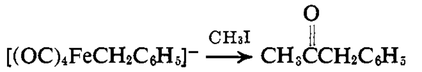
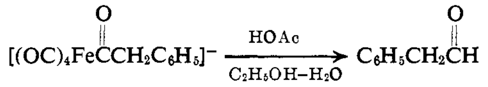
the utilization of these reagents in selective organic reactions.

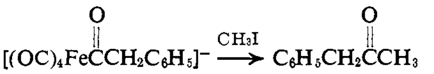
The isolation of these acyl and alkyl anions permitted us to demonstrate their role as intermediates in aldehyde and ketone syntheses, eq 1–3.[9]



$$[(OC)_4FeCH_2C_6H_5]^- \xrightarrow{CH_3I} CH_3\overset{\overset{\displaystyle O}{\|}}{C}CH_2C_6H_5 \qquad (1)$$



$$[(OC)_4Fe\overset{\overset{\displaystyle O}{\|}}{C}CH_2C_6H_5]^- \xrightarrow[C_2H_5OH-H_2O]{HOAc} C_6H_5CH_2\overset{\overset{\displaystyle O}{\|}}{C}H \qquad (2)$$



$$[(OC)_4Fe\overset{\overset{\displaystyle O}{\|}}{C}CH_2C_6H_5]^- \xrightarrow{CH_3I} C_6H_5CH_2\overset{\overset{\displaystyle O}{\|}}{C}CH_3 \qquad (3)$$

Acknowledgment. This work was supported by the National Science Foundation (Grant No. GP20273X). We are also indebted to D. Clark, R. G. Komoto, and S. R. Winter for assistance.

[9] The products were identified by their infrared spectra and 2,4-DNP derivatives. Yields from reactions 1, 2, and 3 were 75, 86, and 73%, respectively.

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Gas-Phase Aromatic Substitutions by Brominium Ions from the Isomeric Transition of ^{80m}Br

Sir:

The use of labeled, gaseous ions, such as HeT^+ and R^+, resulting from the nuclear decay of suitable tritiated precursors provides a unique tool for the study of electrophilic reactions in gaseous systems at atmospheric pressure,[1–4] and seems to fill to a certain extent the gap between solution chemistry and mass spectrometric methods.

We have now extended the scope of the research to another electrophile, the gaseous brominium ion, which can be conveniently obtained *via* the isomeric transition (IT) of ^{80m}Br (T = 4.4 hr). The chemical consequences of the IT of ^{80m}Br are unusually well known, and represent a typical example of the nuclear phenomena, which can be broadly described as "inner shell ionization."[5] In particular, the IT of ^{80m}Br contained in molecules such as CH_3Br is known to cause their instantaneous Coulomb explosion, giving rise to ^{80}Br ions with a preferred charge of +7.[6] When the decay occurs in a sufficiently large excess of a rare gas, having an ionization potential (IP) intermediate between the first and the second IP of Br, the charge of the daughter ions can be rapidly reduced to unity by charge-exchange processes,[7] while the excess kinetic energy (some electron volts) resulting from the explosion is taken away by unreactive collisions. The thermal $^{80}Br^+$ ion eventually obtained represents a valuable gaseous electrophile, whose products can be easily traced due to their radioactivity.

This communication presents the preliminary results of a study on gas-phase bromination of benzene, toluene, and the halobenzenes by brominium ions, resulting from the IT of ^{80m}Br in $CH_3{}^{80m}Br$. The methyl bromide was prepared by neutron activation of CH_3Br,[8] purified by preparative glc, and allowed to decay in a gaseous system containing typically 95 mol % Ar, 2.5 mol % of the substrate, and 2.5 mol % of the CH_3-^{80m}Br. After a reaction time of about 30 min, the products were rapidly separated with a 4-m Igepal CO-880 column at 120–150°, using a discontinuous radio gas chromatographic technique.[8,9] The yields of the products, *i.e.*, the ratio of their activity to the activity of the ^{80}Br daughter ions formed during the reaction, were calculated from the known initial activity of the $CH_3{}^{80m}Br$, the half-life of ^{80m}Br, and the reaction time, suitable corrections being allowed for the decay of the 17.6-min ^{80}Br. Half-life and γ-spectrometric measurements confirmed that the products were free from isotopic impurities, *e.g.*, ^{82}Br and the parent ^{80m}Br, indicating that their formation occurred exclusively *via* the daughter ions from IT. The isomeric distribution given in Table I was insensitive to the addition of radical (I_2, Br_2) and electron (SF_6) scavengers, providing evidence against a contribution from thermal Br atoms and radiolytic processes. In addition to the substitution products, $C_6H_5{}^{80}Br$ was also formed from all the substrates, its yields increasing in the order $C_6H_5F < C_6H_5$-$CH_3 < C_6H_5Cl$ (*cf.* footnote *a* of Table I) and decreasing at the highest concentrations of the moderator. However, in contrast to homolytic substitution by hot halogen atoms,[9–11] the yields from halogen for hydrogen substitution are generally higher than those from halogen for halogen substitution. Competition experiments gave an apparent $k_{toluene}/k_{benzene}$ value[12] of about 2, while the reactivity ratio of the halobenzenes was close to unity.[13] The following reaction scheme is suggested for the formation of the aromatic products.[14]

$$CH_3{}^{80m}Br \xrightarrow{IT} [^{80}Br]_{exc}{}^{n+} \xrightarrow[\text{many collisions}]{+\,Ar} {}^{80}Br^+ \qquad (1)$$

$$^{80}Br^+ + C_6H_5X \longrightarrow [C_6H_5X^{80}Br]_{exc}{}^+ \qquad (2)$$

$$[C_6H_5X^{80}Br]_{exc}{}^+ \longrightarrow \text{fragments} \qquad (3a)$$

$$[C_6H_5X^{80}Br]_{exc}{}^+ \xrightarrow{+M} [C_6H_5X^{80}Br]^+ + M^* \qquad (3b)$$

$$[C_6H_5X^{80}Br]^+ + C_6H_5X \longrightarrow C_6H_4XBr + C_6H_6X^+ \qquad (4)$$

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[7] In addition to compelling theoretical considerations, preliminary mass spectrometric data indicate that the charge of the $^{80}Br^+$ ions from the decay of $CCl_3{}^{80m}Br$ is effectively reduced to unity by the addition of Ar or Ne. No stable adduct could be formed from the reaction of multiply charged brominium ions with the substrate.

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[12] The toluene reactivity includes the contribution of the side chain (*cf.* Table I).

[13] Accurate data would require the knowledge of all the decomposition products, resulting from the fragmentation of the excited arenonium ions.

[14] A contribution from long-lived, excited states of the brominium ion cannot be completely ruled out.

Table I. Isomer Distribution from the Gas-Phase Attack of $^{80}Br^+$ Ions

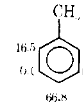
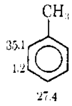
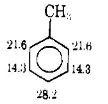
Substrate	Yields,[a] %			
C_6H_5F[b]	o-$C_6H_4FBr^*$, 28.8	m-$C_6H_4FBr^*$, 30.0	p-$C_6H_4FBr^*$, 41.2	
C_6H_5Cl	o-$C_6H_4ClBr^*$, 33.0	m-$C_6H_4ClBr^*$, 33.0	p-$C_6H_4ClBr^*$, 34.0	
C_6H_5Br	o-$C_6H_4BrBr^*$, 34.5	m-$C_6H_4BrBr^*$, 33.4	p-$C_6H_4BrBr^*$, 32.1	
$C_6H_5CH_3$	o-$C_6H_4(CH_3)Br^*$, 33.8	m-$C_6H_4(CH_3)Br^*$, 22.4	p-$C_6H_4(CH_3)Br^*$, 22.2	$C_6H_5CH_2Br^*$, 21.6

[a] Relative yields from several individual runs, whose standard deviation is about 10%. The absolute yields (in per cent of the total ^{80}Br daughter ions formed) are the following: o-, m-, p-$C_6H_4{}^{80}BrF$ = 2.83%; o-, m-, p-$C_6H_4{}^{80}BrCl$ = 1.90%; o-, m-, p-$C_6H_4{}^{80}BrBr$ = 0.81%; o-, m-, p-$C_6H_4{}^{80}Br(CH_3)$ = 4.23%. The ^{80}Br-labeled bromobenzene yields are 0.38 for fluorobenzene, 0.67 for chlorobenzene, and 1.16 for toluene. In addition, ^{80}Br-labeled methylene bromide was formed in all systems, with yields ranging from 2 to 6%. The unidentified ^{80}Br activity is mainly contained in inorganic products ($^{80}BrBr$, $H^{80}Br$). [b] The gaseous system was kept at 760 Torr and at room temperature for C_6H_5F and $C_6H_5CH_3$, at 50° for C_6H_5Cl, and at 65° for C_6H_5Br; composition: 95 mol % Ar, 2.5 mol % C_6H_5X, 2.5 mol % $CH_3{}^{80m}Br$.

While $\Delta H°$ values of the arenonium ions are not known, the exothermicity of the overall process including steps 2 and 4 can be roughly estimated around -80 kcal mol^{-1} for X = H, and -95 kcal mol^{-1} for X = CH_3,[15-17] as compared to -113 and -115, respectively, in the case of HeT^+.

As a whole, the reactivity of the $^{80}Br^+$ ($\Delta H° = 300$ kcal mol^{-1}) is comparable to that of HeT^+ ($\Delta H° = 323$ kcal mol^{-1}) and related reagents[18] such as D_2T^+ ($\Delta H° = 256$ kcal mol^{-1}), showing the typical features of a gas-phase electrophilic attack. The positional selectivity is very low by solution chemistry standards as shown in the case of toluene by the data of Table II. On the other hand, a measurable ortho–para orientation characterizes the bromination, as the tritiodeprotonation, of toluene and the halobenzenes. The two reactions differ in some respects, as the $^{80}Br^+$ attack on toluene gives rise to higher yields of side-chain substituted products and to a more extensive replacement of the substituent group. Furthermore, the ortho : para ratio in the bromination of the halobenzenes increases in the order $C_6H_5F < C_6H_5Cl < C_6H_5Br$, despite the increasing bulk of the substituent, in significant agreement with the trend prevailing in solution. However, apart from these differences, probably arising from the different exothermicity of the attack, and the different ability of bromine and tritium to undergo fast intramolecular shifts within the excited arenonium ion, the $^{80}Br^+$ attack retains the main feature of tritiodeprotonation, *i.e.*, the unusual correlation between *positional* and *substrate* selectivity illustrated by the lack of discrimination between benzene and the halobenzenes, in contrast with the para : 0.5 meta ratio $\simeq 2$ characteristic of the latter substrates.

Table II. Comparison of Solution and Gas-Phase Bromination of Toluene

	Solution		Gas phase
	Molecular bromination[a]	Positive bromination[b]	Unsolvated positive bromination *via* $CH_3{}^{80m}Br \xrightarrow{IT} {}^{80}Br^{n+} \xrightarrow{Ar} {}^{80}Br^+$
			
$\dfrac{k_{C_6H_5CH_3}}{k_{C_6H_6}}$	605	36	2.1

[a] H. C. Brown and L. M. Stock, *J. Amer. Chem. Soc.*, **79**, 1421 (1957). [b] P. B. D. de la Mare and J. T. Harvey, *J. Chem. Soc.*, 36 (1956).

The present results suggest that the gas-phase electrophilic attack involves two kinetically distinct steps, *i.e.*, the preliminary formation of a reagent–substrate complex, which determines the *intermolecular* selectivity, followed by the competition of the individual reaction centers for the electrophile, which regulates the *intramolecular* selectivity. The suggestion is reminiscent of the π-complex theory of Olah,[19] whose extension to the gas phase was been actually proposed in recent mass spectrometric[20] and radiolytic[21] studies. However, taking into account the physical features of the ion–molecule interaction in the gas phase, we are rather inclined to extend to the $^{80}Br^+$ attack the model recently suggested for the tritiodeprotonation,[18] based on the intervention of a long-lived ion–molecule complex, whose formation requires no activation energy, depending on long-range electrostatic interactions. The forces that determine the formation of the complex, and therefore the competition of different substrates for the electrophile include, according to a recent treatment by Dugan and Magee,[22] and Dugan and Rice,[23] ion–dipole and ion–induced-dipole interactions, whose relative contributions depend, *inter alia*, on the permanent dipole and the electronic polarizability of the substrate. At large ion–molecule separations the ion–dipole term predominates, *irrespective of the sign of the dipole*,[24] which can help explain how substrates with an appreciably permanent dipole, like halobenzenes, successfully compete with benzene, despite the fact that the

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(24) The interaction potential is given by the expression

$$-V = \frac{\mu e \cos \gamma}{4\pi\epsilon_0 r^2} + \frac{\alpha e^2}{8\pi\epsilon_0 r^4}$$

where r is the separation, γ the angle between the dipole (negative end) and the separation vector, and α and γ the permanent dipole and the polarizability of the substrate, respectively. Owing to the molecular rotation, cos γ changes during the interaction yet its mean value remains positive at significant separations (*cf.* ref 23).

negative end of the dipole points away from the ring, which causes a severe deactivation in solution. Once trapped into the "electrostatic cage," the electrophile attacks the individual reaction centers according to competitive processes, characterized by activation energies determined by the electron density at the reaction site, which depends, in turn, on inductive and mesomeric factors analogous to those invoked to explain the selectivity of conventional electrophilic substitutions.

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Stereochemistry of the Nucleophilic Substitution of Vinylic Bromides with Copper

Sir:

Organometallic compounds undergo alkylation and it was shown[1] that Co(I) acts as a nucleophile in an S_N2 reaction which proceeds with inversion of configuration at the attacked carbon. The coupling of arylcopper,[2–5] vinylcopper,[3,4] and alkylcopper[3,5] compounds with alkyl and vinyl halides was explained[3,5] as involving the formation of "ate" complexes[6] by a nucleophilic substitution at carbon in the first step of the reaction, followed by a coupling of the carbons linked to the copper in the "ate" complex. Such a coupling was demonstrated[7] to proceed with retention of configuration in vinylic compounds.[7] The inversion of configuration observed in the coupling of diphenylcopper lithium with (−)-2-bromobutane was interpreted as an inversion during the process of the nucleophilic substitution of bromine with copper, followed by coupling with retention of configuration. There is, however, no proof for the nucleophilic substitution of bromine by copper, since the carbon linked to copper in the "ate" complex has enhanced nucleophilic character[4,8–11] and a direct substitution by carbon is possible.

We report now that nucleophilic substitution of a vinylic bromine with copper proceeds with retention of configuration.

Table I. Reactions of Dimethylcopper Lithium with Vinylic Bromides[a]

Substrate	Temp, °C (*t*, hr)[b]	Products (% of total product)
I	−80 (5)	III (23); V (77)
II	−80 (0.5)	IV (5); VI (95)
IX	−80 (3)	XI (13); XIII (87)
X	−80 (0.5)	XII (5); VI (95)
X[c,d]	−100 (0.5)	XIV (20); X (80)
I[e]	−80 (20)	III (25); V (13); VII (62)
IX[e]	−80 (3)	XI (11); XIII (12); XV (77)
IX[e]	−80 (3); 20 (18)	XI (15); XIII (6); V (6); VII (73)
XVII	−5 (1.5)	XIX (65)[f]
XVIII	−80 (1.5)	XX (90)[f]
XXI	−5 (0.5)	XIX (31); XXIII (41)[f]
XXI	−5 (2)	XIX (68); XXIII (5)[f]
XXII	−80 (0.5)	XX (83); XXIV (12)[f]
XVIII[e]	−80 (1.5)	XXV (90)[f]

[a] A 0.5 *M* ethereal solution (4.0 ml) of the substrate was injected slowly with a syringe into a 0.25 *M* ethereal solution (40 ml) of dimethylcopper lithium which was stirred in a bath kept at the temperature indicated. The reaction products were treated with acidified water at the reaction temperature. Analysis of the products was by nmr. The yields of the reactions were higher than 85% except for the reactions with methyl α-bromocrotonates (about 50% yield). [b] Temperature and duration of the reaction with $(CH_3)_2CuLi$. [c] The reaction was decomposed with methanol at the reaction temperature before being treated with acidified water. [d] This reaction was carried out using a ratio of $X/(CH_3)_2CuLi$ = 1/1.4. [e] The reaction product was treated with acidified D_2O at the temperature of the reaction. [f] Other unidentified products were also formed.

trans-α-Bromocinnamic acid (I)[12] reacted with dimethylcopper lithium at −80° (Table I) to give, after treatment of the reaction product with acidified water, *trans*-α-methylcinnamic acid[13,14] (III) and *trans*-cinnamic acid (V). Similarly, methyl *trans*-α-bromocinnamate (II) gave methyl *trans*-α-methylcinnamate (IV) and methyl *trans*-cinnamate (VI). Treatment of the reaction mixture from I with acidified D_2O instead of water yielded the α-deuterated *trans*-cinnamic acid (VII). A similar reaction performed on *cis*-α-bromocinnamic acid (IX) gave the corresponding *cis*-α-methylcinnamic acid[15] (XI) and *cis*-cinnamic acid (XIII), both with retention of configuration. Again, treatment of the reaction mixture from IX with D_2O gave the α-deuterated *cis*-cinnamic acid (XV), proving that cinnamic acids are formed from organometallic intermediates. The organometallic compound XVI is not configurationally stable at room temperature in the presence of excess copper reagent. Such an isomerization of an α-vinylic copper derivative of a cinnamic acid has been observed before, with methyllithium.[9]

Treatment of methyl *cis*-α-bromocinnamate (X) with dimethylcopper lithium gave, under the conditions of the reaction used with the acid IX, methyl *trans*-cinnamate (VI) with inversion, and also the α-methyl derivative XII with retention of configuration. The trans ester resulted from an isomerization process, since at −100° some of the cis ester XIV was also obtained. Confirmation for this process was obtained on using a

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(14) Nmr (CCl_4) δ 12.0 (COOH), 7.8 (=CH), 7.4 (C_6H_5), 2.15 (=CCH_3, doublet, *J* = 1.5 Hz).

(15) Nmr (CCl_4) δ 12.0 (COOH), 7.5 (C_6H_5), 6.8 (=CH), 2.15 (=CCH_3, doublet, *J* = 1.5 Hz). This compound was previously (ref 16) assigned the trans configuration.

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