independently or related by symmetry to another bond, the results are internally consistent in all cases and can only be compared in pairs. That is, naphthalene (XI) and our compound (VII) fall into one class, having either no annelation or symmetrical annelation at both sides, while III and IV are fused at a single side of the naphthalene nucleus. Note that our measured values of g, h, i, and j are statistically identical, as would be expected for this molecule. In all four cases our measured values are somewhat larger ($\sim 3\sigma$) than those found by Cruikshank and Sparks[14] for naphthalene, which would be predicted for a small increase in the double-bond order at bonds a, c, d, and f of our compound (VII). In all the annelated systems, bond k is larger than that observed in naphthalene.

Finally, excellent agreement is also found between the cyclobutene moiety of VII and the analogous portions of similar molecules.[1,14,21,22] The shared bond is invariably longer when the fusion is to a naphthalene group, as opposed to a benzene group. Since the saturated C-C bond lengths are essentially the same in all cases, this results in necessarily smaller internal angles adjacent to the points of fusion in the cyclobutene group for IV and VII. Slightly longer bonds C(3)-C(4) and C(5)-C(6) are noted in VII than in all the other studies, but the reason for this is not apparent. In all cases, the shared bond is considerably longer than the value of 1.33 Å determined by gas phase electron diffraction for the double bond of cyclobutene.[23]

No unusually short intermolecular contacts are noted in VII. The planarity of the molecule allows for close packing in the lattice, as can be seen in Figure 2, and may account for trends found in the melting point behavior of the substituted naphthalenes and benzenes.[2]

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Liquid-Phase Reactions of Free Methyl Cations from the Decay of Methane-t_4. Alternative Alkylation Sites in Halobenzenes

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Abstract: The reaction of free methyl cations, generated from the decay of multitritiated methane dissolved in liquid halobenzenes, gives the corresponding labeled halotoluenes together with methyl halides, toluene, and minor amounts of decomposition products. The attack of the reagent on the n-type nucleophilic centers displays a remarkable selectivity, following the trend $\mathrm{Br} > \mathrm{Cl} > \mathrm{F}$, in agreement with the HSAB principle. Ring alkylation is characterized by an appreciable positional selectivity, which is in contrast with the scarce substrate discrimination. The reactivity ratios deduced from the competition experiments depend on the composition of the system, the selectivity of the reagent increasing with the concentration of halobenzenes. This trend is explained by the intervention of methylphenylhalonium ions, which, besides being intermediates for the formation of methyl halides, are also methylating agents and are more selective than free methyl cations.

The reactivity of electrophilic carbon toward aromatic substrates has been the object of continued interest for many years. Depending upon the experimental conditions (the reagent, the medium, the catalyst etc.), a large variety of alkylating species were either postulated or identified as responsible for the attack on the aromatic substrate.[1] Terms such as polarized molecules, polarized complexes and ion pairs,[2] and incipient and "hot" carbonium ions[3] were coined to describe reagents where carbon electrophilicity is promoted by the use of poorly solvating media[4] and methods favoring the formation of charged species as free of external influence as possible in solution.

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Since the major uncertainties affecting these classical studies concern the degree of ionization, the extent of solvation, and ion pairing of the "charged" reagent, it appeared useful to investigate the reactivity of free carbocations bearing a +1 charge, spontaneously and randomly generated within homogeneous aromatic substrates, in the absence of any counterions. This can be accomplished with a nuclear technique, based on the β decay of a constituent atom in a multitritiated precursor, dissolved in trace concentration within the liquid substrate.

The present paper describes the behavior of one such powerful reagent, the methyl cation, freed in solution by the decay of multitritiated methane and allowed to react with typical substrates such as fluoro-, chloro-, and bromobenzene, which bear both π and n nucleophilic centers. This approach leads to formation of carbonium ions that display conceivably no memory with respect to antecedents, since the leaving group is a ^{3}He atom and the counterion is represented by a far-removed electron. The method is also suitable for generating *exactly the same* ionic reagent independent of the environment and therefore for establishing *experimental* correlations between gas-phase and solution behavior of a given reagent–substrate pair.

Experimental Section

Materials. Methane-t_4, used as a precursor of the methyl cations, was prepared according to Cacace et al.[5] The isotopic composition was measured by radio gas chromatography and mass spectrometry, and corresponded to 60.4% CT_4, 29.4% CT_3H, 8.1% CH_2T_2, and 2.0% CH_3T, with a standard deviation of 1%.

The aromatic compounds employed either as substrates or as standards in the gas chromatographic analyses were research-grade chemicals from Merck A. G. and were used without further purification.

Preparation of the Samples. The liquid samples were prepared by dissolving 0.6 mCi of tritiated methane, diluted with inactive CH_4 to a specific activity of 0.22 Ci/mmol, into 2 mL of the carefully degassed substrate(s).

The solutions were stored in the dark at 22 °C for 8–10 months in Pyrex vials, equipped with a capillary arm closed by a mercury plug in order to eliminate any gas bubbles within the system.

Analysis of Products. The liquid samples were degassed at low temperature and washed with inactive methane to remove the undecayed CT_4 and other gases. A Hewlett-Packard Model 7620 gas chromatograph, equipped with a hot-wire detector in series with a 10-mL internal-flow proportional counter, heated at 120 °C, was used for the analyses. The GLC separations were carried out using helium as a carrier gas, the activity of the effluents being monitored by employing a CH_4/He 1:1 counting-gas mixture, obtained by adding a methane makeup flow to the outlet of the hot-wire detector.

A correction factor was applied to the counter response for the halobenzenes, present in bulk, to allow for their appreciable quenching. The appropriate calibration curve was determined by monitoring the counter signal from an external radiation source as a function of the amount of each halogenated compound.

The total activity of the crude reaction mixtures was independently measured with a Packard Tri-Carb scintillation spectrometer.

The mixtures were fractionated on three different 5-mm i.d. gas chromatographic glass columns: (A) 12-m Bentone 38 (6%) + silicon oil DC 200 (20%) on Chromosorb W-AW-DMCS, 60–80 mesh; (B) 12-m 4,4′-azoxydianisole (20%) on Chromosorb W-AW-DMCS, 60–80 mesh; (C) 8-m tricresyl phosphate (20%) on Chromosorb W-AW-DMCS, 60–80 mesh.

The separations on column B, which contained a liquid-crystal phase, were obtained by heating the oven of the gas chromatograph at 135 °C, then allowing the temperature to slowly decrease to 90 °C.

The products from the reactions of fluorobenzene and its mixtures with toluene were fractionated on columns A, (at 130 °C) and B. The former column resolved all the products except the isomeric fluorotoluenes, and the latter separated *m*- and *p*-fluorotoluene, but not toluene, from *o*-fluorotoluene. Combination of the two separations allowed complete resolution of the mixture.

In the case of chlorobenzene, columns A at 140 °C, B, and C at 118 °C were used; neither A nor B could achieve separation of chlorobenzene from *o*-xylene, which required column C. This column, however, did not resolve the pairs *m*-/*p*-xylene and *m*-/*p*-chlorotoluene.

Full resolution of the products from bromobenzene was achieved with columns A and B.

Results and Discussion

Nature of the Reagent. Labeled methyl cations were formed, as reported earlier,[6–9] from the spontaneous decay of a tritium atom contained in a CT_4 molecule giving a 82% yield, largely independent of the environment. The activity balance was provided by molecular tritium (6%) and by reactive fragments as CT_2^+, CT_2, CT^+, T^+, T, and HeT^+. The CT_3^+ ions were expected to be formed in their electronic ground state and to have no appreciable translational energy, whereas they might be in a vibrationally excited state whose upper energy limit can be estimated at 32 kcal mol^{-1}.[8] The low specific activity level employed in the present study makes the contribution of radiolytic processes to the formation of labeled products safely negligible. Therefore, the activity observed in the products was essentially due to the reactions of the decay fragments with the substrate(s). Any contribution from the reactions of ionic intermediates with tritiated methane was practically negligible, due to the very low concentration of the labeled precursor within the liquid system.

The *absolute yields,* expressed as the ratio of the total activity recovered in the end products to the activity originally contained in the decay-produced methyl cations, were well reproducible and amounted to 57 ± 4% for all systems investigated.[10] Furthermore, the total activity of the crude reaction mixture, measured by liquid scintillation spectrometry, closely matched the combined activity of the individual products identified by radio GLC. This showed that high-boiling labeled products, such as polymers, etc., are not formed in appreciable yields. The activity balance must therefore be accounted for by some gaseous products removed from the system together with the undecayed CT_4 by the degassing procedure.

Conceivably, there are at least two "blind" (i.e., not leading to labeled final products) exothermic reaction channels which could account for the activity loss, namely, electron transfer (eq 1) and hydride ion abstraction reaction (eq 2).

$$CT_3^+ + C_6H_5X \longrightarrow CT_3 + C_6H_5X^+ \qquad (1)$$

$$CT_3^+ + C_6H_5X \longrightarrow CT_3H + C_6H_4X^+ \qquad (2)$$

$$(X = F, Cl, Br)$$

Reaction 1 would lead to the *inactive* aromatic molecular ion and to CT_3 radicals, whose contribution, if any, to the identified products should be negligible, since no significant difference in the absolute yields of end products has been observed in the presence of increasing toluene concentrations. Since toluene is known[11] to trap methyl radicals efficiently by fast and quantitative H atom abstraction giving benzyl radical and CT_3H, the yields are expected to depend markedly on the toluene concentration if any radical channel were to contribute appreciably to formation of the products.

On the other hand, hydride-ion abstraction (eq 2) may well account for the formation of gaseous products, in particular partially tritiated methanes,[12] together with fragmentation of excited intermediates (vide infra).

From a comparison between the experimental yields (57% × 0.82 = 47%) and the overall activity of those decay fragments which could react with the aromatic compounds to yield methylated products, e.g., CT_2, CT_2^+ ($\leq$5%,) it can be concluded that *CT_3^+ is the major source of the measured radioactive products.* Even if one makes the extreme assumption that all activity in CT_2 and CT_2^+ species leads to observed

Table I. Tritiated Products from the Reaction of CT_3^+ Decay Ions with Halobenzenes (C_6H_5X, X = F, Cl, Br) in the Liquid Phase

X	rel yields of products[a] (activity %)						isomeric composition of halotoluenes, %		
X	methyl halide	benzene	toluene	halobenzene	halotoluenes	unidentified products[b]	ortho	meta	para
X = F	0.4	0.5	0.7	13.8	78.4	6.2	44.3	22.3	33.4
	0.1	0.3	0.7	13.5	78.7	5.9	43.8	23.1	33.1
X = Cl	6.1	2.3	8.6	12.9	70.2		39.4	24.1	36.5
	6.2	1.9	8.6	12.2	71.3		40.8	24.5	34.7
X = Br	29.6	3.7	11.7	4.6	50.2		40.3	25.0	34.7
	24.6	3.6	12.2	6.3	53.3		41.1	25.5	33.4

[a] Expressed as a percentage of the total activity recovered in the isolated products. Standard deviation of data, ca. 10%. [b] The reported activity corresponds to two unidentified adjacent peaks, whose retention times on both GC columns employed are greater but very close to that of the *p*-fluorotoluene, i.e., the last eluted isomer.

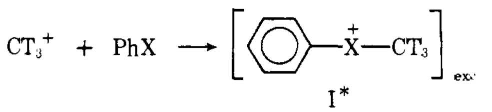
products, their maximum contribution would be of the same order of magnitude as the experimental error (ca. 10%).

Reactions of Methyl Cations with the Halobenzenes. Table 1 gives the yields of the products from the decay of tritiated methane in the presence of the halogenated aromatic substrates. The yields are expressed as percentage of the total activity recovered in the products and represent the average of at least three runs, with a standard deviation of ca. 10%.

The bulk of the recovered activity was essentially contained in the methylated products, including the halotoluenes, the methyl halides, and toluene itself which experimentally confirms that methyl cations are indeed the predominant reactive species among the decay fragments. The identified products showed that the substrates behave as ambident nucleophiles, offering both π and n centers to the attack of the charged electrophile, whose selectivity depends on the nature of the halogen substituent.

An interesting feature, not directly evident in traditional Friedel-Crafts alkylations, is the attack of the reagent on the halogen atoms, leading eventually to the corresponding methyl halides.

The actual isolation of these products suggested the formation of the intermediate halonium ion (I) where bond formation takes place between the methyl carbon and the halogen substituent (eq 3).



I*

(3)

In principle, ions 1, excited by the exothermicity of the attack,[12] could either directly decompose to yield methyl halides and phenyl cations

$$I^* \rightarrow CT_3X + Ph^+ \quad (4)$$

or, especially in the liquid phase, undergo collisional stabilization and, eventually, nucleophilic displacement by another molecule of the substrate, present in large excess.

The appreciably lower yields of methyl halide, especially MeBr, from gas-phase experiments,[12] under conditions where dissociative processes are favored, do not indicate any relevant contribution of reaction 4. The formation of methyl halides therefore is likely to take place via a bimolecular process, involving displacement of the CT_3X moiety of ion I by a nucleophile, which in the present case is the halobenzene itself (eq 5).[13]

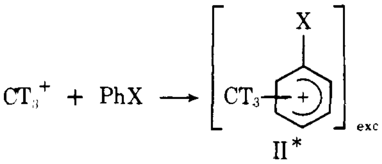
$$1 + PhX \rightarrow CT_3X + Ph_2X^+ \quad (5)$$

The displacement of the PhX moiety which occurs in competition with reaction 5 will be discussed in the following section.

In this connection, Olah and Melby[14] have already provided direct evidence for the formation of methylphenylbromonium ions, similar to 1, in methyl fluoroantimoniate-SO_2 solutions, and suggested their role as alkylating intermediates in Friedel-Crafts reactions.

The attack of the free methyl cations on the halogen substituent is characterized by the reactivity order F $\ll$ Cl < Br, which finds an interesting rationalization in the HSAB principle,[15] in that it can be associated to the softness scale of the halogen-atom bases, considering that CH_3^+ represents the *softest* positively charged carbon acid.

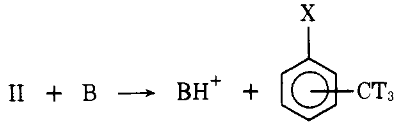
It is suggested that formation of the halotoluenes, the major labeled products, involves primary attack of the methyl cations on the aromatic ring (eq 6).[16]



II*

$\Delta H_6^\circ \simeq -80$ kcal mol^{-1} (6)

The excited arenium ion II*, following collisional deactivation, eventually loses a proton to a base, e.g., another substrate molecule.

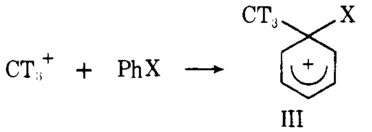


(7)

The isomeric composition of the halotoluenes, given in Table 1, is rather independent of the nature of the halogen substituent and characterized by a predominant ortho-para orientation. Since partial isomerization of the highly excited arenium ions II cannot be excluded, the observed para:meta ratio of ca. 3:2 must be regarded as a *lower limit* of the positional selectivity of the free methyl cation in its liquid-phase attack on halobenzenes.

The formation of toluene, which represents the other product bearing the labeled methyl group, finds analogy in the methyldemethylation[8] and methylde-*tert*-butylation[9] processes observed in the liquid-phase reaction of the CT_3^+ cation with toluene and *tert*-butylbenzene. The relative yields of toluene from the halobenzenes are higher in the liquid than in the gas phase[12] and follow the trend PhF $\ll$ PhCl < PhBr.

In agreement with the mechanism suggested by Speranza and Cacace[17] for the gas-phase protodehalogenation of halobenzenes, formation of toluene may be traced to the attack of the decay ions on the ring position bearing the halogen atom.



III

(8)

Among the many conceivable routes leading from III to toluene, the halogen cation (X^+) transfer (eq 9) to another

Table II. Tritiated Products from the Reaction of CT_3^+ Decay Ions with Toluene/Halobenzene (C_6H_5X, X = F, Cl, Br) Mixtures in the Liquid Phase

	system composition,[a] mol %		rel yields of products[b] (activity %)							
	halobenzene	toluene	methyl halide	benzene	toluene	halobenzene	unidentified products	ethylbenzene	xylenes	halotoluenes
X = F	9	91	≤0.2	0.4	14.8	1.3	2.3	5.8	71.7	3.5
	50	50	0.5	0.5	8.4	6.4	5.3	1.1	57.3	20.5
	91	9	1.1	0.8	2.2	12.6	6.3		19.1	57.2
X = Cl	9	91	1.3	0.7	14.9	0.8	1.6	4.9	71.3	5.0
	50	50	2.3	1.3	13.4	5.0	1.0	2.8	53.6	21.2
	91	9	5.4	1.8	9.7	10.3			19.6	53.1
X = Br	9	91	5.7	0.9	16.8	0.8		5.1	66.4	4.4
	50	50	13.5	2.0	16.2	4.2		1.8	46.2	16.1
	91	9	22.1	3.0	12.4	5.0			15.5	42.7

[a] The systems contained 2.7 mmol of methane dissolved in 2.0 mL of the liquid substrates. [b] See Table I.

Table III. Isomeric Composition of Products from Liquid-Phase Competitions

	system composition, mol %		isomeric composition of products, %						apparent rel rates of ring methylation[a]
			xylenes			halotoluenes			
	PhX	$PhCH_3$	ortho	meta	para	ortho	meta	para	
X = F	9	91	41.0	27.3	31.7		not measured		0.49
	50	50	39.1	26.4	34.5	48.0	23.3	28.7	0.36
	91	9	38.6	26.0	35.4	43.0	26.1	30.9	0.30
X = Cl	9	91	43.2	26.2	30.6	44.6	22.5	32.9	0.67
	50	50	42.9	26.7	30.4	43.0	24.0	33.0	0.38
	91	9	43.4	25.0	31.5	42.4	23.4	34.2	0.26
X = Br	9	91	41.3	58.7			not measured		0.66
	50	50	42.1	57.9		40.7	25.1	34.2	0.35
	91	9	39.0	61.0		40.7	27.4	31.9	0.28

[a] Calculated as ($[C_7H_8]/[C_6H_5X]$) ($XC_6H_4CT_3$ activity/$C_6H_5CT_3$ activity).

Table IV. Overall Reactivity of Halobenzenes Relative to Toluene in Competition Experiments

PhX/$PhCH_3$	rel reactivity[a] F	Cl	Br
0.1	0.40	0.72	1.40
1.0	0.32	0.45	0.67
10	0.29	0.32	0.45

[a] Calculated as follows: ($[PhCH_3]/[PhX]$)[(activity of methylated products from PhX)/(activity of methylated products from $PhCH_3$)].

substrate molecule accounts for (1) the higher toluene yields in the liquid compared to the gaseous phase, owing to the expected predominance of intermolecular processes over unimolecular fragmentation, and (2) the observed reactivity trend, reflecting the energy scale for heterolytic C–X bond breaking, i.e., F ≫ Cl > Br.

$$\mathrm{II} + \mathrm{PhX} \rightarrow \mathrm{PhCT_3} + \mathrm{C_6H_5X_2^+} \quad (9)$$

The yields of the labeled substrate and of benzene are too low to allow any correlation with dissociation processes involving the methyl cations, since these products could also arise from the reactions of other parasitic species formed from the decay of methane.

Halobenzenes–Toluene Competitions. In order to evaluate its substrate selectivity, the reagent was allowed to react with mixtures of the individual halobenzenes with toluene. The relative yields of products are reported in Table II.

Toluene was used in the place of benzene as a reference compound to evaluate simultaneously both the substrate selectivity and the isomeric composition of the products. Use of benzene would lead to the formation of large amounts of labeled toluene from direct alkylation, thus obscuring the formation of the same product from the methyldehalogenation reaction of the halobenzenes.

Table III shows the isomeric compositions of the halotoluenes and of the xylenes formed, together with the apparent relative rates of alkylation measured at different ratios of the aromatic substrates.

In the following discussion, the *overall reactivity* of the aromatic substrates toward the methyl cation is defined as the sum of all channels leading to products containing the labeled methyl group. For its evaluation, the contribution from each of the competing partners towards the yield of toluene must be taken into account. Since the activity of C_7H_8 formed is found to depend linearly on the molar fraction of toluene, this separation could be accomplished by linear regression analysis of the data. The calculated yields of toluene from toluene itself are in good agreement with those from benzene–toluene competitions,[8] indicating that this reaction channel is reasonably independent of the competing partner.

Table IV summarizes the overall reactivity of the halobenzenes relative to toluene, at various system compositions. It is apparent from the data that the overall substrate reactivity follows the order PhBr > PhCl > PhF, and is strongly dependent on the system composition, the apparent reactivity of toluene increasing at low $[C_7H_8]$ values.

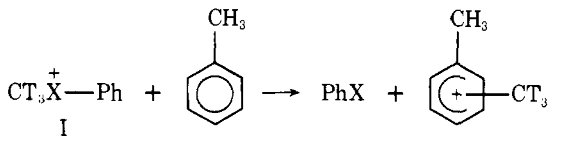
Comparison with the data of Table II shows that the appreciable difference among the reactivities of halobenzenes is largely determined by the different reactivities on the "n" centers and, less significantly, by the methyldehalogenation channel. On the contrary, the concentration dependence is the same as for competitive ring methylation shown in the last column of Table III, supporting the occurrence of some kind of coupling between the alkylation channels of halobenzenes and toluene.

The observed trend suggests a gradual rise in the substrate selectivity of the reagent as the concentration of halobenzene increases, the effect being more pronounced for bromo- and chloro- than for fluorobenzene.

Simple transalkylation between haloarenium ions II and toluene would instead be expected to favor the more activated toluene when its molar fraction is greater, and would not markedly depend on the nature of the halogen substituent, in contrast with the experimental findings.

The intervention of methylarylhalonium ions I, on the contrary, can explain, at least on qualitative grounds, the observed effects of the relative concentration of substrates and the nature of the substituent.

In fact, ions I, apart from the methyl halide nucleophilic displacement eq 5, are known from solution-chemistry studies[14] to undergo irreversible alkylation of the aromatic ring via reaction 10, and therefore are likely to represent a methylating reagent more selective than the free methyl cation, thus favoring toluene alkylation.



I

(10)

Their contribution becomes more relevant at high halobenzene concentrations and, in addition, is expected to fit the observed trend Br > Cl > F.

Apart from the observed reactivity variations with the molar ratios of the competing aromatic compounds, the methyl cation displays a remarkably low substrate selectivity, as indicated by the apparent rates of alkylation relative to toluene, that never exceed a value of 0.7. Although the competition experiments do not allow establishment of a reactivity scale for the direct ring alkylation of the halobenzenes by the free methyl cation, owing to the concurrent alkylation by halonium ions, the absolute halotoluene yields in neat halobenzene indicate a PhF:PhCl:PhBr reactivity ratio of 1.5:1.3:1. These figures are comparable, although lower, with those measured for other strong alkylating agents, e.g., in the $GaBr_3$-catalyzed ethylation of the same substrates in $C_2H_4Cl_2$, yielding the ratio 2.1:1.6:1.[18]

The isomeric composition of the xylenes and of the halotoluenes from the competition experiments is essentially the same as from the neat substrates, indicating that positional selectivity is less affected than substrate selectivity by the nature of the alkylating species.

These findings suggest that the factors influencing the substrate selectivity can be treated separately from those determining the isomeric composition of the products, i.e., the formation of the σ complexes.

In the present case, where the extremely reactive electrophile is randomly generated "in situ" within a large excess of liquid aromatic compounds, the reaction obviously occurs in the absence of macroscopic diffusion or mixing effects.[19] On the other hand, the nature of the reagent, free of a counterion and essentially unsolvated,[7-9] lends support to the possibility that the substrate selectivity largely reflects the relative rate of formation of the encounter complexes with the competing aromatic compounds, i.e., is simply determined by the capture cross section of the substrate for the methyl cation. Furthermore, the overall substrate reactivity is deeply influenced by the direct attack of the electrophile on the halogen atom, in close analogy with the appreciable gas-phase reactivity of many gaseous cations toward n centers such as the oxygen atoms of phenol and anisole,[20,21] and the halogen atom of the halobenzenes.[17]

The present liquid-phase results display surprising analogies with those of gas-phase aromatic substitutions by charged electrophiles, that are generally characterized by low substrate selectivity, which is in contrast with a significant positional selectivity.[22-26]

This similarity is remarkable in view of the profound differences between the two environments, in particular their different ability to stabilize highly excited intermediates like those from reaction 6, and the specific long-range ion-molecule interactions typical of the gas phase.

In conclusion, the present work has examined the reactions of originally free methyl cations toward fluoro-, chloro-, and bromobenzene in the liquid phase, showing the ability of the reagent (1) to alkylate both π-type and n-type nucleophilic centers, yielding respectively halotoluenes and methyl halides with appreciable selectivity among the halogen atoms, and (2) to promote methyldehalogenation of the substrates. The intervention of methylphenylhalonium ions as methylating agents has been deduced from the competition experiments with toluene, to account for the observed variations in the relative ring alkylation rates with the composition of the system.

Appreciable positional selectivity and low substrate discrimination are typical features of the electrophilic aromatic substitution by bona fide free methyl cations, which represent, to my knowledge, the most powerful carbocations hitherto produced in solution.

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Demonstration of Woodward–Hoffmann Behavior in the Pulsed, Infrared Laser Induced Reaction of *cis*-3,4-Dichlorocyclobutene[1]

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Abstract: The pulsed, infrared laser induced reaction of *cis*-3,4-dichlorocyclobutene has been demonstrated to produce *cis,-trans*-1,4-dichloro-1,3-butadiene as the only detectable product even though the reaction system was not at thermal equilibrium. This is the isomer predicted by the Woodward–Hoffmann rules of conservation of orbital symmetry for a thermally allowed, ground-state, conrotatory ring opening. Even at relatively short laser pulses, reaction via a higher energy, nonallowed channel or biradical intermediate could not be made competitive within the experimental detection limit.

There is currently much interest in multiple photon infrared photochemistry which can, perhaps, be best typified as the photochemistry of the ground electronic state. Excitation with intense, pulsed, infrared laser radiation has been shown to promote molecules to high vibrational levels of the ground electronic state as a result of the absorption of many infrared photons. Much interest has centered on laser isotope separation, understanding the multiphoton absorption process, and chemical reactions induced or augmented by infrared laser radiation.[3] We have been interested in characterizing the influence of intense infrared radiation on organic systems and report in this work the effect of pulsed irradiation on *cis*-3,4-dichlorocyclobutene (**1**). Of particular concern was the behavior of this compound with respect to the Woodward–Hoffmann rules[4] concerning the conservation of orbital symmetry when induced to react in the strong field created by the megawatt infrared laser.

Experimental Section

cis-3,4-Dichlorocyclobutene (**1**) was synthesized according to well-established procedures.[5] Heating 3 Torr of **1** for 4 h at 175 °C in a 15 cm × 16 mm diameter Pyrex tube fitted with a Teflon valve and Viton O-ring produced a pure sample of *cis,trans*-1,4-dichloro-1,3-butadiene (**2**). Isomerizing **2** with a trace of I_2 at 100 °C according to the procedure of Bartlett and Wallbillich[6] produced a mixture of **2**, *cis-cis*-1,4-dichloro-1,3-butadiene (**3**), and *trans,trans*-1,4-dichloro-1,3-butadiene (**4**). The three isomers could be separated from each other and from **1** utilizing a 20 ft × ¼ in. 10% Carbowax 20M column at 80 °C with a Varian Model 2700 gas chromatograph equipped with a flame ionization detector. The retention times of **1**, **2**, **3**, and **4** were 63.3, 24.0, 18.3, and 26.5 min, respectively. The gas chromatographic analyses of the laser reactions were complicated somewhat by small amounts of the three isomeric butadienes either in the starting material or formed during the analyses. Blank runs were conducted routinely and all laser reactions corrected accordingly. The reported results are estimated to be reliable to ±5%.

All infrared irradiations were performed with a Lumonics Model 203 CO_2 laser. The P(48) line of the 001-100 transition (916.58 cm^{-1}) was utilized to excite **1**. Mild focusing of the laser beam was accomplished with a 50-cm focal length BaF_2 lens; the sample cell was positioned at various distances between the lens and the focal point to vary the effective fluence within the cell. Several irradiations were conducted utilizing a 7.5-cm focal length BaF_2 lens which focused the laser beam within the reaction cell. Most experiments were performed using a CO_2–He–n_2 gas mix in the laser which produced a pulse shape consisting of a sharp initial spike of ~160 ns fwhm followed by a long tail of ~2500 ns (Figure 1A); removing the N_2 from the mix essentially eliminated the tail (Figure 1B). In the long pulse, approximately half the energy is contained within the initial spike and half within the tail. Pulse energies were measured with a Scientech Model 360001 power meter and temporal profiles of the pulses were determined by a photon drag detector. Samples for laser irradiation were prepared by standard vacuum line techniques and contained in 10 cm × 2.0 cm diameter Pyrex cells fitted with NaCl windows.

Results and Discussion

The use of a megawatt, pulsed, infrared laser as an energy source to drive organic chemical reactions is a recent development. Heretofore, the requisite energy to induce nonspontaneous reactions has usually been deposited in the form of either simple heat or ultraviolet-visible photons. It is not obvious that a chemical reaction initiated by the high vibrational excitation produced by an intense pulsed infrared beam will proceed in the same fashion as from simple heating which produces vibrational, rotational, and translational excitation in accordance with a Boltzmann population.

There are a number of classes of concerted organic reactions which yield totally different products and/or stereochemistry depending on whether the reactions are induced by thermal or photochemical means. The Woodward–Hoffmann rules of conservation of orbital symmetry[4] unequivocally account for these differences on the basis of symmetry properties of the ground and electronically excited states.

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