The Reactions of Cyclopropyl(methyl)bromonium Ion with Benzene in the Gas Phase

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The thermal gaseous cyclo-$C_3H_5BrCH_3^+$ ion, formed by the reaction of $CH_3ClCH_3^+$ ion, but not of $CH_3FCH_3^+$ ion, with cyclopropyl bromide, reacts with benzene as a methylating and as an allylating agent with equal facility. The loss of the cyclic structure results either from a concerted ring cleavage during the attack or from rearrangement of cyclopropylarenium ion after the attack. The methylating ability of cyclopropyl(methyl)bromonium ion toward benzene falls between those of dimethylfluoronium and dimethylchloronium ions, *i.e.* $CH_3FCH_3^+$ > cyclo-C_3H_5-$BrCH_3^+$ > $CH_3ClCH_3^+$.

THE ionic chemistry of cyclopropane and its derivatives has attracted great interest in recent years. Yet, few reports are available about positive ion reactions during which the participation of the cyclopropane ring throughout the process has been proved beyond doubt by the identification of the species involved. For gas-phase reactions unambiguous evidence is restricted to the tritonation of cyclopropane [1] and its *cis*- and *trans*-dimethyl derivatives,[2] and to the rearrangement of cyclopropyl(methyl)bromonium ion, formed by the methylation of cyclopropyl bromide with dimethylfluoronium and dimethylchloronium ions.[3] The extent of reaction (3a—c) depends on the excitation energy of ions $(1a)_{\text{exc.}}$ and $(1b)_{\text{exc.}}$: the higher the excitation energy, the more the rearrangement processes (3b—c) are favoured. Ion $(1a)_{\text{exc.}}$ is more excited than ion $(1b)_{\text{exc.}}$ because reaction (1) is more exoenergetic than reaction (2); in consequence, ion $(1a)_{\text{exc.}}$ is found to yield cyclo-C_3H_6 and cyclo-$C_3H_5CH_3$ more than CH_3Br, contrary to what happens for $(1b)_{\text{exc.}}$.[3]

$$CH_3FCH_3^+ + \text{cyclo-}C_3H_5Br \longrightarrow \underset{(1a)_{\text{exc.}}}{(\text{cyclo-}C_3H_5BrCH_3)^+_{\text{exc.}}} \qquad (1)$$

$$CH_3ClCH_3^+ + \text{cyclo-}C_3H_5Br \longrightarrow \underset{(1b)_{\text{exc.}}}{(\text{cyclo-}C_3H_5BrCH_3)^+_{\text{exc.}}} \qquad (2)$$

Ion (1a) formed by reaction (1) is of higher energy that ion (1b) formed by reaction (2)

$$\underset{(1)_{\text{exc.}}}{(\text{cyclo-}C_3H_5BrCH_3)^+_{\text{exc.}}} \xrightarrow{[M]} \begin{cases} CH_3Br & (+C_3H_5^+) \quad (3a) \\ \text{cyclo-}C_3H_6 & (+CH_2Br^+) \quad (3b) \\ \text{cyclo-}C_3H_5CH_3 & (+Br^+) \quad (3c) \end{cases}$$

Cyclopropyl(methyl)bromonium ion is known to be stable in the condensed phase but its reactivity is still unknown; [4] at the near atmospheric pressures used by us to generate it free of counterions the possibility exists that, at least in part, it becomes thermalized by collision and reacts further with suitable nucleophiles. We report herein the reactions of thermal cyclopropyl(methyl)bromonium ions with benzene that lead to stable neutral products. Our aim was also to establish whether the positively charged C_3H_5 group was transferred with or without retention of the cyclic structure. Finally, we compare our results with those obtained from the attack of allyl ions on C_6H_6 in ion cyclotron resonance (i.c.r.) experiments.[5]

EXPERIMENTAL

Materials.—Methyl fluoride, methyl chloride, and ammonia (Matheson), oxygen (SIO), and cyclopropyl bromide (Merck-Schuchardt) were high purity products, used as received. G.l.c. analysis, carried out under the analytical conditions, confirmed their purity.

Sample Preparation.—Pyrex bulbs (0.4 l), connected to a vacuum line, were outgassed to 10^{-3} Torr, then filled with the desired gases and sealed, according to the procedure described in detail elsewhere.[6] Oxygen was added as a thermal radical scavenger; some experiments were run in the presence of ammonia, a good scavenger of positive ions, to establish the ionic character of the processes under investigation. Cyclopropyl bromide and benzene were added as liquids contained in small, fragile Pyrex ampoules, which were broken by shaking before irradiation.

Irradiations.—The gaseous mixtures were irradiated with ^{60}Co γ-rays in a 220 Gammacell (Atomic Energy of Canada Ltd.) at 37 °C and at a constant dose rate of 0.34 Mrad h^{-1} (1.39×10^{-5} eV g^{-1} s^{-1}), measured with a Fricke dosimeter, and received a total dose of 4.8 Mrad.

Analysis.—After irradiation the mixtures were analysed by g.l.c. A Carlo Erba instrument (model 2 450), equipped with an f.i.d. detector and 6 m × 2 mm i.d. stainless steel column packed with ICO-880 (C. Erba), was operated under several conditions to detect any reasonable compound which could be found after radiolysis. The following conditions were used for quantitative analysis: the oven temperature was set at 60 °C for 19 min, then linearly programmed to 90 °C at 39 °C min^{-1}; the initial flow rate was 3.9 l h^{-1}. The products were identified by comparison of the retention volumes of authentic samples, and their quantities were measured from peak areas. The yields were calculated as *G* values, *i.e.* the number of molecules formed per 100 eV of absorbed radiation energy. Additional analyses were carried out on a Porapak Q column under the analytical conditions described previously.[3]

RESULTS

Table 1 shows the experimental conditions and yields of products formed by the reactions of cyclo-$C_3H_5BrCH_3^+$ with benzene. At least three independent samples were prepared, irradiated, and analysed three or four times. Thus, the yields are the mean values of all the measurements, and are reproducible within a standard deviation of 10% except for the lowest values which may be less precise. The presence of oxygen rules out any significant interference of radical reactions, and the ionic character of the processes under investigation is further confirmed by the 75—90% depletion of the yields when ammonia is added.

In Table 2 some results are compared with those obtained previously.

TABLE 1

Product yields in the γ-radiolysis of CH_3X–cyclo-C_3H_5Br–PhH gaseous mixtures

	System composition [a]				Product yields (10^2 G) [b]	
X	CH_3X p/Torr	cyclo-C_3H_5Br p/Torr	PhH p/Torr	NH_3 p/Torr	$PhCH_3$	$PhCH_2CH{=}CH_2$
F	720	6	2		23.00	N.d. [c]
F	720	10	3		23.00	N.d.
F	720	10	3	1	9.00	N.d.
Cl	720	10	3		8.20	9.3
Cl	720	10	3	1	2.20	2.4

[a] O_2 15 Torr. Radiation dose 4.8 Mrad. [b] G = number of molecules produced per 100 eV of absorbed radiation energy. [c] N.d. = not detectable, $G \leqslant 10^{-4}$.

TABLE 2

Product yields in the γ-radiolysis of CH_3X–cyclo-C_3H_5Br, CH_3X–PhH, and CH_3X–cyclo-C_3H_5Br–PhH gaseous mixtures

	System composition [a]			Product yield (10^2 G) [b]				
X	CH_3X p/Torr	cyclo-C_3H_5Br p/Torr	PhH p/Torr	CH_3Br	cyclo-C_3H_6	cyclo-$C_3H_5CH_3$	$PhCH_3$	Reference
F	720	3		2.29	40.50	6.30		3
F	760 [c]		1—2				104.9	7
F	720	10	3	2.15	42.00	5.60	23.00	This work
Cl	720	3		6.22	0.85	3.34		3
Cl	760 [c]		1—2				0.58	7
Cl	720	10	3	9.50	0.95	2.95	8.10	This work

[a,b] As in Table 1. [c] O_2, 4 Torr; radiation dose, 4.8 Mrad.

DISCUSSION

The Formation of the Reagent Ions.—Dimethylfluoronium and dimethylchloronium ions, produced by the γ-radiolysis of the corresponding methyl halides,[6,7] are known to transfer the methyl cation to substrates which are more nucleophilic than the parent halogenomethanes themselves.[3,6-8] Cyclopropyl bromide and benzene are present in traces, and the dimethylhalogenonium $(1a)_{exc.}$ and $(1b)_{exc.}$ ions must undergo many collisions before being able to react with the additives; in other words, the latter react only with the thermal alkylhalogenonium ions. Since $G(CH_3XCH_3^+)$ is not known, the absolute yields of the final compounds are of little significance. On the other hand the relative yields of each product in each system as a function of the halide X and the presence of benzene are the relevant factors.

The Formation of Toluene.—Benzene can compete with cyclopropyl bromide for dimethylhalogenonium ions, and in addition to equations (1) and (2) the reactions (4) and (5) must also be considered. Table 2 shows

$$CH_3FCH_3^+ + PhH \longrightarrow (PhHCH_3)^+_{exc.} + CH_3F \quad (4)$$

$$CH_3ClCH_3^+ + PhH \longrightarrow (PhHCH_3)^+_{exc.} + CH_3Cl \quad (5)$$

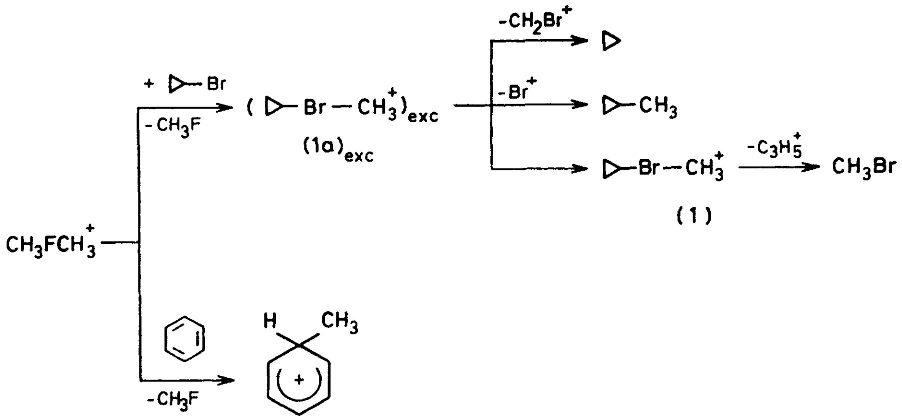
that $G(C_7H_8)$ in $(CH_3F + \text{cyclo-}C_3H_5Br + C_6H_6)$ is lower than in $(CH_3F + C_6H_6)$,[7] but in $(CH_3Cl + \text{cyclo-}C_3H_5Br + C_6H_6)$ is much higher than in $(CH_3Cl + C_6H_6)$.[7] Furthermore, in the former system the yields of the aliphatic product are independent of the presence of benzene, whereas only $G(CH_3Br)$ is increased and practically equal to $G(C_7H_8)$ and $G(C_6H_5CH_2CHCH_2)$ in the latter system. The results are rationalized as follows. In CH_3F toluene is formed only in reaction (4), followed by equations (6) and (7).

$$(PhHCH_3)^+_{ex.} \xrightarrow{[M]} PhHCH_3^+ \quad (6)$$

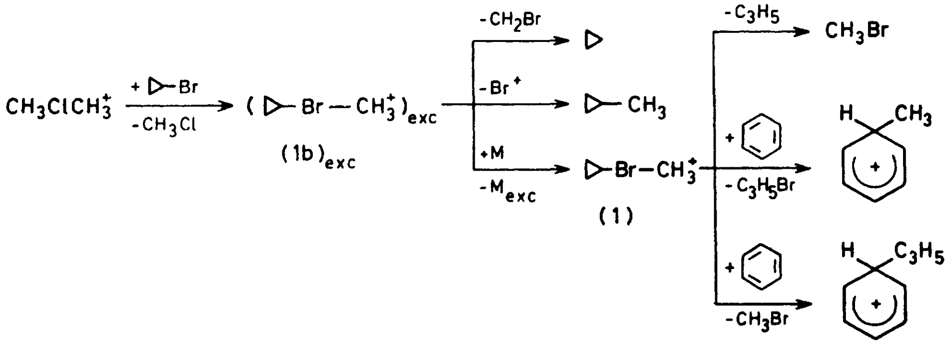
$$PhHCH_3^+ \xrightarrow[-BH^+]{+B:} PhCH_3 \quad (7)$$

Ion $(1a)_{exc.}$ either rearranges according to equations (3b and c), or, after thermalization, decomposes according to equation (3a) without attacking benzene because of the much greater reactivity of dimethylfluoronium ions. Thus, as far as the formation of toluene is concerned, the overall effect of cyclopropyl bromide is to prevent some $CH_3FCH_3^+$ ions from reacting with C_6H_6, and for this reason we have found $G(C_7H_8)$ lower than that measured by Speranza *et al.*[7] Scheme 1 outlines the mechanism through which the products are formed in methyl fluoride. On the other hand, reaction (5) is not very efficient,[7] and dimethylchloronium ion yields ion $(1b)_{exc.}$ in equation (2) which can be easily thermalized by collisions because of its lower energy. Ion (1) either

$$(1b)_{exc.} \xrightarrow{[M]} (1) \quad (8)$$



SCHEME 1



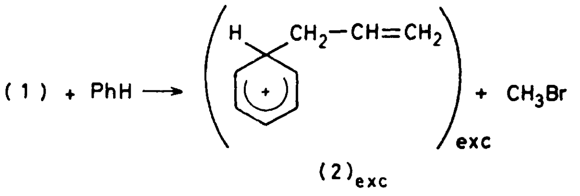
SCHEME 2

decomposes according to equations (3a—c), or reacts with benzene, reaction (9). In conclusion, the results are

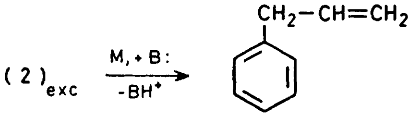
$$(1) + PhH \longrightarrow (PhHCH_3)^+_{exc.} + cyclo\text{-}C_3H_5Br \quad (9)$$

consistent with cyclo-$C_3H_5BrCH_3^+$ ion being a better methylating agent of benzene than $CH_3ClCH_3^+$ ion. Scheme 2 outlines the mechanisms through which the products are formed in CH_3Cl.

The Formation of 3-*Phenylprop*-1-*ene*.—In our previous work [3] no sign of ring cleavage was given by product analysis. Thus, an ion containing a linear C_3H_5 group can be ruled out as the precursor of 3-phenylprop-1-ene. Significantly, the latter has been found only in the CH_3Cl system, where long lived cyclopropyl(methyl)-bromonium ions are able to react with benzene, but not in the CH_3F system, where the efficient methylation of C_6H_6 by $CH_3FCH_3^+$ ion is favoured. However, the results suggest that cyclopropyl(methyl)bromonium ion, when it is possible, transfers a positively charged C_3H_5 group, which loses the initial cyclic identity in the course of the reaction either in the concerted mechanism (10) and (11) or in the rearrangement of the Wheland intermediate $(3)_{exc.}$ [reactions (12), (13), and (11). The cyclopropyl ⟶ allyl transition involves little or no activation energy,[9] and the greater stability of the linear *versus* the cyclic structure is widely recognized.[9a,c-f] Therefore, the exothermicity of reaction (12) can surely provide, if required, the energy necessary to the rearrangement process (13). From the present experiments we are not able to distinguish between the concerted and the rearrangement mechanism. We can only



(10)



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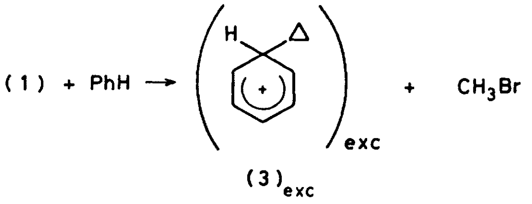
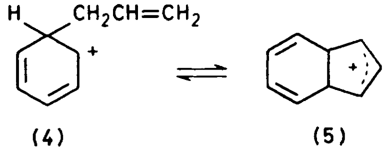


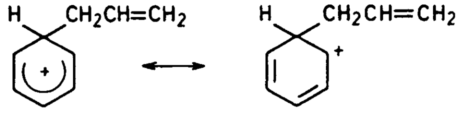
(12)

$$(3)_{exc} \longrightarrow (2)_{exc} \quad (13)$$

conclude that cyclopropyl(methyl)bromonium ion behaves as an allylating, and not a cyclopropylating, agent toward benzene, and that this ability is equal to its methylating power, as shown in Table 1 by the yields of toluene and 3-phenylprop-1-ene in the CH_3Cl system. In Scheme 2 the described mechanism is also outlined.



(4) (5) (14)



(2) (4) (15)

Comparison with I.c.r. Results.—When allyl ions were allowed to react with benzene in i.c.r. experiments,[5] it was proposed that the resulting ionic complex was formed by two equilibrating isomers (4) and (5) which collapsed into ($C_7H_7^+ + C_2H_4$). No changes in the mechanism occurred when $C_9H_{11}^+$ ion underwent several collisions with the bath molecules at low pressures, and the nature of this ion differed from those of the charged species produced by Uccella and Williams,[10] as inferred by the fragmentation paths. We note that delocalisation of the positive charge in (5) is unlikely, (4) is one of the resonant structures of the Wheland intermediate (2) [reaction (15)] and that two significant differences exist between the i.c.r. and the present experiments, the identity of the allylating agent and the value of the pressure. Under the radiolytic conditions the Wheland intermediate (2) has to be formed in the course of reactions (10) and (11), or (12), (13), and (11); otherwise, 3-phenylprop-1-ene would not be found among the neutral products, according to present knowledge of gas-phase electrophilic attack on arenes, even when the aromatic ring reacts with powerful positive ions.[11-14] The results in Tables 1 and 2 do not support the occurrence of the rearrangement process (14) at high pressures, which would lead to the formation of the neutral compounds derived from species (5). At the same time, the contribution of the resonant structure (4) should not be significant, since the neutral compounds derived from (4), *e.g.* 3-(cyclohexa-2,4-dienyl)prop-1-ene, are not found. On the other hand, under i.c.r. conditions, where unimolecular processes prevail, it seems reasonable to assume that the rearrangement process (14) takes place, hindered by collisional stabilization at higher pressures. Finally, one could also postulate that the $C_9H_{11}^+$ ion was the precourser of toluene through the mechanism [equation (16)—(18)] proposed by Houriet *et al.*[5] In contrast to this hypothesis is

$$(1) + \mathrm{PhH} \longrightarrow (2) \longleftrightarrow (4) \rightleftharpoons (5) + CH_3Br \tag{16}$$

$$(2) \longleftrightarrow (4) \rightleftharpoons (5) \longrightarrow C_7H_7^+ + C_2H_4 \tag{17}$$

$$C_7H_7^+ \xrightarrow[-A^+]{+AH} \mathrm{PhCH_3} \tag{18}$$

the fact that the main source of $C_7H_7^+$ and C_2H_4 should be, as in the case of i.c.r. experiments, ion (5), the presence of which was not proven by the present results. Furthermore, ethylene, the neutral product in equation (17), was never found by us.

Conclusions.—Gaseous cyclopropyl(methyl)bromonium ions, generated free of counterions by the reactions of dimethylhalogenonium ions with cyclopropyl bromide, react with benzene, and behave as methylating and allylating agents with equal ability. The trend of methylating ability toward benzene of the alkylhalogenonium ions investigated in this work is found to be $CH_3FCH_3^+ > \text{cyclo-}C_3H_5BrCH_3^+ > CH_3ClCH_3^+$. The question still remains whether the cyclopropyl ring is cleaved during attack on the arene in a concerted mode or after the formation of the cyclopropylbenzenium ion in a rearrangement process.

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