12. Substrate and Positional Selectivity of Free Phenylium Ions toward Arenes in the Gas and Liquid Phases

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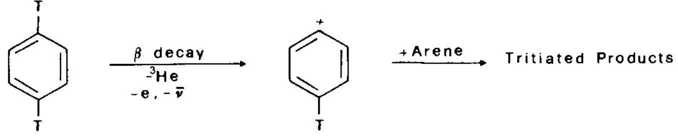
A nuclear technique, based on the spontaneous decay of tritiated precursors that allows the generation of free carbenium ion of exactly the same nature in different environments, has been exploited in a comparative study of aromatic phenylation by free phenylium ions, both in the gas phase at various pressures and in the liquid phase. The differences between the reactivity pattern of the phenylium ion in the two environments can essentially be reduced to significant ion-neutral electrostatic interaction in the gas phase and, to the much greater efficiency of collisional stabilization, in the condensed phase, allowing a larger fraction of the excited ionic intermediates, from the highly exothermic attack of phenylium ion on the competing arenes, to survive dissociation and isomerization. The mechanism of the major competitive processes promoted by phenylium-ion attack on arenes, *i.e.* phenyldehydrogenation and phenyldephenylation, are discussed, together with the substrate and positional selectivity displayed by the nuclear-decay-formed phenylium ion toward the selected arenes. The kinetic and mechanistic features of aromatic phenylation, deduced from the present decay experiments, are compared with those of related phenylation reactions carried out in the dilute gas state and in solution.

Introduction. – Spontaneous β decay of a tritium atom, covalently bound in a specific position in an organic compound, affords a convenient means to produce free carbocations of defined structure in both gaseous and condensed phases and to study their intrinsic reactivity properties by tracer techniques [1]. The method was recently applied to gather otherwise hardly accessible information upon unimolecular automerization of a gaseous phenylium ion **1** [2], generated from decay in [1,4-T_2]benzene [3] *(Scheme 1)*, and its reactivity features toward σ-, π-, and n-type acceptors [4]. The relevant data point to the high reactivity of the phenylium ion toward all types of nucleophilic centers, with a distinct preference for the *n*- and π-type sites of the substrate.

Scheme 1



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We now report the extension of the study to the gas- and liquid-phase ionic phenylation of substituted arenes. The investigation has been primarily undertaken to bring the inter- and intramolecular selectivity of **1** toward compounds containing different σ-, π-, and n-type nucleophilic centers, such as fluorobenzene, chlorobenzene, anisole, toluene, and *p*-xylene, to a sharper focus. From a comparative analysis of the results obtained from the gas- and liquid-phase experiments, we expect to gain first insight into inter- and intramolecular isomerization of the primary phenylated adducts from attack of **1** on the selected aromatic compounds.

Additional interest is attached to this study, owing to the possibility to extend directly the reactivity data of the tritiated free phenylium ion **1** to those obtained under similar conditions from the dediazoniation of benzenediazonium-ion salts, wherein solvated phenylium ion is often recognized to be a major ionic intermediate [5].

Experimental. – *Materials.* The key substrate for the nuclear-decay experiments, namely [1,4-T_2]benzene, was synthesized and purified according to [3b]. The aromatic compounds employed either as substrates or as standards in GC analyses were research-grade chemicals from *Merck AG* and *Aldrich Chemical Co.*, and were used without further purification. Other aromatic compounds not commercially available, such as isomeric methoxybiphenyls, fluorobiphenyls, and dimethylbiphenyls were prepared following modified versions of well-established synthetic procedures [6].

Growth of the Decay Products. The procedure followed to prepare the gaseous and liquid samples were analogous to those described in [2b]. The vessels were stored in the dark for 10–16 months at 100° (gaseous samples) and r.t. (liquid samples).

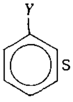
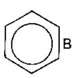
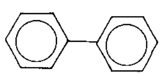
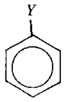
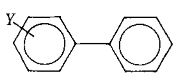
Radiochemical Analysis of Products. After the storage period, the ampules were opened and their content analyzed by radio-GC and radio-HPLC procedures. A *Carlo Erba Fractovap 4200* gas chromatograph equipped with a high-sensitivity hot-wire detector in series with a 10-ml internal-flow *Berthold* proportional counter, heated at 180°, was used for the radio-GC analyses. A *Varian Vista 5500* high-pressure liquid chromatograph equipped with a 254-nm UV detector in series with a *Berthold LB 503 HS* flow liquid scintillation counter was used for the radio-HPLC analyses.

The identity of the tritiated products was established by coincidence of their retention volumes with those of authentic reference compounds on the following columns: *i)* GC: 4 m × $\frac{1}{8}$ inch stainless steel column packed with 10% *SP 1000* on *Supelcoport* (80–100 mesh), operated at 60°; *ii)* GC: 2 m × $\frac{1}{8}$ inch stainless steel column packed with 5% *SP 1200* + 5% *Bentone 34* on *Supelcoport* (100–120 mesh), operated at 120°; *iii)* HPLC: 25 cm × 5 mm *Alltech Rosil C-18 HL* from *Alltech*, Italy, using $MeOH/H_2O$ 3:2. The absolute yields of the tritiated products correspond to the ratio of their activity to the activity of the labelled decay ion formed during the storage period within the decay samples.

Results. – *Table 1* shows the absolute and relative yields of tritiated products recovered from the liquid decay samples, containing mixtures of each selected substituted arene (S = fluorobenzene (F), chlorobenzene (C), toluene (T), or anisole (A)) and benzene (B), used as competing substrate. The results concerning similar competition experiments, carried out in the gas phase at 100° in the pressure range of 17–113 Torr, are given in *Tables 2* (F), *3* (C), *4* (T), and *5* (X = *para*-xylene). Reaction conditions were chosen to span over one order of magnitude for the relative concentrations of the two competing aromatic substrates. Occasionally, *ca.* 4–5 mol-% of a powerful ion trap, such as NH_3, were added to the mixtures.

The overall absolute yields of the tritiated aromatic products from the liquid systems of *Table 1* are generally quite close to the theoretical limit and are found to depend upon the nature of the substituent group Y in S, increasing in the order: 69% (Y = Me), 70% (Y = MeO), 80% (Y = F), 100% (Y = Cl). In the corresponding gaseous samples *(Tables 2–5)*, the absolute yields of the tritiated aromatic products appear to be appreciably lower, amounting to 38–50% (F), 35–50% (C), 36–43% (T), and 30–64% (X). Such decreases are counterbalanced by a considerable increase of the yield of low-boiling tritiated products, invariably accompanying formation of the aromatic derivatives. In general, it has been observed that the combined activity of the aromatic and of the

Table 1. *Tritiated-Product Distribution from Attack of Phenylium Ions on Liquid Arenes* (T = 25°)

System composition[a]		Relative yields of product [%][b]			Overall absolute yield [%][c]	Kinetic parameters		
								
([S]/[B] = 1) Y		BIP	ST	YBIP o [%]; m [%]; p [%]		α[d]	β[e]	γ[f]
F	(F)	62	5	33 (47; 20; 33)	80	0.7	0.5	0.3
Cl	(C)	47	22	31 (50; 29; 21)	100	1.6	0.7	1.4
Me	(T)	46	1	53 (44; 30; 26)	69	1.2	1.1	0.04
MeO	(A)	14	6 +45 (DPE)[g]	35 (65; 13; 22)	70	6.6	2.5	1.7

[a] The systems contained 1 mCi of [1,4-T_2]benzene (specific activity: 90 mCi mmol^{-1}). Liquid arenes saturated with O_2, used as a radical scavenger. In some cases, variable amounts of NH_3 added to the liquid mixture did not cause any significant difference in the relative yields of labelled products.

[b] Expressed as a percentage of the total activity of the recovered aromatic products; standard deviation of data, *ca.* 10%.

[c] Expressed as the percent ratio of the total activity of the final aromatic products to the activity originally contained in the nuclear-decay formed phenylium ion reactant.

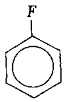
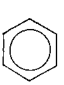
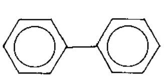
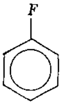
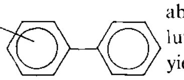
[d] $\alpha = ([\mathrm{YBIP}] + 2[\mathrm{ST}])[\mathrm{B}]/[\mathrm{BIP}][\mathrm{S}]$; in the case of A, $\alpha = ([\mathrm{YBIP}] + [\mathrm{DPE}] + 2[\mathrm{ST}])[\mathrm{B}]/[\mathrm{BIP}][\mathrm{S}]$.

[e] $\beta = [\mathrm{YBIP}][\mathrm{B}]/[\mathrm{BIP}][\mathrm{S}]$.

[f] $\gamma = 2[\mathrm{ST}]/[\mathrm{YBIP}]$; in the case of A, $\gamma = (2[\mathrm{ST}] + [\mathrm{DPE}])/[\mathrm{YBIP}]$.

[g] DPE = diphenyl ether.

Table 2. *Tritiated-Product Distribution from Gas-Phase Attack of Phenylium Ions on Fluorobenzene* (T = 100°)

System composition[a]			Relative yields of product [%][b]			Over-all abso-lute yield [%][c]	Kinetic parameters		
		[S]/[B]							
S [Torr]	B		BIP	ST	YBIP o [%]; m [%]; p [%]		α[d]	β[e]	γ[f]
23	2	11.5	7	37	56 (17; 75; 8)	50	1.6	0.7	1.3
50	32	1.6	38	17	45 (25; 70; 5)	50	1.3	0.8	0.8
40	41	1.0[g]	38	21	41 (23; 71; 6)	33	2.2	1.1	1.0
39	46	0.9	50	18	32 (23; 72; 5)	46	1.6	0.7	1.1
22	51	0.4	81	5	14 (22; 76; 2)	38	0.7	0.4	0.7
							1.5 ± 0.8	0.7 ± 0.4	1.0 ± 0.3

[a] All gaseous systems contain [1,4-T_2]benzene (1 mCi; specific activity: 90 mCi·mol^{-1}) and O_2 (4 Torr).

[b] See *Footnote b* of *Table 1*.

[c] See *Footnote c* of *Table 1*.

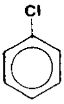
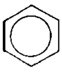
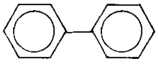
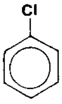
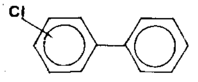
[d] See *Footnote d* of *Table 1*.

[e] See *Footnote e* of *Table 1*.

[f] See *Footnote f* of *Table 1*.

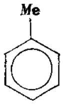
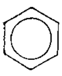
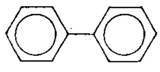
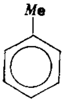
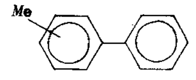
[g] 4–5 mol-% NH_3 added to the gaseous mixture.

Table 3. *Tritiated-Product Distribution from Gas-Phase Attack of Phenylium Ions on Chlorobenzene* ($T = 100°$)

System composition a)			Relative yields of products [%] b)			Overall absolute yield [%] c)	Kinetic parameters		
 S [Torr]	 B	$\frac{[S]}{[B]}$	 BIP	 ST	 YBIP *o* [%]; *m* [%]; *p* [%]		α d)	β e)	γ f)
11	2	5.5	14	65	21 (10; 82; 8)	38	2.0	0.3	6.2
33	10	3.3	29	53	18 (6; 90; 4)	44	1.3	0.2	5.9
30	31	1.0g)	48	38	14 (15; 80; 5)	31	1.9	0.3	5.4
32	36	0.9	55	33	12 (12; 84; 4)	35	1.6	0.2	5.5
8	50	0.2	88	9	3 (0; 100; 0)	50	1.5	0.3	6.0
							1.7 ± 0.4	0.3 ± 0.1	5.8 ± 0.4

a) See *Footnote a* of *Table 2*. b) See *Footnote b* of *Table 1*. c) See *Footnote c* of *Table 1*. d) See *Footnote d* of *Table 1*. e) See *Footnote e* of *Table 1*. f) See *Footnote f* of *Table 1*. g) See *Footnote g* of *Table 2*.

Table 4. *Tritiated-Product Distribution from Gas-Phase Attack of Phenylium Ions on Toluene* ($T = 100°$)

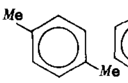
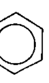
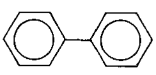
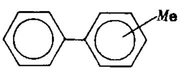
System composition a)			Relative yields of products [%] b)			Overall absolute yield [%] c)	Kinetic parameters		
 S [Torr]	 B	$\frac{[S]}{[B]}$	 BIP	 ST	 YBIP *o* [%]; *m* [%]; *p* [%]		α d)	β e)	γ f)
50	14	3.6	21	27	52 (4; 87; 9)	39	1.4	0.7	1.0
20	7	2.9	26	26	48 (8; 82; 10)	42	1.3	0.6	1.1
28	30	0.9	47	18	35 (4; 85; 11)	36	1.6	0.8	1.0
42	53	0.8g)	45	22	33 (10; 77; 13)	33	2.1	0.9	1.3
19	32	0.6	60	14	26 (6; 83; 11)	42	1.5	0.7	1.1
12	50	0.3	78	7	15 (2; 85; 13)	43	1.6	0.8	0.9
							1.6 ± 0.5	0.7 ± 0.2	1.1 ± 0.2

a) See *Footnote a* of *Table 2*. b) See *Footnote b* of *Table 1*. c) See *Footnote c* of *Table 1*. d) See *Footnote d* of *Table 1*. e) See *Footnote e* of *Table 1*. f) See *Footnote f* of *Table 1*. g) See *Footnote g* of *Table 2*.

low-boiling fraction of the samples accounts for over 80% of the theoretical yield, the remainder being presumably provided by polymerization products and by the formation of monotritiated benzene, *via* hydride-ion transfer from the aromatic substrate to **1**, whose activity cannot be discriminated from that contained in the undecayed [1,4-T_2]benzene.

Inspection of *Tables 1–5* reveals that attack of **1** on the selected substituted arenes S leads exclusively to the formation of two classes of tritiated derivatives, namely isomeric substituted biphenyls (YBIP) and the tritiated parent compound (ST). The ST class includes labelled diphenyl ether as well which is formed in *ca.* 30% of absolute yields in the liquid samples with anisole as the substrate *(Table 1)*. In all competition experiments,

Table 5. *Tritiated-Product Distribution from Gas-Phase Attack of Phenylium Ions on* para-*Xylene* ($T = 100°$)

System composition[a])			Relative yields of products [%][b])			Overall absolute yield	Kinetic parameters		
		$\frac{[S]}{[B]}$		Tritiated Alkylbenzenes[h])					
S [Torr]	B		BIP	ST	YBIP (2,5 [%]; 3,5 [%]; 3,4 [%]; 2,4 [%]; 2,3 [%])	[%][c])	α[d])	β[e])	γ[f])
20	6	3.3	26	33	41 (31; 44; 10; 5; 7; 3)	30	1.2	0.5	1.6
36	42	0.9	59	15	26 (57; 23; 6; 5; 6; 3)	64	1.1	0.5	1.1
34	32	1.1[g])	53	17	30 (64; 22; 2; 6; 4; 2)	26	1.1	0.5	1.1
40	69	0.6	60	21	19 (60; 20; 4; 6; 8; 2)	30	1.7	0.5	2.2
8	85	0.1	89	6	5 (57; 30; 4; 3; 6; 0)	35	2.0	0.6	2.4
							1.4 ± 0.6	0.5 ± 0.1	1.7 ± 0.7

[a]) See *Footnote a* of *Table 2.* [b]) See *Footnote b* of *Table 1.* [c]) See *Footnote c* of *Table 1.* [d]) See *Footnote d* of *Table 1.* [e]) See *Footnote e* of *Table 1.* [f]) See *Footnote f* of *Table 1.* [g]) See *Footnote g* of *Table 2.* [h]) Tritiated alkylbenzenes are mainly toluene and isomeric xylenes.

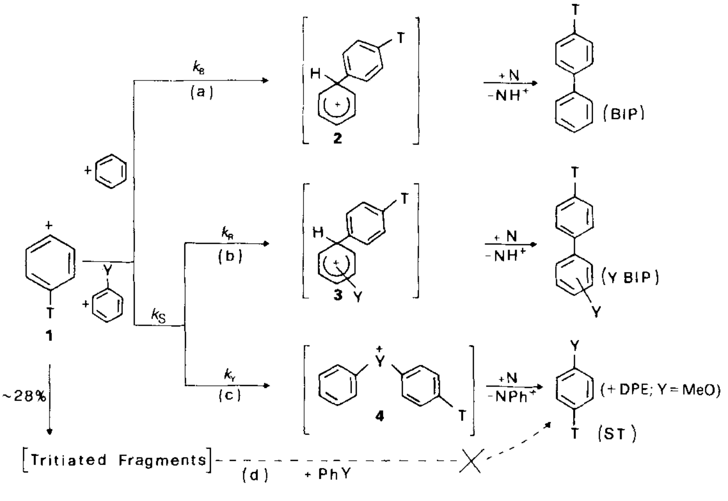
these products are accompanied by comparable yields of unsubstituted biphenyl (BIP), from attack of **1** on the benzene competitor B. A measure of the relative extent of the reaction pathways leading to the formation of labelled YBIP and ST from S, and of tritiated BIP from B, is provided by the α factors of *Tables 1–5*, expressed by the ([YBIP] + 2 [ST]) [B]/[BIP][S] ratios. In the liquid systems *(Table 1)*, the α factors increase in the order: F (0.7) < T (1.2) < C (1.6) < A (6.6). In the gaseous samples *(Tables 2–5)*, they barely exceed unity in all cases, *i.e.* F (1.5 ± 0.8), T (1.6 ± 0.5), C (1.7 ± 0.4), X (1.4 ± 0.6). Under all experimental conditions, the α factors appear essentially independent upon the [S]/[B] ratios and the presence of the added base NH_3, as demonstrated by the rather limited oscillation intervals quoted. Restricting the analysis to the relative extent of ring phenylation observed in the competing substrates, the β factors of *Tables 1–5* report the [YBIP][B]/[BIP][S] ratios, measured from the competition experiments. The β values are found to increase in the order: F (0.5) < C (0.7) < T (1.1) < A (2.5) in the liquid systems *(Table 1)*, whereas, in the gas phase, they never exceed unity, increasing in the order: C (0.3 ± 0.1) < X (0.5 ± 0.1) < F (0.7 ± 0.4) ≈ T (0.7 ± 0.2).

The relative distribution of the [ST] and [YBIP] products from the substituted arene S is represented by the γ factors of *Tables 1–5*, expressed by the 2 [ST]/[YBIP] ratios. The γ factors appear to depend upon the nature of the Y substituent of S in both the liquid and the gaseous systems. A rather similar trend is observed in both phases, where the γ values are found to increase in the Y order: Me (0.04) < F (0.3) < Cl (1.4) < MeO (1.7). However, the absolute γ value for each individual substrate significantly increases in passing from the solution to the gaseous phase, *i.e.* Me (1.1 ± 0.2) ≈ F (1.0 ± 0.3) < Me_2 (1.7 ± 0.7) < Cl (5.8 ± 0.4).

Finally, the isomeric composition of the substituted biphenyls YBIP from S recovered in the liquid systems follows the classical *ortho-para* distribution of electrophilic aromatic substitution in condensed phase *(Table 1)*. However, when the reaction is carried out in the gas phase at 100°, predominant formation of the *meta*-YBIP is invariably observed, whose relative yield increases in the Y order: F (70–76%) < Me (77–87%) < Cl (80–100%). Under the same conditions, attack of gaseous **1** on *β*-xylene (X, *Table 5*) promotes extensive Me-group transfers within the corresponding adduct, as demonstrated by the recovery of significant yields of all isomeric dimethylbiphenyls, with both Me groups on the same ring.

Discussion. – *Phenylium-Ion Attack on Aromatic Substrates.* Since the concentration of [1,4-T_2]benzene and, therefore, the specific activity of the systems have been deliberately kept at very low levels, the otherwise conceivable contribution of radiolytic processes to the formation of *tritiated* products is practically suppressed1). Consequently, in this study, the labelled phenylium ion **1** represents the only significant source of the tritiated products detected. The nature and the properties of **1** produced by nuclear decay in [1,4-T_2]benzene *(Scheme 1)* have been previously described in detail [2–4].

Scheme 2



Any reaction scheme for the attack of **1** on the selected aromatic substrates should account for the formation of significant yields of both the labelled biphenyl derivatives YBIP and BIP and the tritiated parent compound ST, under all experimental conditions. While attack of **1** to the system of the competing substrates appears to be the most direct route to YBIP and BIP (*Paths a* and *b* in *Scheme 2*), the tritiated substrate ST may conceivably arise from two different pathways, namely a quasi-resonant Ph-group displacement after attack of **1** at the Y substituent of the substrate (*Path c* in *Scheme 2*) or,

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1) Radiolytic processes are entirely negligible as a source of *tritiated* products in comparison with the decay of the labelled parent, provided that the concentration of the latter and, therefore, the specific activity of the systems are sufficiently low. For a discussion on this topic, see [1].

alternatively, by ring-tritonation of S by some acidic species arising from extensive fragmentation of the primary daughter ion from nuclear decay in [1,4-T_2]benzene (*Path d* in *Scheme 2*)[2]). However, that *Path d* in *Scheme 2* can be only a negligible route to ST is demonstrated by the exceedingly low yields of ST formed in the liquid toluene/benzene samples (*ca.* 0.7%, *Table 1*) and in some gaseous decay mixture under favorable conditions (*cf. ca.* 1.5% of tritiated fluorobenzene in the last entry of *Table 2*). It is, therefore, concluded that the phenylation pattern occurring in the decay systems involves competitive attack of **1** on the nucleophilic sites of the present aromatic compounds, *i.e.* their π systems (*Paths a* and *b* in *Scheme 2*) and their substituents (*Path c* in *Scheme 2*), giving the corresponding protonated biphenyls **2** and **3** and the Y-phenylated parent compound **4**, respectively, both excited by the exothermicity of their formation process[3]).

According to the proposed reaction pattern, kinetic significance can be attached to the α factors measured in the competition experiments, provided that the efficiency of cross-disproportionation and Ph-group transfer among the ionic intermediates **2**, **3**, and **4** is low with respect to neutralization (second steps of *Paths a, b,* and *c* in *Scheme 2*)[4]). This condition is attained in the present study, as demonstrated by the relatively high yields of labelled products and by the approximate constancy of the α, β, and γ factors (*Tables 2–5*) for each competition system as a function of the relative concentration of the components ([S], [B], and [NH_3]). On these grounds, the factors of *Tables 1–5* correspond in first approximation to the $(k_R + k_Y)/k_B$ ratios of the competing *Paths a* and *b + c* in *Scheme 2,* whereas a measure of the apparent k_Y/k_R ratios of the competing *Paths b* and *c* in *Scheme 2* can be conveniently provided by the γ factors, in view of the equal tendency of excited **4** to release either a labelled or an unlabelled Ph moiety. An estimate of the apparent k_R/k_B ratios of the ring phenylation *Paths a* and *b* in *Scheme 2* may arise from the β values of *Tables 1–5*.

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[2]) The β^- particle from the decay event possesses high energy and leaves the atom in a time short relative to periods of orbital-electron motion (0.1–0.01 of a period). This suddenly changes the nuclear charge and consequently perturbs the electrostatic environment of the surrounding cloud of electrons. Usually, the cloud of electrons will contract adiabatically to accomodate itself to the increased nuclear charge, but sometimes excited electronic state or ionization ('shake off') may result [7]. 'Shake-off' effects in the decay of [1,4-T_2]benzene produces over 30 different charged fragments in *ca.* 28% of nuclear events [3a]. Part of these fragments may retain a T-atom. Some of them might in principle act as *Bronsted* acids toward the aromatic substrate yielding eventually ST (*Path d in Scheme 1*).

[3]) An exothermicity of $-\Delta H^\circ = 52–77$ kcal·mol^{-1} is estimated for the formation of the protonated biphenyl **2** (*Path a*), using a value of $\Delta H_f^\circ = 244–270$ kcal·mol^{-1} for the formation of **1** (which depends on its vibrational energy, *cf.* [2]), and the value of 213 kcal·mol^{-1} for the ΔH°_f of the protonated biphenyl **2** (*cf.* [8]). Even a rough estimate of the enthalpy changes of the first steps of *Path b* and *c* in *Scheme 1* is prevented owing to the lack of reliable data for the ΔH_f° values of the corresponding intermediates **3** and **4**. However, since the gas-phase basicities of the selected arenes S exceed that of benzene, it is likely that $-\Delta H^\circ$ of the *Path b* leading to **3** (Y = F, Cl, Me, Me_2, or MeO) exceeds 52 kcal·mol^{-1}. Furthermore, since the addition of **1** to the n-center of CH_3Y (Y = F, Cl, or MeO) is quoted in [2] to be exothermic by several tens of kcal/mol, it is plausible that attack of **1** at the n-center of C_6H_5Y (Y = F, Cl, or MeO) to yield the relevant onium ion **4** is similarly exothermic. The same conclusion applies to the insertion of **1** into the side chain of toluene and *p*-xylene, if it is considered that for the insertion of **1** in CH_4 $-\Delta H^\circ = 45–70$ kcal·mol^{-1} [4d].

[4]) Proton transfer from ground-state arenium ions **2** and **3** to the competing aromatics, which are the major components of the decay mixtures, is a process several kcal/mol endothermic. However, the process may occur, if excited **2** and **3** are involved. Other proton acceptors N available to ions **2** and **3** could be the added NH_3 or any basic species formed from self-radiolysis of the decay sample.

Substrate and Positional Selectivity. The α, β, and γ kinetic parameters and the relative distribution of the tritiated products outlined in *Tables 1–5* provide an interesting picture of the substrate and positional selectivity of the attack of a free phenylium ion **1** on the selected arenes in both the liquid and the gas phase as well as of any intramolecular isomerization process taking place in the ensuing phenylated intermediates, *e.g.* **3**.

According to the relevant β factors *(Table 1)*, the liquid-phase attack of **1** on arenes follows the typical pattern of classical electrophilic aromatic substitutions in condensed media by powerful electrophiles [9]. In fact, they indicate a distinct preference of the ionic electrophile for the most activated aromatic ring (F < C < B < T < A). As expected, the presence of a substituent in S influences the overall ring-phenylation rate, according to the order: F < Cl < H < Me < MeO. However, the formation of appreciable yields of labelled ST products in the liquid decay systems points to a direct attack of **1** at the substituent group (*Path c* in *Scheme 1*) to an extent, represented by the γ factors of *Table 1*, which seems to parallel the relative nucleophilicity of the substituent group (Me ≪ F < Cl < MeO)⁵).

While attack of **1** at the Y group of toluene, fluorobenzene, and chlorobenzene leads eventually to the exclusive formation of the labelled parent compound ST, phenylation at the O-atom of anisole produces the diphenylmethyl oxonium intermediate **4** (Y = MeO), which undergoes neutralization to give predominantly diphenyl ether (DPE; 88%) and minor yields of tritiated anisole (12%). This distribution indicates that a Me group is transferred from **4** to a suitable acceptor N over seven times faster than a Ph moiety, in agreement with the well-established higher propensity of a C_{sp^3} *vs.* C_{sp^2} to undergo nucleophilic displacement.

Combination of the directing effects of the aromatic ring and the substituent group Y of S leads to an overall relative rate of attack of **1** on the liquid arene, expressed by the α factors of *Table 1*, increasing in the order: F < B < T < C < A.

Agreement of the data of *Table 1* with the reactivity model of common electrophilic substitutions in condensed phase is extended as well to the positional selectivity of **1** in its attack to the ring positions of S. The ring-site selectivity of **1**, deduced from the isomeric distribution of the substituted biphenyls YBIP recovered in the liquid decay systems, must be regarded as a lower limit, owing to the possible occurrence of intramolecular isomerization processes *(e.g. Scheme 3)* of a fraction of the initially formed *ortho-* and *para*-substituted intermediates **3** to the *meta*-substituted isomer **5**, which is the thermodynamically most stable structure [13]. However, the negligible effects on the relative distribution of the tritiated phenylation products, observed by addition of the very powerful base (NH_3) to the liquid mixture, exclude the occurrence of the isomerization in the liquid samples at 25° to any significant extent. On these grounds, it is concluded that the isomeric distribution of YBIP in *Table 1* reflects the actual selectivity of **1** for the ring positions of S. An attempt to quantify the reactivity order of the selected arenes toward ring phenylation in the liquid phase is given in *Table 6*, which lists the phenylation partial rate factors referred to benzene, calculated in the assumption that formation of *o*-**3**, *m*-**3**,

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[5] An approximate estimate of the relative nucleophilicity of substituent groups can be provided by the gas-phase methyl-cation affinities of model compounds, such as CH_3CH_3, CH_3F, CH_3Cl, and CH_3OCH_3, carrying the groups in question. The methyl cation affinities of these model compounds, as defined in [10], increase in the order: CH_3CH_3 (< 50 kcal·mol^{-1} [8]) < CH_3F (59 kcal·mol^{-1} [11]) < CH_3Cl (64 kcal·mol^{-1} [12]) < CH_3OCH_3 (*ca.* 90 kcal·mol^{-1} [8]).

Scheme 3

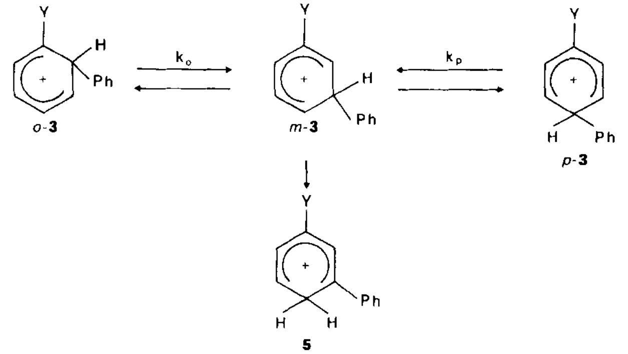
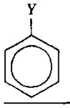


Table 6. *Partial Rate Factors for Attack of Phenylium Ions to the π-System of Liquid Arenes* ($T = 25°$)

Substrate 	Relative ring-phenylation rate $\beta = k_R/k_B$	Partial rate factors[a]) f_o	f_m	f_p
Y = F	0.5	0.7	0.3	1.1
Y = Cl	0.7	1.0	0.6	0.8
Y = Me	1.1	1.5	1.0	1.8
Y = MeO	2.5	4.9	1.0	3.3

[a]) $f_o = [\beta(\% \, o)] \times 3$; $f_m = [\beta(\% \, m)] \times 3$; $f_p = [\beta(\% \, p)] \times 6$.

and *p*-**3** by attack of **1** at the corresponding ring positions of S is rate-determining. The partial rate factors in *Table 6* are in substantial agreement with the classical *ortho-para* directing effects of the F, Cl, Me, and MeO groups in electrophilic aromatic substitutions. Thus, although deactivating, the Cl-atom is an *ortho-para*-directing substituent as well as F, which, however, results slightly activating at the *para*-positions, in agreement with the relevant σ^+ constants [13]. Other *ortho-para*-orienting substituents are the activating Me and MeO groups, which, however, have no net effects at the corresponding *meta*-positions, as shown by their f_m values of 1.0.

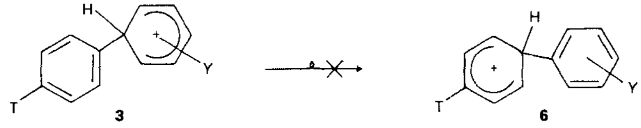
In contrast with the efficiency of collisional deactivation and neutralization of the primary excited ionic intermediates **2**, **3**, and **4**, observed in the liquid, the gas-phase picture is dominated by extensive isomerization and fragmentation processes affecting the primary excited adducts from attack of **1** on S. Such trend is well-documented by substantial decrease of the absolute yields of the tritiated aromatic products recovered in the gaseous systems at 100°, which is counterbalanced by a parallel increase of the yields of fragmentation products. Furthermore, the overall relative reactivity of the arenes toward the phenylation channel is significantly modified with respect to the liquid phase, as shown by the α factors of *Tables 2–4*, all ranging around 1.5–1.7, and the composition of isomeric YBIP is also shifted in favor of the *meta*-isomer, which becomes by far the most abundant (70–100%).

All such differences can be reasonably traced to the typical features of ionic processes in the gas phase at relatively low pressures. In these media, ion-molecule reactions are dominated by preliminary long-range electrostatic interactions, which lead to an encounter complex, characterized by an energy minimum on the potential energy surface, at a rate corresponding to the physical capture cross section. In agreement with the α factors in *Tables 2–4,* similar rate coefficients can be expected for reactions involving a given ionic species, such as **1**, and molecules such as the selected arenes with comparable polarizability and dipole momentum [14]. According to the comparatively large amounts of the labelled ST products recovered in the gaseous systems with respect to the liquid ones, it can be suggested that electrostatic interaction between **1** and the arene is characterized by an extensive attractive region around the Y substituent.

In the dilute gas state, the encounter complex, excited by the exothermicity of the ion-molecule electrostatic interactions, may unimolecularly dissociate into the products or, alternatively, rearrange itself to give a thermodynamically more stable isomer *(Scheme 3)* well before collisional quenching and neutralization take place. This accounts for the exceedingly high yields of the *meta*-YBIP isomers recovered in the gaseous mixtures, whose formation is favored at low pressures and in the absence of the added base, *i.e.* NH_3. It is, therefore, suggested that, after attack of **1** on the gaseous arene occurring at the encounter rate, the ensuing electrostatic adduct evolves to the isomeric σ-bonded intermediates **3** at individual rates following the inherent site selectivity of **1** shown in *Table 1*. Subsequent intramolecular isomerization of excited **3** to the most stable structure **5** profoundly modifies the isomeric distribution of the phenylated products, recovered in the gaseous decay samples.

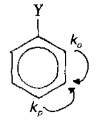
Observation of extensive intramolecular isomerization within the ring-phenylated intermediates **3** in the dilute gas state excludes the occurrence of alternative isomerization channels, including the conceivable transannular H transfer *(Scheme 4)*, even when energetically allowed (Y = F or Cl). Indeed, in contrast to experimental evidence, occurrence of the transannular H transfer *(Scheme 4)* to a significant extent would lead to the arenium ion **6** family, wherein the original positional relationship between the Y and Ph substituents of its immediate precursor **3** is maintained and cannot be further modified. Inadequate orientation between the C_{sp^3}–H bond and the π-orbitals of the tritiated Ph moiety of **3** may be responsible for the comparatively slow transannular H shift *(Scheme 4)*.

Scheme 4



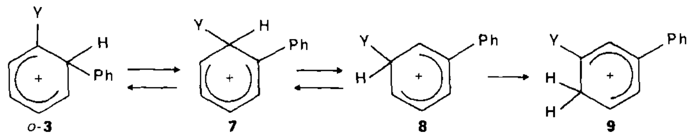
According to the isomerization pattern in *Scheme 4*, the apparent extent of the Ph-group intramolecular transfer within excited primary intermediates **3** (Y = F, Cl, Me), measured in the gas phase at 100° in the absence of NH_3 can be roughly estimated from relative yields of the *ortho*- and *para*-YBIP, when the phenylation reaction is carried out at 25° in the liquid phase in the presence of NH_3 or at 100° in the dilute gas phase in the absence of added bases. Under the latter conditions, the *ortho*- and *para*-YBIP decrease by factors that would reflect approximately the relative contribution ($k_o[3_o]$ *vs.* $k_p[3_p]$) of

Table 7. *Relative Intramolecular Isomerization Rate Constants* (T = 100°)

	Y	F	Cl	CH_3
	$\frac{k_o}{k_p}$	0.6 ± 0.2	1.1 ± 0.2	1.5 ± 0.4

the isomerization steps in *Scheme 3* to the population of the ionic precursor *m*-**3** of *meta*-YBIP. On these grounds, we can evaluate the apparent k_o/k_p rate constant ratios for each individual system, whose relevant figures are shown in *Table 7*. According to the reported figures, the relative tendency of excited **3** to undergo $o \to m$ (k_o) *vs.* $p \to m$ (k_p) Ph shifts increases in the order: F < Cl < Me. This may reflect both the particular effect of the substituent Y upon the positive charge distribution in the corresponding σ complexes **3** and the steric effect arising from the proximity of the relatively large Me and Cl groups when adjacent to a Ph moiety. An additional explanation can be found in the possibility that Me or Cl shifts may be involved in the isomerization pattern of excited **3** (*Scheme 5*). Of course, this contribution is expected to be more significant in *o*-**3** than in *p*-**3** and as the relative mobility of the Y group with respect to the Ph moiety increases. Possible occurrence of the process in *Scheme 5* (Y = Me), accompanying the major isomerization sequence in *Scheme 3*, is verified by analysis of the isomeric distribution of dimethylbiphenyls from attack of **1** on *para*-xylene in the gas phase at 100° (*Table 5*). Isolation of all isomeric biphenyls with the two Me groups on the unlabelled ring, other than the expected 2,5-isomer, indicates extensive Me transfers accompanying isomerization of the primary adducts. Ancillary radiolytic experiments, carried out by protonating 2,3-dimethylbiphenyl with $C_nH_5^+$ (n = 1,2) ions in the gas phase ($P(CH_4)$ = 50 Torr) at 100°, conclusively demonstrate that both Ph (2,3→3,4) and Me groups (2,3→3,4) participate in the isomerization pattern, with a relative efficiency exceeding 10.

Scheme 5



Comparison with Related Gas- and Condensed-Phase Studies. The results outlined in the previous sections provide a definite answer to the question concerning the competition between the nucleophilic centers of several aromatic compounds toward a specific phenylating reactant, the nuclear-decay formed 'free' phenylium ion **1**, in the liquid phase, in the absence of extraneous effects due to specific ion solvation and ion-counterion pairing, which may affect the intrinsic reactivity scale of the ionic electrophile. The conclusions reached in previous studies [2] [4] of a highly reactive phenylium ion **1** with a pronounced selectivity for the n- and π-type nucleophilic centers are confirmed in the present investigation. Thus, **1** displays a measurable substrate discrimination coupled with a distinct positional selectivity toward arenes, in the liquid phase at 25°, which contrasts with the lack of substrate selectivity observed in the gas-phase at 100°. This difference suggests that, while the gas-phase phenylation process is governed by the rate-determining formation of an electrostatic adduct [14], in the liquid phase the individual positions of the aromatic substrate compete for the electrophile in the rate-determining step. A further difference between aromatic phenylation in the gas phase and in solution is provided by the largely different efficiency in collisional deactivation and neutralization of the ionic intermediates, typical of the two phases. In fact, the population of the primary phenylated intermediates in *Scheme 2*, excited by the exothermicity of their formation processes well above activation energy for intramolecular proton, Ph, and Y (= Cl, Me) transfers, tends towards an equilibrium isomeric composition characterized by a predominance of ST and of the *meta*-isomer of YBIP, the extent of conversion depending on the time available for intramolecular isomerization, before collisional deactivation and neutralization take place. This accounts for the prevalent *ortho-para*-orientation in liquid-phase phenylation, where efficient collisional deactivation and fast neutralization helps to preserve the initial kinetic composition of the primary phenylated intermediates, and for the pressure, temperature, and base effects on the distribution of phenylated products observed in the gas-phase.

In the light of these conclusions, comparison of the present results with those of related investigation on gas-phase phenylation of alkylbenzenes [15], while revealing a substantial qualitative agreement between the two sets of experiments, allows us to point out some inconsistencies concerning the interpretation of the data given in [15]. Here, kinetic significance is attributed to a product composition, which refers to gas-phase experiments, wherein extensive isomerization and fragmentation profoundly alter the initial kinetic distribution of the primary ionic intermediates. As a consequence, no correspondence can be established between the relative reactivity of the individual positions of toluene toward attack of **1** and the relevant partial rate factors reported in [15] ($f_o = 1.61$; $f_m = 2.36$; $f_p = 1.64$), taking into account in addition that they refer to a phenylation process carried out in the gas phase, where the rate-determining step concerns the primary electrostatic adduct and not the σ-bonded intermediates **3**.

The present results concerning the liquid-phase experiments closely parallel those of solution-chemistry studies on related phenylation processes, especially if comparison is restricted to kinetic investigation of homogeneous and heterogeneous phenylation of arenes with benzenediazonium tetrafluoroborate [16]. A most intriguing difference is provided by the $f_m = 1.0$ values measured in the present study for toluene and anisole at 25°, which contrast with the appreciably lower ones ($f_m = 0.43$ (T and A) [16a] and $f_m = 0.85$ (T), $f_m = 0.48$ [16b]), measured at 60–66°. The $f_m = 1.0$ values, measured in the decay experiments in the liquid phase, indicate an equal activation for the *meta* positions of toluene and anisole and the positions of benzene toward electrophilic attack of a phenylium ion, as theoretically predicted. Therefore, the assumptions advanced in [16a,b], such as a I_π effect in the aromatic [17], the occurrence of a spirocyclopropane phenonium ion from insertion of a diradical phenyl cation [18] to an aromatic 'double bond', or nonstatistical distribution of the competing arenes in the liquid cage surrounding the phenylating reactant, are any longer required. In the light of the present data, the most likely explanation for the $f_m < 1$ value measures in [16a,b] remains a differential complexing ability of the competing aromatics by the BF_3 acid, liberated in the decomposition of benzenediazonium salt [16a], that, by modifying the relative proportions of uncomplexed arenes in the vicinity of the reactive ion, provides *apparent* rate-constant ratios unrelated to the intrinsic reactivity scale.

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