvation of the reagent, tend to approach those observed in the gas phase. Thus, the ½ ortho:para ratio increases from 0.42 for the isopropylation of toluene with i-C_3H_7Br–$SnCl_4$ in tetramethylsulfone[5] to 0.62 with i-C_3H_7Br–$SnCl_4$ in nitromethane,[5] to 0.93 with i-C_3H_7Br–$TiCl_4$ in CS_2, which is very close to the 1.0 value measured in the gas phase.

The trend is confirmed by the scarce data on isopropylation of *m*-xylene, where substitution at the sterically hindered position 2, not observed with i-C_3H_7Br–$AlCl_3$ in nitromethane, increases to 15.8% with C_3H_6–$AlCl_3$ in the same solvent, to be compared with the 23–27% value measured in the gas phase.

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(16) For instance, in C_3H_8 (720 Torr), NH_3 (5 Torr), and O_2 (2 Torr), the yields

of isopropylated and *n*-propylated products are in the ratio of ca. 20:1 for toluene, and ca. 10:1 for the xylenes. Interestingly, the isomeric composition of products is similar, except for a somewhat higher extent of ortho substitution for *n*-propylation.

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(19) For instance, in the case of toluene, $\Delta H^\circ \simeq -9$ kcal mol^{-1} for protonation, and -14 kcal mol^{-1} for hydride ion abstraction. For the protonation of xylenes, $\Delta H^\circ \simeq -12$ kcal mol^{-1} (cf. ref 20).

(20) Values arrived at calculating ΔH_f° of I from the ΔH_f° values of dimethylisopropylbenzenes, deduced from D. R. Stull, E. F. Westrum Jr., and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds", Wiley, New York, N.Y., 1969, and using the gas-phase PA of xylenes, according to (a) R. Yamdagni and P. Kebarle, *J. Am. Chem. Soc.*, **98**, 1320 (1976), and (b) J. L. Devlin III, J. F. Wolf, R. W. Taft, and W. J. Hehre, *J. Am. Chem. Soc.*, **98**, 1990 (1976). Isopropylation of toluene is estimated to be less exothermic by at least 6 kcal mol^{-1} with respect to that of *m*-xylene.

(21) Alkylation of cumene by $i\text{-}C_3H_7^+$ has been observed by M. S. B. Munson and F. H. Field, *J. Am. Chem. Soc.*, **89**, 1047 (1967), in methane at 1 Torr.

(22) ΔH° for cumene protonation with CH_5^+ is ca. -53 kcal mol^{-1} and the excitation energy is of course distributed between the product, i.e., the arenium ion and CH_4.

(23) Theoretical and experimental data suggest that an additional methyl substituent increases appreciably the gas-phase proton affinity of an arene. In addition to ref 20b, *cf.* (a) S.-L. Chang and J. L. Franklin, *J. Am. Chem. Soc.*, **94**, 6630 (1972), and (b) J. L. Devlin III, J. F. Wolf, R. W. Taft, and W. J. Hehre, *J. Am. Chem. Soc.*, **98**, 1990 (1976). On the relative instability of ipso-alkylated ions, cf. D. Heidrich, M. Grimmer, and B. Sommer, *Tetrahedron*, **32**, 2027 (1976).

(24) The activation energy for 1,2-hydrogen shifts in arenium ions is comparatively low, e.g., only 10–11 kcal mol^{-1} in methylbenzenium ions, as measured in acidic solutions by C. MacLean and E. L. Mackor, *Discuss. Faraday Soc.*, **34**, 165 (1962). See also, for gaseous cations, F. H. Field in "Ion–Molecule Reactions", Vol. 1, J. L. Franklin, Ed., Butterworths, London, 1972, p 283.

(25) The free energy of activation for 1,2-methyl group shifts in methylbenzenium ions, measured in HF–SbF_5 systems by D. M. Brouwer, *Recl. Trav. Chim. Pays-Bas*, **87**, 611 (1968) ranges from 15 to 22 kcal mol^{-1}. Consequently, the difference between the activation energies for the migration of the methyl and, respectively, the isopropyl group is necessarily much lower than the excitation energy of the arenium ions from the alkylation process 1.

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Rearrangement and Equilibria of Ions Formed from Side-Chain Substituted β-Phenylethyl Chlorides under Stable Ion Conditions[1]

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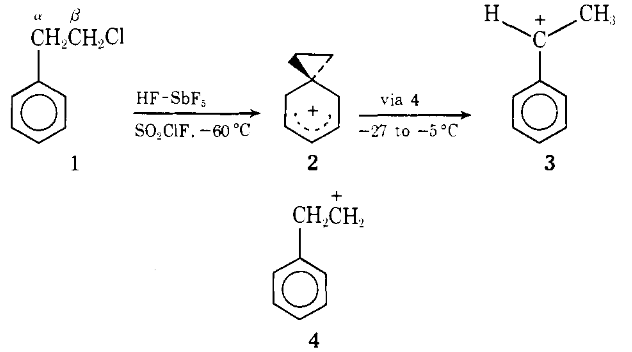
Abstract: Ionization of a series of β-arylethyl chlorides, substituted at C_α and/or C_β by methyl groups, with aryl = phenyl and *p*-methoxyphenyl, has been studied under stable ion conditions. The 1-aryl-2-chloropropanes and 3-aryl-2-chlorobutanes ionize exclusively to rearranged benzyl cations. Under these same conditions, neophyl chloride and 2-chloro-2-methyl-1-phenylpropane undergo competing ionization–rearrangement and protolytic cleavage reactions. The ethyl-*p*-methoxyphenyl carbenium ion (**9**) was found to be 8–10 kcal/mol more stable than the isomeric 1-*p*-methoxyphenyl-2-propyl cation (**10**) and this relatively small energy difference is regarded as strong support for π bridging in **10**. Benzylic and/or equilibrating cations are formed upon ionization of 3-aryl-2-chloro-2,3-dimethylbutanes. The relative stabilities are determined by the para substituent; methoxy exclusively forms the static benzyl cation, protonated methoxy (HO^+CH_3) the degenerate equilibrating β-phenylethyl cations, while the ion derived from the parent (phenyl) system is equilibrating with contributions from both benzyl and β-phenylethyl cations. There is no evidence for formation of σ-bridged ethylenearenium ions from any of the side-chain substituted β-phenylethyl systems studied.

Ionizations performed under "stable ion" conditions can potentially yield information unobtainable from normal solvolytic studies. Specifically, the exceedingly long ion lifetimes allow rearrangements which may be too slow to occur during solvolyses to be studied, thus experimental determination of energy differences between thermodynamically favored ions and their highly unstable transformation intermediates becomes feasible. Consider the recent study from our laboratories[3] where 2-chloroethylbenzene (**1**) was found to quantitatively ionize in fluoroantimonic acid (HF–SbF_5) to the ethylenebenzenium ion (**2**).[4] Subsequently, **2** was observed to rearrange to the methylphenylcarbenium ion (**3**) via the highly unstable intermediate **4**. This rearrangement has no solvolytic analogy;[5] the "hot" carbocations formed by deaminative acetolysis of 2-phenylethylamine, where 18% of products derive from **3**, do not rearrange via **2**.

The energy of activation for the transformation of **2** to **3** was found to be only 13.0 kcal/mol.[3] This value, which must closely approximate the energy difference between **2** and **4**, encouraged us to examine some derivatives of **1** in the anticipation that relative energies of substituted ions derived from **2** to **4** could be elucidated. Accordingly, we chose derivatives of **1** substituted by groups able to stabilize these ions by electron donation, namely methyl groups at C_α and/or C_β, and a *p*-methoxy group on the aromatic ring. Although the energy of all ions corresponding to **2**, **3**, and **4** should thus be lowered, energy differences should still be experimentally detectable.



Previous studies of alkylated 2-phenylethyl systems under stable ion conditions were hampered by the formation of only benzylic ions (cf., **3**) or complex equilibria involving ions of type **3**, **4**, and possibly **2**.[5d] In the work we present in this study,