for the different electrostatic adducts between $CH_3ClCH_3^+$ and M ($=E_r^M$) or X ($=E_r^X$).[10] Moreover, the empirical k_{obsd} is better expressed by the $k_c k_p/(k_b + k_p)$ term of Figure 1a, rather than by the $k_p K_{eq}$ term of Figure 1b, valid for thermally activated reactions involving a fast pre-equilibrium step. In this connection, the apparent k_M/k_X ratios and their temperature-dependence trend have no relationship with the relative height of the internal "chemical" activation energies $E^\ddagger_0$, since reflecting instead the interplay between the $|E^\ddagger_0 - E_r|$ and $|E_0 - E_r|$ energy gaps for any given electrostatic adduct, and their sensitivity to temperature.

This is reflected in empirical k_M/k_X ratios and the corresponding $\Delta E^\ddagger_0$ values, which are significantly lower than those measured under high-pressure conditions, where collision frequency is high, the reaction is thermally activated, and the temperature-dependence trend of k_{obsd} reflects the actual "chemical" activation energies $E^\ddagger_0$. This conclusion is corroborated by the k_M/k_X ratios, measured at 100 °C, as a function of the total pressure of the irradiated system (Figure 3). The monotonic increase of the apparent k_M/k_X values with the pressure from ca. 2.8, measured under low-pressure conditions (0.5–1.2 Torr),[7b] to a constant value of 9.8 above 300 Torr, is explained by the transition from an electrostatically activated to a thermally activated methylation reaction 1, with the latter regime prevailing above 300 Torr. Above this limit, the empirical quantity $\Delta E^\ddagger_0$ from the Arrhenius plot of Figure 2 represents a reasonably accurate estimate of the actual $E^\ddagger_0(X) - E^\ddagger_0(M)$ difference. Below this limit, this correspondence is not any longer warranted, raising the phenomenological $\Delta E^\ddagger_0$ quantity from the interplay of several kinetic factors, linked not only to the specific potential energy profile governing the reaction under those conditions (curve a vs curve b of Figure 1a,b) but also to the hardly predictable residual internal energy distribution E_r of the ionic species involved.

In conclusion, the results of this study underline the kinetic interest attached to the exploration of the high-pressure limit of ion–molecule reactions and of its dependence upon the reaction temperature, in view of the drastic transition from electrostatic to thermal activation for ionic processes in the gas phase. Attainment of thermal activation in gas-phase ion–molecule reactions serves one of the major purposes of this field, namely to provide generalized and simplified models for related ionic processes in condensed media, which after all are themselves driven by thermal activation mechanisms.

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Registry No. $CH_3ClCH_3^+$, 24400-15-5; CH_3Cl, 74-87-3; mesitylene, 108-67-8; *p*-xylene, 106-42-3.

Gas-Phase Acid-Induced Nucleophilic Displacement Reactions. 7.[1] Structural and Stereochemical Evidence for the Existence and the Relative Stability of Alkylenebenzenium Ions in the Gas Phase

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Abstract: A comprehensive investigation on the existence and the relative stability of gaseous 2,3-butylene- and 1,2-propylenebenzenium ions was carried out by establishing the structural features and the stereochemistry of acid-induced displacement by CH_3OH on isomeric 3-phenylbutyl-2 onium and β-phenylpropyl onium intermediates. The latter were obtained in the gas phase from the reaction of radiolytically formed GA^+ ($GA^+ = D_3^+$, $C_nH_5^+$ (n = 1, 2), i-$C_3H_7^+$, and $CH_3FCH_3^+$) acids with isomeric 3-phenyl-2-chlorobutanes and β-phenyl-Y-propanes (Y = Cl, OH). The analysis of the isomeric distribution of the neutral substitution products allows the establishment of extensive phenyl-group participation in the displacement process, occurring in competition with methyl and hydrogen 1,2-transfers. The participating ability of a phenyl moiety adjacent to the substitution center is found to depend essentially upon the configuration of the precursor and to be related to its gas-phase nucleophilicity. The occurrence of relatively stable cyclic alkylenebenzenium ions as static intermediates in these displacement reactions is suggested by the particular isomeric and stereoisomeric distribution of the products and by its comparison with that obtained from open-chain isomeric ions. The results obtained from the present gas-phase experiments are discussed in the light of those from related gas-phase and solution studies.

The involvement of an aromatic ring leading to a bridged benzenium ion in the solvolysis of β-arylalkyl systems has been a matter of intense investigation and lively debate in the last decades.[3] The original proposal by Cram[4] that the intermediates in these reactions were π-bridged alkylenebenzenium ions **9** (eq 1) was criticized by Brown,[5] who suggested that the experimental data could alternatively be rationalized in terms of weakly π-bridged, rapidly equilibrating ions. Further solvolytic studies led to the conclusion that a continuous spectrum of species exists, from open to completely bridged ions, depending upon solvent and substitution in the ion.[6] Environmental factors intervene as well in the sensitive balance between aryl-assisted and solvent-assisted

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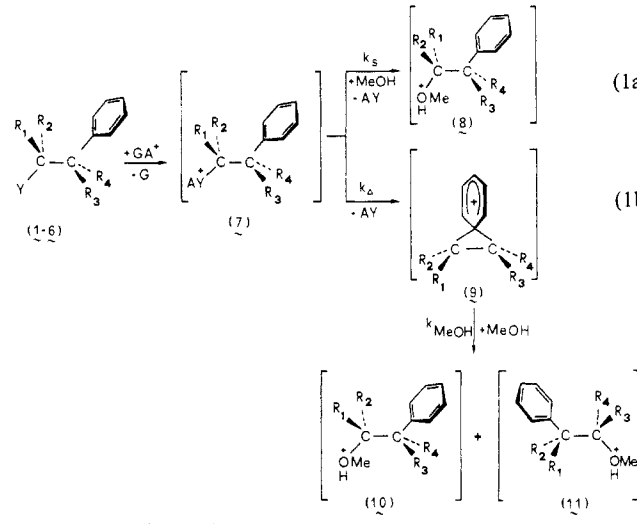
pathways, typical of many of the β-arylalkyl solvolyses.[7]

The precise characterization of the σ- and π-bridged alkylenebenzenium transients and of their role in anchimerically assisted β-arylalkyl solvolysis was obtained only after the introduction of low-nucleophilicity solvent systems, such as the superacidic media.[8] The exceedingly long ion lifetimes attainable under such conditions allow rearrangements which may be too slow to be studied under normal solvolytic conditions, thus experimental determination of energy differences between thermodynamically favored ions and their highly unstable transformation intermediates becomes feasible.[9] However, in spite of their low nucleophilic reactivity, both superacidic solvent and counterion do nevertheless physically interact with the long-lived ionic species present so as to alter appreciably their relative stability levels.

Theoretical evaluation of the geometry and the relative energetics of the bridged and open structures of gaseous β-arylalkyl cations has been restricted to the unsubstituted β-phenylethyl system.[10] Unfortunately, even in this simple case, different theoretical approaches led to contradictory results.

From the above considerations, a detailed investigation on the existence and the stability of alkylenearenium ions and their conceivable isomers in the gas phase appears of special interest, because it would allow evaluation of the intrinsic features of these species under conditions excluding the interference of the solvent and the counterion effects, which invariably complicate condensed-phase studies. As a matter of fact, gas-phase studies have been carried out to ascertain whether the simplest member of the alkylenearenium ion family, namely the ethylenebenzenium ion, were an actual minimum on the $C_8H_9^+$ potential energy surface.[11] The experimental technique employed was invariably the collisional activation (CA) mass spectrometry of the $C_8H_9^+$ fragments obtained by electron impact on a variety of β-phenylethyl precursors. Although, in some cases, the relevant CA spectral data of $C_8H_9^+$ ions could not exclude intervention of a transient ethylenebenzenium structure, nevertheless these experiments provided no conclusive evidence about its general occurrence as a stable intermediate, since the spectral data appear to be profoundly affected by the ionizing electron energy and by the specific nature of the β-phenylethyl precursor.

These considerations, and the relevance of the problem, have prompted us to exploit a different experimental approach for establishing the occurrence of the alkylenearenium ions **9** (eq 1) as well as other conceivable bridged isomers in the gas phase and for evaluating any structural and environmental effects on their relative stability. In the previous papers of this series,[12] the stereochemistry of gas-phase acid-induced bimolecular nucleophilic displacements at saturated carbon and its dependence on the presence of nucleophilic groups adjacent to the reaction center have been investigated by a gas-phase radiolytic technique[13] that, unlike ordinary mass spectrometric methods, is specifically designed to allow the actual isolation and structural identification of the neutral reaction products. The high stereospecificity of these processes suggested application of such a technique for a quantitative evaluation of the extent of phenyl-group participation (eq 1) on the reasonable presumption that neighboring-group participation gives net retention of configuration resulting from two inversions as in eq 1b. Thus, once the mechanistic details of all



$GA^+ = D_3^+, CH_5^+, C_2H_5^+, CH_3FCH_3^+, i\text{-}C_3H_7^+$

	Y	R_1	R_2	R_3	R_4	config
1	Cl	H	CH_3	CH_3	H	erythro
2	Cl	H	CH_3	H	CH_3	threo
3	Cl	H	CH_3	H	H	
4	Cl	H	H	CH_3	H	
5	OH	H	CH_3	H	H	
6	OH	H	H	CH_3	H	

the processes following attack of radiolytically generated gaseous acids GA^+ on the nucleophilic sites of the β-arylalkyl substrates **1–6** are thoroughly examined, the isomeric and stereoisomeric distribution of the neutral end products can be easily linked to the extent of reaction proceeding via a bridged alkylenearenium intermediate **9** and, therefore, to the extent of adjacent aryl-group participation to the nucleophilic displacement process.

In this paper, this approach is applied to ascertain the occurrence, the stability, and the isomerization of 1,2-propylene- and 2,3-butylenebenzenium ion **9** in the gas phase, by analysis of the structural and stereochemical features accompanying nucleophilic displacement on the corresponding isomeric β-phenylpropyl and 3-phenylbutyl-2 onium ions **7** of eq 1. A comparative analysis of the structural features accompanying decomposition of the corresponding β-phenylethyl onium ions (**7**: R_1–R_4 = H) under gas-phase and solvolytic conditions is left to the following paper.

Experimental Section

Materials. Deuterium, methane, propane, methyl fluoride, oxygen, and trimethylamine were high-purity gases from Matheson Co., used without further purification. Methanol and other compounds, used as substrates or additives in the radiolytic experiments or as standards in chromatographic analyses, were research-grade chemicals from Fluka A.G. and Aldrich-Chemie GmbH. Those compounds, which are not available from commercial sources, such as the substrates **1–5**, and their methoxy derivatives, 2-phenyl-2-methoxybutane, 2-phenyl-2-methoxypropane, 1-phenyl-1-methoxypropane, 1-phenyl-1-methoxy-2-methylpropane, and isomeric phenylbutenes, were synthesized by conventional procedures and their identity checked by mass spectrometric and NMR analysis. Assignment of the absolute configuration of *erythro*-**1** and *threo*-**2** 3-phenyl-2-chlorobutanes was made possible by the solvent polarity effects upon the corresponding J_{HH} coupling constants from their

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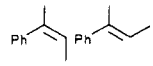
Table I. Product Yields from the Gas-Phase Attack of GA^+ Acids on 3-Phenyl-2-chlorobutanes

system composition[a]			relative distribution of products (%)											total absolute yield	
substrate (Torr)	bulk gas (Torr)	GA^+	CH_3OH (Torr)	 erythro	threo	ret/inv ratio			PhCHO			un-knowns	$10^2G_{(M)}$[b]	%[c]
1 (0.2)	D_2 (750)	D_3^+	0.6	56	n.d.[d]	∞	6	6	3	11	10	n.d.	8	27.8	9
1 (0.3)	CH_4 (700)	$C_nH_5^+$	1.0	85	0.5	160	7	4	0.3	2	n.d.	n.d.	2	60.5	22
1 (0.5)	CH_4 (700)	$C_nH_5^+$	1.6[e]	17	n.d.	∞	0.3	0.5	n.d.	48	18	2	15	10.7	4
1 (0.3)	C_3H_8 (700)	$i\text{-}C_3H_7^+$	1.0	84	n.d.	∞	12	3	n.d.	n.d.	n.d.	n.d.	2	11.6	4
1 (0.5)	C_3H_8 (730)	$i\text{-}C_3H_7^+$	1.0[e]	20	n.d.	∞	0.6	0.6	n.d.	53	16	n.d.	10	16.0	5
1 (0.3)	CH_3F (700)	$CH_3F\text{-}CH_3^+$	0.9	79	n.d.	∞	2	5	2	1	n.d.	n.d.	11	16.0	
2 (0.2)	D_2 (700)	D_3^+	0.8	3	19	6.2	6	10	n.d.	24	14	n.d.	23	32.3	11
2 (0.3)	CH_4 (700)	$C_nH_5^+$	0.4	3	46	14.2	5	23	3	5	8	1	6	59.1	21
2 (0.4)	CH_4 (700)	$C_nH_5^+$	1.5[e]	0.6	7	10.9	n.d.	3	1	41	11	4	32	11.5	4
2 (0.3)	CH_4 (680)	$C_nH_5^+$	1.0	4	44	11.0	12	30	3	3	0.4	1	3	74.4	27
2 (0.2)	CH_4 (160)	$C_nH_5^+$	1.0	3	49	14.0	n.d.	26	5	9	5	n.d.	2	96.3	34
2 (0.3)	CH_4 (700)	$C_nH_5^+$	3.8	2	10	5.0	20	22	7	26	4	n.d.	9	9.6	3
2 (0.3)	C_3H_8 (750)	$i\text{-}C_3H_7^+$	1.1	1	22	23.0	32	17	6	11	2	n.d.	9	9.6	3
2 (0.4)	CH_3F (750)	$CH_3F\text{-}CH_3^+$	1.2	1	37	48.0	0.3	33	2	1	3	n.d.	23	9.4	

[a] O_2: 4 Torr. Radiation dose: 3×10^4 Gy (dose rate: 1×10^4 Gy h^{-1}). [b] $G_{(M)}$ as the number of molecules M produced per 100 eV of absorbed energy. Standard deviation of data, ca. 10%. [c] Total absolute yields estimated by using the $G_{(GA^+)}$ values available from the literature (ref 15). No value for $G_{(CH_3FCH_3^+)}$ is available. [d] n.d. = not detectable ($G_{(M)} \leq 1 \times 10^{-4}$). [e] 4 Torr of NMe_3 added to the gaseous mixture.

^1H NMR spectra. The same approach could not be used to establish the absolute configuration of the erythro and threo forms of both 3-phenylbutan-2-ols and their methyl ethers, since no such distinct dependence of the relevant J_{HH} coupling constants with solvent polarity could be obtained. In these cases, assignment of the absolute configuration was obtained by resorting to an indirect chemical derivatization procedure.[14] Isomeric 3-phenylbutan-2-ols were converted into their chlorinated forms, *erythro*-**1** and *threo*-**2**, by treatment with $SOCl_2$. Since the $SOCl_2$ chlorination of alcohols proceeds with retention of configuration, NMR discrimination of **1** and **2** allows for immediate assignment of the absolute configuration of their individual alcoholic precursors. Once the absolute configuration of 3-phenylbutan-2-ols is established, that of their methyl ethers can be easily determined by using derivatization procedures with well-established stereochemistry. Thus, *erythro*-3-phenylbutan-2-ol was converted into its *erythro*-*p*-toluensulfonate and this into the threo form of 3-phenyl-2-methoxybutane by treatment with CH_3ONa/CH_3OH. The same stereoisomer of 3-phenyl-2-methoxybutane was obtained by converting *threo*-3-phenylbutan-2-ol into its threo sodium salt and by treating the latter with CH_3I. A similar chemical procedure was used to characterize the erythro stereoisomer of 3-phenyl-2-methoxybutane.

Before irradiation, the starting substrates **1**–**6** were repeatedly purified by preparative gas chromatography on the following columns: i, 20% DC-200 + 6% Bentone 34 on 60–80 mesh Chromosorb W-AW, 2 m; ii, 5% diisodecylphthalate + 5% Bentone 34 on 60–80 mesh Chromosorb W-AW, 4 m. Their purity was checked by GLC, using flame ionization detection (FID).

Procedure. The gaseous mixtures were prepared by conventional techniques, using a greaseless vacuum line. The reagents and the additives were introduced into carefully outgassed 250-mL Pyrex bulbs, each equipped with a break-seal tip. The bulbs were filled with the required amount of the appropriate bulk gas (D_2, CH_4, C_3H_8, or CH_3F), cooled to the liquid-nitrogen temperature, and sealed off. The irradiations were carried out at a temperature of 37.5 °C in a 220 Gammacell from Nuclear Canada Ltd., at a dose rate of 1×10^4 Gy h^{-1} to a total dose of 3×10^4 Gy, as determined by a neopentane dosimeter.

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Product Analysis. The analysis of the irradiation products was performed by injecting measured portions of the homogeneous reaction mixture into a Perkin-Elmer Model Sigma 1 gas chromatograph, equipped with a FID detector. In order to prevent selective losses of the reaction products by adsorption on the glass of the reaction bulb (and to obtain reproducible and meaningful reaction yields), the analysis was repeated after careful washing of the bulb walls with 0.3-mL aliquots of freshly purified ethyl acetate. Satisfactory agreement between the results of the gaseous mixture and the ethyl acetate solution analysis was found in all runs. The products were identified by comparison of their retention volumes with those of authentic standard compounds. Appropriate calibration curves for the detector response were employed to measure the yields of each product. The identity of the products was further confirmed by GLC–mass spectrometry, using a Hewlett-Packard HP 5982 A mass spectrometer.

The following columns were employed for the GLC analyses: (i) a 2 m long, 2 mm i.d. glass column, packed with 10% SP 2100 + 6% Bentone 38 on 100–120 mesh Chromosorb W-AW, operated at 100 °C; (ii) a 2 m long, 3.2 mm i.d. stainless steel column, packed with 5% SP 1200 + 5% Bentone 34 on 100–120 mesh Supelcoport support, operated at 100 °C.

Results

Table I reports the absolute and relative yields of the products formed from diastereoisomeric 3-phenyl-2-chlorobutanes **1** and **2** undergoing gas-phase attack from the radiolytically produced GA^+ acids, in the presence of CH_3OH as the nucleophile and NMe_3 as a base, when required. The data concerning the irradiation of the gaseous mixtures containing isomeric β-phenylchloropropanes **3** and **4** and β-phenylpropanols **5** and **6** are listed in Table II. Both tables give $G_{(M)}$ values, expressed as the number of molecules of the product M formed per 100 eV of energy absorbed by the gaseous mixture at a total dose of 3×10^4 Gy (dose rate: 1×10^4 Gy h^{-1}). The reported figures represent the mean $G_{(M)}$ values obtained from several separate irradiations, carried out under the same experimental conditions, whose reproducibility is expressed by the standard deviations quoted.

Table II. Product Yields from the Gas-Phase Attack of GA^+ Acids on β-Phenylchloropropanes and β-Phenylpropanols

system composition[a]			relative distribution of products (%)											total absolute yield	
substrate (Torr)	bulk gas (Torr)	GA^+	CH_3OH (Torr)	MeO Ph	MeO Ph	(β/α) ratio	OMe Ph	PhCHO	OMe Ph	Ph	Ph	Ph	Ph	$10^2G_{(M)}$[b]	%[c]
3 (0.5)	D_2 (750)	D_3^+	2.5	26	41	0.6	n.d.[d]	27	n.d.	n.d.	n.d.	3	2	120.7	40
3 (0.6)	CH_4 (700)	$C_nH_5^+$	0.7	55	30	1.8	n.d.	13	0.2	0.6	n.d.	n.d.	1	143.0	51
3 (0.2)	CH_4 (180)	$C_nH_5^+$	0.7	46	28	1.6	n.d.	21	n.d.	1	n.d.	2	2	156.0	56
3 (0.5)	CH_4 (720)	$C_nH_5^+$	1.9[e]	20	6	3.1	n.d.	12	n.d.	20	n.d.	5	38	55.8	20
3 (0.6)	CH_4 (750)	$C_nH_5^+$	2.1	53	32	1.6	n.d.	15	n.d.	0.4	n.d.	n.d.	n.d.	108.4	39
3 (0.6)	CH_4 (730)	$C_nH_5^+$	5.2	54	25	2.1	n.d.	21	n.d.	n.d.	n.d.	n.d.	n.d.	63.0	22
3 (0.5)	C_3H_8 (700)	$i\text{-}C_3H_7^+$	2.0	54	5	10.9	n.d.	38	n.d.	2	n.d.	1	n.d.	23.9	8
3 (0.6)	CH_3F (700)	$CH_3F\text{-}CH_3^+$	1.9	58	30	1.9	n.d.	10	n.d.	0.6	n.d.	n.d.	1	27.5	
4 (0.5)	D_2 (750)	D_3^+	2.5	40	21	1.9	2	n.d.	n.d.	n.d.	37	n.d.	n.d.	29.9	10
4 (0.5)	CH_4 (700)	$C_nH_5^+$	0.5	76	16	4.8	n.d.	6	1	n.d.	0.5	n.d.	1	101.8	36
4 (0.2)	CH_4 (155)	$C_nH_5^+$	0.8	51	17	3.1	6	8	2	4	13	n.d.	n.d.	84.4	30
4 (0.5)	CH_4 (700)	$C_nH_5^+$	1.9[e]	29	3	10.0	n.d.	3	n.d.	24	31	1	9	29.3	10
4 (0.5)	CH_4 (750)	$C_nH_5^+$	2.0	72	14	5.3	5	5	n.d.	0.6	3	n.d.	n.d.	65.3	23
4 (0.6)	CH_4 (720)	$C_nH_5^+$	4.8	76	15	5.2	n.d.	5	3	n.d.	n.d.	1	n.d.	46.0	16
4 (0.5)	C_3H_8 (690)	$i\text{-}C_3H_7^+$	2.4	78	1	78.4	1	6	1	11	1	n.d.	n.d.	15.3	5
4 (0.5)	CH_3F (700)	$CH_3F\text{-}CH_3^+$	2.1	70	2	27.9	n.d.	23	n.d.	n.d.	4	n.d.	n.d.	27.2	
5 (0.3)	CH_4 (700)	$C_nH_5^+$	2.1	36	39	0.9	n.d.	25	n.d.	n.d.	n.d.	n.d.	n.d.	67.6	24
6 (0.3)	CH_4 (700)	$C_nH_5^+$	2.0	58	26	2.2	7	10	n.d.	n.d.	n.d.	n.d.	n.d.	12.5	4

[a] O_2: 4 Torr. Radiation dose: 3×10^4 Gy (dose rate: 1×10^4 Gy h^{-1}). [b] $G_{(M)}$ as the number of molecules M produced per 100 eV of absorbed energy. Standard deviation of data, ca. 10%. [c] Total absolute yields estimated by using the $G_{(GA^+)}$ values available from the literature (ref 15). No value for $G_{(CH_3FCH_3^+)}$ is available. [d] n.d. = not detectable ($G_{(M)} \leq 1 \times 10^{-4}$). [e] 4 Torr of NMe_3 added to the gaseous mixture.

Serial irradiations carried out at doses ranging from 1×10^4 to 1×10^5 Gy showed an essential constancy of both the absolute $G_{(M)}$ values and the relative distribution of the products. The tables summarize also the total absolute yields of the irradiation products, expressed by the percent ratio of their $G_{(M)}$ values to the $G_{(GA^+)}$ of their gaseous acid precursors available from literature.[15] The results of these calculations, while largely approximate,[16] represent nevertheless an estimate of the relative efficiency order of the reaction channels, leading to the corresponding products.

The ionic character of these reactions is demonstrated by the sharp decrease of the overall yields (from ca. 50% to over 80%) caused by addition to the gaseous mixture of 0.6 mol % of NMe_3, an efficient Brønsted acid interceptor. Additional evidence is provided by the significant decrease of the yields caused by an increase of the relative concentration of the nucleophile CH_3OH, which efficiently competes with the substrates **1**–**6** for the GA^+ acids.

Inspection of Table I reveals that the substitution products from stereoisomeric 3-phenyl-2-chlorobutanes **1** and **2** are mostly 3-phenyl-2-methoxy derivatives, together with minor amounts of 2-phenyl-2-methoxybutane and 1-phenyl-1-methoxy-2-methylpropane, accompanied by variable yields of elimination (isomeric phenylbutenes) and oxidation products (benzaldehyde). In the CH_3F, C_3H_8, and CH_4 runs, appreciable yields of ring-alkylated products are formed as well. Since their formation is not directly relevant to the present study, these products do not appear in Table I and will not be discussed further.

Concerning the relative distribution of the products, it should be noted that *erythro*-**1** gives rise to substitution derivatives, whose yield is invariably *higher* than that of the corresponding substitution products from the threo isomer **2**. In general, the relative yields of the substitution products exceed those of isomeric phenylbutenes, except when NMe_3 is present in the gaseous systems.

Among the substitution products, it is possible to discriminate those whose formation apparently does not involve side-chain structural reorganization, namely the isomeric 3-phenyl-2-methoxybutanes, from those, such as 2-phenyl-2-methoxybutane and 1-phenyl-1-methoxy-2-methylpropane, whose formation sequence involves necessarily a side-chain isomerization step. In general, the relative yields of these latter substitution products are found to depend on many factors, including the nature of the bulk component of the irradiated gas and the configuration of the starting substrate.

Direct information on the stereochemistry of the substitution processes is obtained from the (ret/inv) values of Table I, indicating the retained versus inverted 3-phenyl-2-methoxybutane yield ratios. Their inspection reveals that both **1** and **2** give predominantly their retained substituted derivative (83–100%) and that the stereoselectivity of the process is more pronounced for the erythro isomer **1** ((ret/inv) ≥ ca 160) than for the threo isomer **2** ($5 <$ (ret/inv) < 48). While the stereospecificity of the substitution process on the erythro isomer **1** is found to be rather

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(16) There are considerable uncertainties as to the radiation dose actually absorbed by the gas and to the pressure dependence of the known $G_{(GA^+)}$ values (ref 15). In addition, there are several reaction channels available for GA^+ acids following their attack on the substrates **1**–**6** that represent only one of the nucleophiles present in the system.

independent upon both the nature of the GA^+ acid and the concentration of the CH_3OH nucleophile, that of the threo isomer **2** appears to be influenced appreciably by the nature of the GA^+ acid, the concentration of CH_3OH, and, to a lesser extent, the total pressure of the system. In general, the (ret/inv) ratio from **2** increases in passing from the D_2 systems (=6.2) to the CH_4 (=5–14), C_3H_8 (=23), and CH_3F samples (=48). In addition, the substitution stereospecificity appears to increase by decreasing the CH_3OH concentration and the total pressure of the irradiated sample.

No evident effect of the pressure of the base NMe_3 upon the stereospecificity of the substitution process is observable.

A product pattern, analogous to that encountered in the gaseous systems with **1** and **2** (Table I), arises from the radiolytic samples containing **3–6**, as the starting substrates (Table II). Again, major amounts of substitution products are recovered from the mixtures, together with less abundant elimination (phenylpropenes), fragmentation ((α-methoxyethyl)benzene), and oxidation derivatives (benzaldehyde). In the CH_3F, C_3H_8, and CH_4 systems, these products are accompanied by appreciable amounts of ring-alkylation derivatives. In the absence of NMe_3, the overall relative substitution yield (60–90%) exceeds that of the accompanying secondary products (10–40%) and appears rather independent upon the nature of the starting compounds. On the contrary, the total absolute yield of the substitution products is strongly affected by the nature of the leaving group Y (21–33% for Y = Cl (**3** and **4**); 4–18% for Y = OH (**5** and **6**) in CH_4 systems) and to a lesser extent by the structure of the starting substrate.

In analogy with the isomeric distribution of the substitution products from 3-phenyl-2-chlorobutanes **1** and **2**, it is possible to discern two different categories of substituted products from substrates **3–6**, namely those, such as 1-phenyl-2-methoxypropane, where the phenyl substituent is adjacent to the functional group as in the starting substrate and those, such as 1-phenyl-1-methoxypropane and 2-phenyl-2-methoxypropane, where this relationship is lost by side-chain structural rearrangements. In general, the relative abundance of these isomerized substitution products depends upon the nature of the bulk component of the gaseous mixture and on the nature and the structure of the starting compounds, increasing from **3–4** to **5–6** and, within the same series, from the 1-phenyl-Y-propanes **4–6** to their isomers **3–5**. An overall view of this multifaceted correlation is provided by the β/α values of Table II, which represent the ratios between the yield of the 1-phenyl-2-methoxypropane (β) and that of the 1-phenyl-1-methoxypropane (α), i.e., the predominant isomerized substitution product.

Finally, while the expected methoxy derivative of 1-phenyl-2-Y-propanes **3** and **5**, namely the 1-phenyl-2-methoxypropane (β), is invariably recovered in high yields among the products from the corresponding precursors, no evidence was obtained for the formation of 2-phenyl-1-methoxypropane from 2-phenyl-1-Y-propane precursors **4** and **6**, in spite of a specific search.

Discussion

Nature of the Substitution Process. As outlined in previous papers,[12] the conditions typical of the present experiments, in particular the low concentrations of the substrate (ca. 0.1%) diluted with a large excess of the bulk gas (D_2, CH_4, C_3H_8, or CH_3F), excludes direct radiolysis of the starting compounds **1–6** as a significant route to the products of Tables I and II. The presence of an efficient thermal radical scavenger, such as oxygen, in the gaseous samples strongly inhibits possible free-radical pathways in favor of the competing ionic reaction pattern, whose role is testified by the marked effect of ion trappers, such as NMe_3 and CH_3OH, on their overall extent.

The role of the stable GA^+ ions from γ-radiolysis of each individual bulk component of the mixture[13,15,17] as gaseous Brønsted (D_3^+, CH_5^+, $C_2H_5^+$, and i-$C_3H_7^+$) and Lewis acids ($C_2H_5^+$, i-$C_3H_7^+$, and $CH_3FCH_3^+$) toward compounds containing n-type centers has been amply demonstrated by ion cyclotron resonance (ICR)[18] and chemical ionization (CIMS)[19] mass spectrometry and by independent radiolytic studies.[12,17,20] The D_3^+ ions ($\Delta H°_f$ = 264 kcal mol^{-1}),[21] as well as CH_5^+ ($\Delta H°_f$ = 216 kcal mol^{-1}),[21] are pure Brønsted acids, attacking all the basic sites of the selected substrates **1–6**, including their n-type center.[22] The $C_2H_5^+$ ions ($\Delta H°_f$ = 216 kcal mol^{-1}),[21] formed together with CH_5^+ in the γ-radiolysis of CH_4, as well as the i-$C_3H_7^+$ ions ($\Delta H°_f$ = 191 kcal mol^{-1})[21] from C_3H_8, are milder Brønsted acids that, in addition to protonation, may add to the selected substrates **1–6**, acting as typical Lewis acids.[23] On the other hand, the $CH_3FCH_3^+$ ion ($\Delta H°_f$ = 146 kcal mol^{-1})[24] from γ-radiolysis of CH_3F behaves exclusively as a pure gaseous Lewis acid, methylating the nucleophilic centers of the substrates **1–6** via processes that are substantially less exothermic than the corresponding protonation by D_3^+, CH_5^+, and $C_2H_5^+$.

The radiolytic GA^+ (D_3^+, $C_nH_5^+$ (n = 1, 2), i-$C_3H_7^+$, and $CH_3FCH_3^+$) acids, thermalized by many unreactive collisions with their parent molecules (D_2, CH_4, C_3H_8, and CH_3F, respectively), eventually attack the substrates **1–6**, present in low concentrations (ca. 0.1 mol %) in the gaseous mixture. Two basic sites are invariably present in the selected substrates, namely the n-type substituent and the phenyl π-ring, which may compete for the gaseous GA^+ acid. To the purposes of the present work, electrophilic GA^+ attack at the π-system of the substrate represents a parasitic reaction channel, whose extent is even not measurable when GA^+ acts as a Brønsted acid. Occurrence of such undesired parasitic processes explains in part the difference between the observed total absolute yields of products (3–56%) and the theoretical one (100%), expected for exclusive attack of GA^+ at the n-type group of the substrate. Another aspect that should be taken into account in explaining such difference is that the starting substrate is only one of the nucleophiles present or formed in the radiolytic mixture. For instance, methanol is invariably present in all systems and efficiently competes with the substrate by reacting with the GA^+ acid at a rate close to the collision limit (eq 2).[25] The oxonium derivative **12** formed is apparently unable to react further with the substrate (**1–6**) to give substitution

$$GA^+ + CH_3OH \xrightarrow[-G]{} \left[CH_3\overset{+}{O}(H)A \right] \xrightarrow[-AY]{1-6} \textbf{(8) or (10–11)} \quad (2)$$

(12)

products, as demonstrated by the evident influence of the nature of GA^+ on the product distribution and the significant decrease of the substituted product yields of Tables I and II by addition of moderate concentrations of methanol. Such effects should in fact be negligible, if the second step of sequence 2 were operative in the irradiated systems. In conclusion, the above considerations, while accounting for the moderate absolute yields of products listed in Tables I and II, are consistent with the previous view[12,18] that

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Table III. Thermochemical Data (kcal mol^{-1})

neutral molecule M	P.A.[a]	M.C.A.[b]	$\Delta H°_f(MH^+)$	$\Delta H°_f(MMe^+)$	$\Delta H°_f(MEt^+)$	$\Delta H°_f(MiPr^+)$
H_2	101		264			
CH_4	132		216			
C_2H_4	163		216			
$CH_3CH{=}CH_2$	180		191			
CH_3F		59[c]		146[c]		
CH_3OH	182	83[d]	136	130[d]	113[d]	ca. 104[e]
i-C_3H_7OH	191	ca. 92[e]	109	ca. 104[e]	ca. 96[e]	85[d]
n-C_3H_7OH	191	ca. 96[e]	114	ca. 108[e]	ca. 103[e]	ca. 91[e]
i-C_3H_7Cl	ca. 170[e]	ca. 72[e]	ca. 162[e]	ca. 154[e]	ca. 144[e]	ca. 133[e]
n-C_3H_7Cl	ca. 170[e]	ca. 72[e]	ca. 166[e]	ca. 158[e]	ca. 153[e]	ca. 141[e]
2-C_4H_9Cl	ca. 171[e]	ca. 73[e]	ca. 157[e]	ca. 149[e]	ca. 140[e]	ca. 128[e]

[a] P.A. = proton affinity; ref 21 and 25. [b] M.C.A. = methyl cation affinity, as defined by Holtz et al. [Holtz, D.; Beauchamp, J. L.; Woodgate, S. D. *J. Am. Chem. Soc.* **1970**, *92*, 7484]. [c] Reference 24. [d] Values calculated from the PAs of the corresponding ethers (ref 21). The heats of formation of the neutrals were taken from the following: Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; Wiley: New York, 1969. [e] Approximate values calculated by using the group additivity rules (Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976).

the substituted products recovered in the present systems arise from the general nucleophilic displacement sequence 1.

Accordingly, the first step of sequence 1 involves the attack of GA^+ at the Y substituent of the substrate. In the absence of specific thermochemical data concerning the heats of formation of the ensuing Y-protonated or -alkylated intermediates **7**, approximate estimates of the enthalpy changes in this first step can be obtained by using the proton and alkyl cation affinities of model compounds (2-chlorobutanes, isomeric chloropropanes and chloropropanols) in the assumption that the β-phenyl substituent exerts the same effect on the neutral precursors **1–6** and on their ionic derivatives **7** (Table III). In this view, it can be concluded that D_3^+ and $C_nH_5^+$ (n = 1, 2) acids attack exothermically all the selected substrates. Protonation enthalpies of **1–4** by D_3^+ range around −70 kcal mol^{-1}.

The $C_nH_5^+$ ions exothermically protonate ($-\Delta H°$ = ca. 38 kcal mol^{-1} (n = 1); $-\Delta H°$ = ca. 7 kcal mol^{-1} (n = 2)) and ethylate ($-\Delta H°$ = 32–33 kcal mol^{-1} (n = 2)) all the selected substrates. Addition of i-$C_3H_7^+$ ions to the n-center of substrates **1–4** is invariably exothermic ($-\Delta H°$ = 19–24 kcal mol^{-1}), whereas proton transfer is endothermic ($\Delta H°$ = ca. 10 kcal mol^{-1}). The methyl-group transfer from $CH_3FCH_3^+$ ion to the n-center of **1–4** is calculated to release ca. 13–14 kcal mol^{-1}. In general, for each individual substrate, the reaction exothermicity increases in the following order: $CH_3FCH_3^+ < i$-$C_3H_7^+ < C_2H_5^+$ (addition) and $C_2H_5^+ < CH_5^+ < D_3^+$ (proton transfer). For each individual GA^+ species the exothermicity increases in the following order: **3**, **4** < **1**, **2** < **5**, **6**.

As discussed in detail in related studies,[12] the thermalized GA^+ acids attack all the nucleophilic centers of substrates **1–6** producing inter alia their protonated and alkylated onium derivatives **7** (eq 1), excited by the exothermicity of their formation processes, which may evolve through a complex reaction pattern, involving isomerization, unimolecular fragmentation, elimination processes, and backside nucleophilic displacements of their leaving group AY by the nucleophiles (e.g., CH_3OH) present in the gas. Among the factors determining the relative extent of such competing processes, the excitation energy of **7** is particularly significant. The highly exothermic attack of D_3^+ ions on **1–4**, in fact, induces extensive fragmentation of the corresponding excited intermediate **7**, while the less exothermic protonation and alkylation of **1–4** by $C_nH_5^+$ and $CH_3FCH_3^+$ ions allows partial collisional stabilization of the related onium ions **7** before attack of the external nucleophile CH_3OH. Another factor is the presence of a powerful base (NMe_3) in the reaction mixture, which enhances significantly the extent of base-induced elimination processes within intermediates **7** to yield substantial amounts of phenylalkenes. In all cases, the presence in the intermediates **7** of Ph, Me, or H groups adjacent to the reaction center may trigger, if energetically allowed, competing anchimeric assistance to the AY leaving group departure (isomerization). In the case of Ph, anchimeric assistance may involve a stable cyclic intermediate, the alkylenebenzenium ion **9** (eq 1).

Nucleophilic Displacements on 3-Phenylbutyl-2-chloronium Ions. The relatively high yield and the stereoisomeric distribution of *erythro*- and *threo*-3-phenyl-2-methoxybutanes formed by attack of GA^+ acids on isomeric 3-phenyl-2-chlorobutanes **1** and **2** in the presence of CH_3OH (Table I) point to a highly efficient assistance of the phenyl group to the CH_3OH-to-AY substitution reaction (eq 1b). These findings are consistent with the general tendency, outlined in previous studies,[12] of nucleophilic vicinal groups for fast participation in gas-phase acid-induced nucleophilic displacements (S_Ni), causing two successive inversions of the configuration of the reaction center(s) and consequently yielding the retained substitution intermediates **10** and **11** (eq 1b).

The almost complete stereospecifity characterizing all the substitution processes occurring on *erythro*-**7** ((ret/inv) ≥ 160) and on *threo*-**7** (5 < (ret/inv) < 48) excludes occurrence of alternative substitution pathways, such as that involving the intermediacy of persistent[26] 3-phenylbutyl-2 cations, from unimolecular fission of the C–Y bond of excited **7**, which subsequently undergoes addition by the external nucleophile CH_3OH. Intermediacy of a persistent 3-phenylbutyl-2 cation would, in fact, lead to the formation of an almost equimolar mixture of inverted and retained ("racemized") 3-phenyl-2-methoxybutane derivatives, rather than the observed predominance of a single stereoisomer. In the same way, the data of Table I reveal that the direct bimolecular CH_3OH-to-AY nucleophilic displacement (eq 1a) (S_N2) hardly competes with the major S_Ni pathways, in view of the very limited yields of inverted substitution products (≤17%), which would be instead predominantly formed by a direct S_N2 process.

In conclusion, the large predominance of retained 3-phenyl-2-methoxybutanes from isomeric **1** and **2** in all systems investigated demonstrates the fast participation of a vicinal phenyl moiety in the gas-phase nucleophilic displacements on intermediates **7**. No information is presently available about the type of interaction between the phenyl moiety and the reaction site established in such participation, whether an intramolecular π-electron positive charge electrostatic interaction or a covalent C_{ring}–C_β bonding.

Nucleophilic Displacements on Isomeric β-Phenylpropyl Onium Intermediates. The conclusions reached in the previous section on the nature and the mechanism of the displacement reactions on the onium derivatives **7** from **1** and **2** apply to those from **3–6** as well (Table II).

Thus, in analogy with the **1–2** systems, direct bimolecular CH_3OH-to-AY nucleophilic displacement on **3** and **5** (S_N2; eq 1a) can be excluded as a significant source of β (Table II), since it is plausible that the efficiency of such S_N2 processes hardly can be affected by replacement of a CH_3 group, adjacent to the reaction center, with a H atom. This conclusion can be extended to the **4** and **6** compounds as well. In fact, despite their higher

(26) As a matter of fact, the present stereochemical data, as well as thermochemical calculations, cannot rule out occurrence of a 3-phenyl-2-butyl cationic transient, collapsing to the corresponding cyclic 2,3-butylenebenzenium ion **9** before single C–C bond rotation in the open cation.

propensity with respect to the **3** and **5** isomers to undergo S_N2 displacements, these compounds do not give rise to the expected S_N2 derivative, i.e., 2-phenyl-1-methoxypropane, at all. The absence of significant yields of 2-phenyl-1-methoxy- and 2-phenyl-2-methoxypropane from **4** and **6** excludes as well the intermediacy of a persistent 2-phenyl-1-propyl cation and of its more stable 2-phenyl-2-propyl isomer from unimolecular fission of the C–Y bond in their onium derivatives **7**. In these systems, as well as in those with **3** and **5**, just variable proportions of 1-phenyl-2-methoxy- (β) and 1-phenyl-1-methoxypropane (α) are mostly formed. A similar product pattern is obtained whether or not occurrence of persistent carbocationic intermediates is energetically allowed (D_2 and CH_4 samples) or forbidden (C_3H_8 and CH_3F systems). This observation lends support to the view that open-chain carbocationic species are hardly involved in the substitution processes, as further demonstrated by the significantly different proportions of β (32%) and α (60%) obtained by direct $C_nH_5^+$ protonation of allylbenzene in the presence of CH_3OH, with respect to those of Table II (β: 53% (**3**), 36% (**5**); α: 32% (**3**), 39% (**5**)).[27]

In conclusion, formation of 1-phenyl-2-methoxypropane (β) in all **3–6** systems can be largely accounted for by fast participation of the phenyl group to the nucleophilic substitution reaction, in complete analogy with the conclusions reached in the butane **1** and **2** systems. An asymmetric 1,2-propylenebenzenium ion **9** is expected to be formed from **3–6** which undergoes subsequent nucleophilic attack by CH_3OH exclusively at the CH_3-substituted carbon to yield the corresponding substituted product β.

Formation, Isomerization, and Reactivity of Gaseous Cyclic Alkylenebenzenium Ions. Once the existence in the gas phase of 2,3-butylene- and 1,2-propylenebenzenium ions **9** from the corresponding onium intermediates **7** is established, it is worthwhile to proceed in the analysis of the factors governing their formation and reactivity in the gas phase. According to the (ret/inv) ratios of Table I, it emerges that formation of the *trans*-2,3-butylenebenzenium intermediate from *erythro*-3-phenylbutyl-2-chloronium ion **7** is a much easier process than that leading to *cis*-2,3-butylenebenzenium ion from the corresponding *threo*-**7** precursor. Further support to this conclusion is the much more abundant yields of secondary elimination and isomerization products accompanying formation of isomeric 3-phenyl-2-methoxybutanes from *threo*-**7** with respect to those from *erythro*-**7**.

Concerning the isomerized substitution products, i.e., 2-phenyl-2-methoxybutanes and 1-phenyl-1-methoxy-2-methylpropane, the question arises as to whether their side-chain isomerization precedes and therefore competes with or follows the formation of 2,3-butylenebenzenium ion **9**. Answering this question is particularly relevant for understanding the factors governing formation of the isomeric cyclic ions **9**.

Information on the isomerization pattern of excited 2,3-butylenebenzenium transients is provided by the results of gas-phase attack of a nuclear decay formed phenylium ion on isomeric 2-butenes. Addition of the phenylium ion to the π-system of butene is a highly exothermic process ($\Delta H^\circ \leq$ ca. −90 kcal mol^{-1}), leading primarily to highly excited 2,3-butylenebenzenium ions, which readily isomerize to give exclusively the thermodynamically most stable 2-phenylbutyl-2 cation.[28] It is therefore conceivable that, if side-chain isomerization within excited 2,3-butylenebenzenium ions from **7** were the main path to formation of the isomerized substitution product, it would produce predominantly the 2-phenyl-2-methoxybutane isomer, in relative yields increasing with the energy level and the lifetime of its ionic precursor, namely at low pressures and in the following order: $CH_3FCH_3^+ < i\text{-}C_3H_7^+ < C_nH_5^+ < D_3^+$. As a matter of fact, 2-phenyl-2-methoxybutane is in general a minor isomerized substitution product, whose yield appears to decrease at low pressure and in the following order: $i\text{-}C_3H_7^+ > C_nH_5^+ > D_3^+$. It is, therefore, concluded that formation of 2,3-butylenebenzenium ions **9**, as well as their isomeric

Chart I

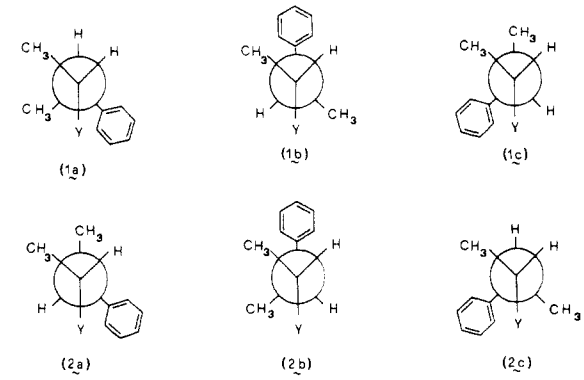
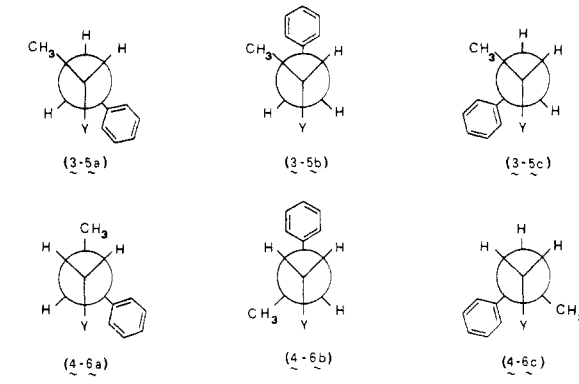


Chart II

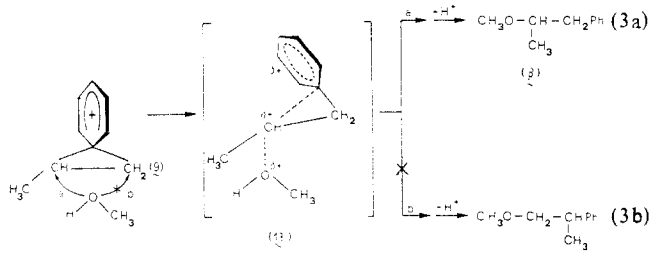


structures, from the corresponding precursors **7** is mainly governed by kinetic factors, deriving from the particular configuration of the ionic precursor **7**.[29] In this view, it is plausible that **1b** is the most stable rotamer of **1** in the gas phase, since it presents only two gauche interactions between bulky groups (Ph, CH_3, Y), whereas **1a** and **1c** are characterized by all gauche interactions (Chart I). Assuming that the onium derivative **7b** of **1b** induces neighboring group participation in a time short with respect to bond rotation, it follows that the favored path is that leading to *trans*-2,3-butylenebenzenium ion **9t**. In gaseous **2**, instead, all gauche interactions are present except in the **2a** rotamer. This situation leads to the predominance of the onium rotamer **7a** over **7b** and **7c**. The corresponding neighboring group trans-anti participations (via CH_3, phenyl, or hydrogen transfer, respectively) take place at rates depending not only on the nucleophilic properties of the participating group but also on the relative population of rotamers **7a**, **7b**, and **7c**. The entire family of isomeric *cis*-2,3-butylenebenzenium (**9c**), 1-phenyl-2-methylpropyl-1, and 2-phenylbutyl-2 cations is formed, which are trapped by the nucleophiles present in the mixture (e.g., CH_3OH) to give eventually the corresponding substitution and elimination derivatives. Structural effects play a significant role in determining the rate constant for the formation of isomeric **9t** and **9c** from their individual precursors *erythro*- and *threo*-**7**, as well. The substantially higher stereospecificity displayed in the formation of *erythro*-3-phenyl-2-methoxybutane from **1** with respect to that observed in the conversion of **2** in *threo*-3-phenyl-2-methoxybutane suggests that the second step (k_Δ) in sequence 1b is intrinsically faster for the erythro form of ion **7** than for the threo one (vide infra). The presence of two eclipsed methyl groups in the transition state leading to **9c** may be responsible for such kinetic difference.

Structural factors in the onium ion **7** from **3–6** determine as well the product pattern of Table II. In fact, conformational analysis of **3–6** indicates that, among the possible staggered rotamers, the **a** and **b** forms are expected to be more stable than the **c** one (Chart II).

(27) Cacace, F., private communication.
(28) Fornarini, S.; Speranza, M., unpublished results.
(29) Cram, D. J.; McCarty, J. E. *J. Am. Chem. Soc.* **1957**, *79*, 2866.

In the framework of the assumptions adopted for the butyl substrates **1** and **2**, it is expected that GA^+ attack on substrates **3–6** induces preferentially H and Ph 1,2-migrations in **3** and **5** and CH_3 and Ph 1,2-shifts in **4** and **6**. Accordingly, 1-phenyl-1-methoxy- (α) and 1-phenyl-2-methoxypropane (β) are mostly formed as substitution products from **3–6**. In addition, the different (β/α) ratios observed in the 1-phenyl-2-Y-propane (**3–5**) and 2-phenyl-1-Y-propane (**4–6**) systems indicate, in complete analogy with the conclusions reached in the butane **1** and **2** experiments, that structural factors may affect the relative efficiency of phenyl-group participation in the corresponding intermediates **7** as well. Inductive and steric factors may be responsible for the comparatively more efficient phenyl-group participation in the onium ions **7** from **4–6b** with respect to those from **3–5b**. This accounts for the higher proportions of β formed from **4–6** (40–78%) with respect to those (26–58%) recovered from **3–5** samples. It is, therefore, concluded that the asymmetric 1,2-propylenebenzenium ion **9** is readily generated by phenyl-group participation within the onium ion **7** from both **4–6** and **3–5**, although at rates decreasing from the first precursors to the latter ones. According to the substituted products distribution, subsequent nucleophilic attack of CH_3OH on the asymmetric 1,2-propylenebenzenium ion **9** takes place exclusively at the methyl-substituted carbon (eq 3). The observed regioselectivity is in



contrast with elementary electron and steric considerations, thus suggesting that the transition state **13** of the substitution process involves a C_{sp^2}–C_{sp^3} bond breaking more pronounced than the concomitant C_{sp^3}–O bond formation and, therefore, development of a partial positive charge at the C_{sp^3} carbon. Within such an hypothesis, it follows that the transition state **12** energy is lowered by the presence of an electron-donating group (i.e. CH_3) at the reaction site and, hence, route (a) is kinetically favored over the alternative pathway (b).

Comparison with Related Gas-Phase and Solution Chemistry Studies. While extensive evidence supports the occurrence of displacement reactions in solution via adjacent phenyl-group participation, identification of anchimerically assisted Ph-3 processes is often controversial. Only in a few instances, in fact, could product analysis, supported by adequate kinetic data, provide firmly an indication of anchimerically assisted reactions by adjacent aryl groups. Most of the difficulties encountered in these cases arise from the fact that the increase in rate associated with Ph participation is not pronounced because often the solvent is itself comparatively basic and nucleophilic, and the displacement rate is quite high even in the absence of participation by the phenyl group. This is particularly relevant for secondary 3-phenyl-2-Y-butane systems (Y = leaving group), wherein assistance of the neighboring group is further contrasted by nucleophilic assistance by the solvent, which is found to affect as well the structure of the bridged transition state.[3-7]

In low-nucleophilicity solvent systems, alkylenebenzenium transients can conveniently be observed, although the resonance energy gained by their benzyl cation isomers is large enough to stabilize these ions with respect to the bridged structure.[8,9]

The present gas-phase results would indicate, in qualitative agreement with most conclusions reached in related solvolytic processes, that, in the absence of solvent, counterion, etc., a vicinal phenyl group is highly efficient in assisting cationic nucleophilic displacements in both primary and secondary systems. Owing to the different origin of the *erythro-* and *threo*-3-phenyl-2-methoxybutanes and of the accompanying isomerized substitution products (2-phenyl-2-methoxybutane) of Table I, the "effective concentration"[30] of the phenyl group adjacent to the reaction center in the onium derivatives **7** of **1** and **2** is essentially expressed by the following equation: $k_\Delta/k_S = (\text{ret/inv})[CH_3OH]$. On these grounds, the "effective concentration" of an adjacent phenyl group in isomeric onium ion **7** from **1** and **2** is determined by the structural properties of the intermediate, ranging from 0.9×10^{-2} to over 7.0×10^{-2} mol L^{-1} for the erythro isomer and from 0.03×10^{-2} to ca. 0.3×10^{-2} mol L^{-1} for the threo one. If comparison is made between these values and those obtained for strictly related bifunctional compounds,[12d] it can be concluded that the participation ability of the phenyl group in the gas phase is intermediate between that of an OH moiety ($k_\Delta/k_S \geq 150 \times 10^{-2}$ mol L^{-1}) and that of a Cl group ($k_\Delta/k_S \leq 0.2 \times 10^{-2}$ mol L^{-1}), reinforcing the hypothesis that the efficiency of a vicinal-group participation process in the gas phase is strictly related to the nucleophilicity of the moiety adjacent to the reaction site.[31]

Conclusions

A stereochemical approach has been adopted for the kinetic investigation of acid-induced nucleophilic displacement processes involving vicinal phenyl-group participation in the gas phase, where interference from environmental factors is excluded. Under such conditions, a vicinal phenyl group is found to anchimerically assist a cationic nucleophilic displacement with a participation efficiency which qualitatively follows the relative gas-phase nucleophilicity scale of their monofunctional models.

The cyclic intermediates involved in the phenyl-group participation from substrates **1–6** display a scarce tendency for isomerization to the corresponding most stable structures, at least at the pressures used in the present experiments (155–760 Torr). This suggests, although it does not prove, that these intermediates have a static alkylenebenzenium structure.

The present results consolidate the knowledge about neighboring-group participation in gas-phase cationic nucleophilic displacements, whose comparison with related solvolytic processes will hopefully allow a rationalization of the effects of the solvent and of counterion encountered in such studies and promote development of quantitative theoretical models for cyclization reactions in the condensed phase.

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Registry No. 1, 5706-91-2; **2**, 5706-90-1; **3**, 10304-81-1; **4**, 824-47-5; **5**, 698-87-3; **6**, 1123-85-9; D_3^+, 12595-96-9; $C_2H_5^+$, 14936-94-8; i-$C_3H_7^+$, 19252-53-0; $CH_3FCH_3^+$, 64710-12-9.

(30) Following classical definitions for solution neighboring group participation processes the k_Δ/k_S ratio of eq 1 is defined as the "effective concentration" of the reactive phenyl moiety of the intermediate **7** in the particular reaction volume about the reaction center C–YA^+, relative to the concentration of the external nucleophile CH_3OH within the same volume. This term represents the actual "reduced" intramolecular reactivity within **7**, once it is referred to a proper intermolecular model, namely to the inherent reactivity of the two reacting moieties of the bifunctional species regarded as if they were not connected by a molecular chain. Adoption of a reasonably good kinetic model for the intermolecular analogue of eq 1b, namely that involving $CH_3ClCH_3^+$ or $(CH_3)_2OH^+$ ion attack on toluene, was hardly possible in the present work, owing to the lack of measurable intermolecular reactivity under the experimental conditions used (ref 17e).

(31) The gas-phase nucleophilicity of the group adjacent to the reaction center is expected to parallel its proton affinity (P.A. (kcal mol^{-1}): 2-C_4H_9Cl, $\simeq$171; toluene, 182–190; 2-C_4H_9OH, $\simeq$191).