nature of the probable disorder is unknown. Likely, in view of the above, the disorder is only a partial one.

Supplementary Material Available. Listings of h, k, l, F_o, and F_c will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number JACS-74-4588.

One Stage Synthesis of Bicyclo[3.2.2]nona-6,8-dien-3-ones. The Silver Trifluoroacetate Induced Reaction of 2-Methoxyallyl Bromide with Arenes

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Abstract: The 2-methoxyallyl cation has been generated from 2-methoxyallyl bromide and silver trifluoroacetate in the presence of sodium carbonate and shown to react with benzene, toluene, *p*-xylene, and mesitylene. On acidic work-up 1-aryl-2-propanones and bicyclo[3.2.2]nona-6,8-dien-3-ones were isolated, whereas nonaqueous work-up gave further products including arylated enol ethers, a simple acyclic hemiketal, namely 2-hydroxy-2-methoxy-1-phenylpropane, possibly bicyclo[3.2.2]nona-2,6,8-trienes and bromine containing by-products. Bicyclo[4.3.0]nona-6,8-dien-3-ones (dihydroindanones), which are the potential products of a 3 + 2 cycloaddition of the 2-methoxyallyl cation to the arene, were not formed. Bicyclo[3.2.2]nona-6,8-dien-3-ones are sensitive to acid and heat, yielding 1-aryl-2-propanones under fairly mild conditions. It is suggested that formation of the bicyclics involves two-pronged electrophilic attack of silver ion and the 2-methoxyallyl cation on opposite faces of the aromatic molecule.

In studying the silver salt promoted formation of allyl cations from allyl halides we noticed several years ago the utility of benzene as a solvent[1a] and considered that benzene-separated ion pairs are formed, which are stabilized by virtue of the favorable interaction of the lowest unoccupied molecular orbital (LUMO) of the cation and the appropriate highest occupied molecular orbital (HOMO) of benzene (Figure 1a).[1b] There arose the intriguing question whether the aromatic sextet might actually be sacrificed under conditions which favored formation of a bicyclic carbocation (Figure 1b). Accordingly, we have investigated the behavior of arenes toward the 2-methoxyallyl cation (Figure 1b, R = OCH_3), which was generated from 2-methoxyallyl bromide and silver trifluoroacetate, and we now report our results in detail.[2] Throughout this paper, compounds **1a–g** refer to the series of products from the reaction with benzene, **2a**, etc., to those from toluene, **3** from *p*-xylene and **4** from mesitylene, while **5a–d** are bromine-containing by-products.

Identification of Products. Basically, the reaction was carried out as described previously,[3] an arene being used instead of the cyclic diene. In order to gain further mechanistic insight, the products were worked up in two ways. In the most simple case (mode of isolation A), the reaction mixture was treated with dilute nitric acid and then extracted with chloroform to yield the known bicyclo[3.2.2]nona-6,8-dien-3-one[4] (**1b**) and 1-phenyl-2-propanone (**1c**) (see Table I and Scheme I, arene = benzene).

Table I. Products from the Reaction with Benzene

Mode of isolation	Retention time R_t	Composition %	Assignment	Formula no.
A. Work-up with dilute HNO_3	1.25	23	Bicyclo[3.2.2]nona-6,8-dien-3-one	**1b**
	≡1.00	77	$PhCH_2COCH_3$	**1c**
B1. Nonaqueous work-up of mother liquor	1.30 −1.25	24	Bicyclo[3.2.2]nona-6,8-dien-3-one[a]	**1b**
	1.00	32	$PhCH_2COCH_3$	**1c**
	0.92	~24	$PhCH_2COH(OCH_3)CH_3$	**1g**
	0.86	Trace	$CH_2BrC(OCH_3)_2CH_2Br$	**5b**
	0.85	8	2-Methoxy-1-phenyl-1-propene[b]	**1e**
	0.73	3	$CH_3C(OCH_3)_2CHBr_2$	**5a**
	0.58	7	2-Methoxy-1-phenyl-1-propene[c]	**1f**
	0.49	2	Benzaldehyde	
B2. Acid treated residue	1.30	71	Bicyclo[3.2.2]nona-6,8-dien-3-one	**1b**
	1.00	26	$PhCH_2COCH_3$	**1c**
	0.92	3	Unknown	

[a] The bicyclic dienone so isolated contained another compound of similar retention time which was possibly 3-methoxybicyclo[3.2.2]nona-2,6,8-triene (**1a**). [b] The phenyl and methyl groups are probably trans to each other; see text. [c] Probably the cis isomer.

On work-up under milder, nonaqueous conditions (mode of isolation B) it became clear that **1b** and **1c** arose from a sequence of sensitive precursors, the identification of which was not trivial, since they were formed in small and changing amounts and tended to be ill-resolved on glc. By using mainly combined glc–ms and

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(1) (a) H. M. R. Hoffmann and D. R. Joy, *J. Chem. Soc. B*, 1182 (1968); (b) D. R. Joy, Ph.D. Thesis, University of London, 1968.

(2) Preliminary account: H. M. R. Hoffmann and A. E. Hill, *Angew. Chem., Int. Ed. Engl.*, **13**, 136 (1974).

(3) A. E. Hill, G. Greenwood, and H. M. R. Hoffmann, *J. Amer. Chem. Soc.*, **95**, 1338 (1973).

(4) A. J. Baker, A. M. Chalmers, W. W. Flood, D. D. MacNicol, A. B. Penrose, and R. A. Raphael, *Chem. Commun.*, 166 (1970).

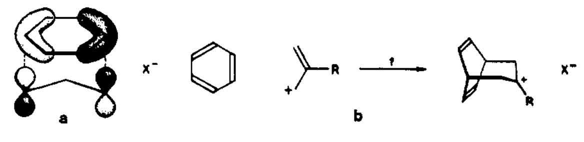
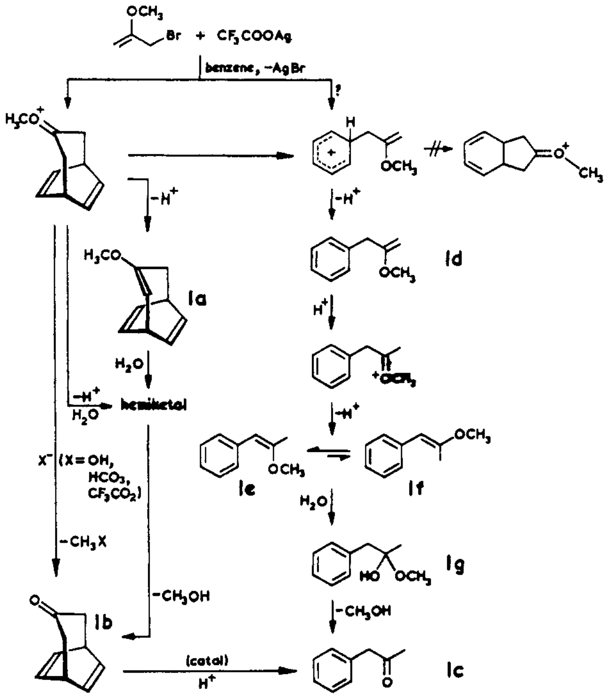


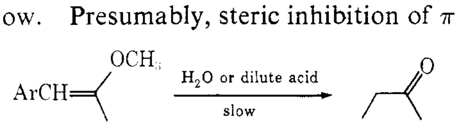
Figure 1. (a) Lowest unoccupied and appropriate highest occupied MO of an allyl cation and benzene, respectively. (b) Bicyclic collapse of a benzene-separated ion pair?

Scheme I. Products and Postulated Intermediates from the Silver Trifluoroacetate Induced Reaction of 2-Methoxyallyl Bromide and Benzene (Simplified)



chemical evidence we were able to identify, in addition to **1b** and **1c**, various isomeric acyclic and possibly bicyclic enol ethers, a hemiketal, and minor brominated by-products.

Of the series of acyclic enol ethers formed 1-mesityl-2-methoxy-1-propene (**4e**) could be handled most readily, because its conversion into 1-mesityl-2-propanone (**4c**) was slow. Presumably, steric inhibition of π overlap is



$$\mathrm{ArCH{=}C(OCH_3)CH_3} \xrightarrow[\text{slow}]{\mathrm{H_2O}\text{ or dilute acid}} \mathrm{ArCH_2C(O)CH_3}$$

4e 4c

Ar = 2,4,6-trimethylphenyl

responsible for the comparative stability of **4e**, which could be collected by preparative glc and even survived treatment with dilute acid on work-up.[5] In contrast, the parent 2-methoxy-1-phenyl-1-propenes were quite labile and could not be obtained free from phenylacetone (**1c**). Furthermore, in this case both trans isomer **1e** (R_t = 0.85) and cis isomer **1f** (R_t = 0.58 or *vice versa*) were found side by side (see Table I). Since semi-empirical molecular orbital (CNDO/2) calculations[6] suggest that *trans*-2-methoxy-1-phenyl-1-propene (the olefinic methyl group and phenyl group are trans) is somewhat more stable than the cis isomer, we assume that the isolated mesityl enol ether **4e** is trans and thence that **1e** (R_t = 0.85) is the trans isomer as well. Consistently, glc pyrolysis of the hemiketal **1g** furnished enol ether **1e** in what is presumably an E1-like elimination, which is known to lead generally to the more stable isomer.

The third conceivable enol ether, namely 2-methoxy-3-phenyl-1-propene (**1d**), was not normally detected and appeared to form phenylacetone (**1c**) most readily. However, on using a silicon oil rather than a Carbowax column, a mass spectrum of an ill-resolved glc peak could be recorded, which is believed to be due to a minor amount of this compound.

Perhaps one of the most interesting products other than the bicyclic is compound **1g** (R_t = 0.92) which on the basis of mass spectral and chemical evidence is a simple acyclic hemiketal, *i.e.*, 2-hydroxy-2-methoxy-1-phenylpropane. Initially, after half of the silver trifluoroacetate had been added, there was only about 5% of the hemiketal present (*cf.* Table II, entry 1). After complete addition of the silver salt the amount of hemiketal rose to 23% (entry 3), whereas addition of water half-way through the reaction raised the proportion of hemiketal to 35% (entry 2), largely at the expense of the acyclic enol ether **1e** and phenylacetone (**1c**). After warming, standing over $CaCl_2$, or vacuum distillation the concentration of the hemiketal decreased, and, significantly, attempts to collect it by preparative glc gave phenylacetone (**1c**) and 2-methoxy-1-phenyl-1-propene (**1e**). The mass spectrum with its weak parent ion at M^{+} 166 and M − 1 ion at 165, but a strong ion at 149 (M − OH) lends further weight to the hemiketal assignment of **1g**.[7]

Finally, the bicyclic dienones isolated by nonaqueous work-up (fraction B1), but not acidic work-up (fraction A) must have been contaminated at least initially with another compound of almost identical retention time. Combined glc–ms showed a fragmentation pattern which was very similar to that of the pure bicyclo[3.2.2]nona-6,8-dien-3-one obtained from acidic work-up. However, the molecular ion of the bicyclic dienone in fraction B1 (*e.g.*, *m/e* 134 for adduct **1b** in the reaction with benzene) was of diminished intensity and a further peak at *m/e* 148 suggested either the presence of 3-methoxybicyclo[3.2.2]nona-2,6,8-triene (**1a**) or facile loss of water from a hemiketal. Judging from the mass spectrum of the acyclic hemiketal **1g** the unknown is more likely to be the bicyclic triene **1a**. Attempts to collect the material together with bicyclo[3.2.2]nona-6,8-dien-3-one (**1b**) by preparative glc on Carbowax 20M were not successful and gave the bicyclic dienone **1b**.

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(5) It has been shown many years ago that enols with mesityl groups attached to the olefinic termini are relatively stable; see R. C. Fuson, *et al.*, *J. Amer. Chem. Soc.*, **62**, 3250 (1940); **66**, 1464 (1944); **67**, 1939 (1945). Note also that simple aliphatic trialkylated enols can be handled more easily than dialkylated ones: H. M. R. Hoffmann and E. A. Schmidt, *J. Amer. Chem. Soc.*, **94**, 1373 (1972); **94**, 7832 (1972); *Angew. Chem., Int. Ed. Engl.*, **12**, 239 (1973). Similarly, aliphatic enol ethers appear to become kinetically more stable with increasing alkylation: T. Okuyama, T. Fueno, H. Nakatsuji, and J. Furukawa, *J. Amer. Chem. Soc.*, **89**, 5826 (1967).

(6) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.

(7) For a discussion of hemiketals, see E. Schmitz and I. Eichorn in "The Chemistry of the Ether Linkage," S. Patai, Ed., Interscience, London, 1967, p 309. See also R. A. Friedel and A. G. Sharkey, Jr., *Anal. Chem.*, **28**, 940 (1956). It would seem worthwhile to generate a few more simple aliphatic hemiketals and to study their kinetic stability in the way we have done this earlier with simple aliphatic enols (see ref 5).

Table II. The Silver Trifluoroacetate Promoted Reaction of 2-Methoxyallyl Bromide and Benzene. Products as a Function of Time and Mode of Work-Up

			Products, % (retention times)						
Entry	Reaction conditions	Work-up	**1b** (1.25)	**1c** (≡1.00)	**1g** (0.92)	**1e** (0.85)	**5a** (0.73)	**1f** (0.58)	PhCHO (0.49)
1	Half of CF_3CO_2Ag added (after 4 hr)	None[a]	7.5	49.0	5.2	23.9	2.7	10.3	1.3
2		Water wash	2.4	39.7	34.3	8.3	4.1	9.9	1.3
3	Complete addition of CF_3CO_2Ag and overnight stirring	None	14.0	40.1	22.9	10.4	4.4	7.0	1.2
4		Water wash	17.0	41.9	24.0	7.7	3.5	4.8	1.2
5		3% acid wash	17.9	47.2	18.4	8.1	2.9	4.4	1.1
6		10% acid wash	14.1	72.5	7.9	0.8	2.8	0.8	1.2

[a] After having stood at 23° overnight the sample contained up to 90% phenylacetone (**1c**).

Discussion

In discussing the mode of formation of the various products one must bear in mind that silver trifluoroacetate is fairly soluble in arenes, least in benzene and most in toluene (Table III). Indeed, work-up of the products from the reaction with toluene was marred by continuous precipitation of silver salts on concentration of the mother liquor. Now it had already been clear from earlier studies that isopentane was advantageous as a cosolvent in many silver salt induced reactions, presumably because it enhances the electrophilic reactivity of silver trifluoroacetate by diminishing its solubility.[8] For this reason the hydrocarbon was also used in the present work. In practice, control of the reactions was best achieved by adding solid silver trifluoroacetate in small portions over an extended period (*ca.* 8 hr) to the reagents. After each addition of the silver salt the temperature was found to rise slightly; one may assume that acid is liberated simultaneously and then neutralized partly, but not completely by the Na_2CO_3 buffer, with evolution of CO_2. The reverse mode of addition, *i.e.*, dropping 2-methoxyallyl bromide into a stirred suspension of the other reagents, caused clagging of the materials with formation of an intractable tar.

Table III. Solubility of Silver Trifluoroacetate in Arenes[a]

Arene	Solubility at 20°, g of $AgOCOCF_3$/mol of arene
Benzene	11
Toluene	55
p-Xylene	21
Mesitylene	31

[a] B. D. Tildesley and A. G. Sharpe, *Research* (*London*), **7**, S9-S10 (1954).

Now silver forms π complexes not only with arenes, but also with olefins. For instance, with norbornadiene the compound $C_7H_8 \cdot 2AgNO_3$ has been characterized, in which the silver is situated exo to each double bond of the bicyclic.[9a] Complex formation of bicyclo[3.2.2]nona-6,8-dien-3-one (**1b**) with silver ion was suggested by the fact that solvent CCl_4 dissolved silver trifluoroacetate in the presence of **1b**, but not in its absence. (In further analogy to the behavior of norbornadiene it was found that **1b** formed an iron–tricarbonyl complex.)

Another facet of the silver complexation comes to light on considering the isomeric bicyclic adducts from *p*-xylene (Table IV). Acidic work-up of the reaction mixture revealed the unsymmetric 6,8-dimethyl derivative **3b** as the major bicyclic product, the ratio **3b**:**3b′** being *ca.* 3:1 in fraction A. In striking contrast, after extracting the silver residues from the nonaqueous work-up with dilute acid (fraction B2), the symmetric 1,5-dimethylated bicyclic **3b′** (which is also the more volatile isomer) predominated with 71%, the ratio **3b**:**3b′** being now *ca.* 1:3. That fraction B2 had been enriched in the symmetric dienone **3b′** can be explained by preferential complexation of **3b′** with silver ion, since it is well-known that increasing alkylation of an ethylenic double bond destabilizes the corresponding silver complex.

Table IV. Products from the Reaction with *p*-Xylene

Mode of isolation	Retention time R_t	Composition %	Assignment	Formula no.
A	≡1.00	69	1-*p*-Xylyl-2-propanone	**3c**
	0.85	24	6,8-Dimethylbicyclo[3.2.2]nona-6,8-dien-3-one	**3b**
	0.56	7	1,5-Dimethylbicyclo[3.2.2]nona-6,8-dien-3-one	**3b′**
B1	1.00	35		**3c**
	0.86	26	6,8-Dimethylbicyclo[3.2.2]nona-6,8-dien-3-one[a]	**3b**
	0.60	29	2-Methoxy-1-*p*-xylyl-1-propene	**3e**
	0.56	6	1,5-Dimethylbicyclo[3.2.2]nona-6,8-dien-3-one[b]	**3b′**
	0.44	2	2,5-Dimethylbenzaldehyde	
	0.33	2	Unknown	
B2	1.00	4		**3c**
	0.85	25		**3b**
	0.54	71		**3b′**

[a] The bicyclic dienone isolated in this fashion contained another compound, presumably 3-methoxy-6,8-dimethylbicyclo[3.2.2]nona-2,6,8-triene (**3a**). [b] Possibly contaminated with the corresponding bicyclic triene (**3a′**).

Consistently, of the two bicyclics derived from tol-

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[8] G. F. P. Kernaghan and H. M. R. Hoffmann, *J. Amer. Chem. Soc.*, **92**, 6988 (1970); H. M. R. Hoffmann, G. F. P. Kernaghan, and G. Greenwood, *J. Chem. Soc. B*, 2257 (1971).

[9] (a) N. C. Baenziger, H. L. Haight, R. Alexander, and J. R. Doyle, *Inorg. Chem.*, **5**, 1399 (1966); (b) M. A. Muhs and F. T. Weiss, *J. Amer. Chem. Soc.*, **84**, 4697 (1962).

uene, the more volatile isomer 1-methylbicyclo[3.2.2]nona-6,8-dien-3-one (**2b′**) was formed as the minor bicyclic product overall (fraction A), but tended to accumulate in the silver residues obtained after nonaqueous work-up (fraction B2, Table XIII).

Quite generally, silver ions may have an important role to play by coordinating and stabilizing the bicyclic dienones and their respective precursors as they arise during the reaction (for the sake of simplicity silver complexation of the olefins has been omitted from Scheme I). It is a difficult question to answer whether benzene itself is coordinated with silver as it combines with the 2-methoxyallyl cation. On steric grounds and from the known structure of the benzene–$AgClO_4$ complex[10] it seems unlikely that Ag^+ and the allyl cation will share the same face of benzene during reaction. Instead, benzene would have to be sandwiched by the metal and 2-methoxyallyl cation before collapse to the bicyclic cation is complete.[10a] In this way, however, silver would wind up on the endo face of the resulting bicyclo[3.2.2]nona-6,8-dien-3-one, and the presumably preferred exo coordination would have to occur in a discrete, subsequent step.

In any event, the bicyclic collapse of benzene will only be complete when the resulting bicyclic cation has shed its *O*-methyl group to a nucleophile or, perhaps less satisfactorily, has formed a hemiketal. The time-dependent, nonaqueous work-up of the reaction mixture showed that acyclic enol ethers predominated during the early stages of the reaction (Table II, entries 1 and 3). After washing with water (entries 2 and 4), which is also liberated during the reaction *via* neutralization of trifluoroacetic acid, *i.e.*

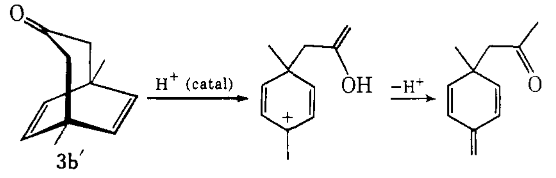
$$2CF_3CO_2H + Na_2CO_3 = 2CF_3CO_2Na + CO_2 + H_2O$$

the proportion of the acyclic hemiketal **1g** increased, while that of the enol ethers **1e** and **1f** decreased. The percentage of bicyclic adduct **1b** appeared to rise most slowly (entry 5) and it may well be that water and thence methanol generated during the reaction are important in trapping the presumed precursor of bicyclo[3.2.2]nona-6,8-dien-3-one (**1b**), *i.e.*, the bicyclic oxonium ion, and in preventing it from breaking up into enol ether or arylpropanone (Scheme I).

Even after isolation in the pure state, bicyclo[3.2.2]nona-6,8-dien-3-ones were found to be unstable toward prolonged exposure to acid and also to heat. For example, in neat deuteriotrifluoroacetic acid the parent bicyclic dienone **1b** was cleanly converted into phenylacetone (**1c**) after 3 hr at room temperature. On the other hand, 1,5-dimethylbicyclo[3.2.2]nona-6,8-dien-3-one (**3b′**) appeared to be relatively resistant toward break up or at least accumulated appreciably in the silver residues. In this instance, aromatization is blocked by the two methyl groups and the compound would have to form a cross-conjugated triene instead (Scheme II).

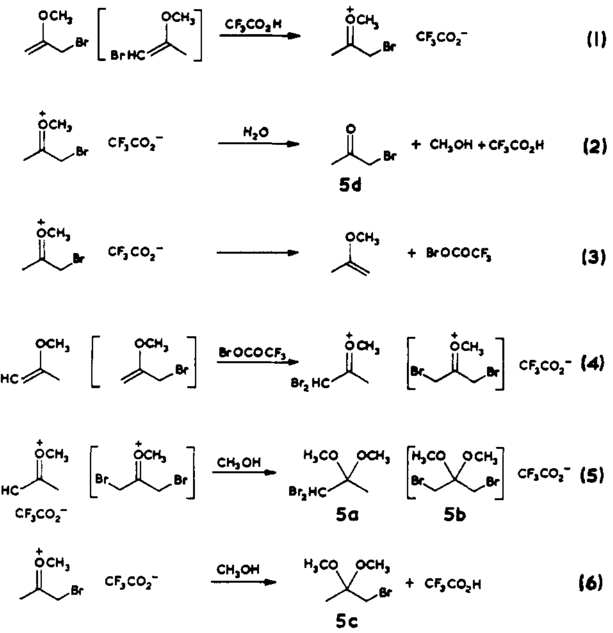
Mass spectrometrically, there was some evidence for a further mode of break-up in that the bicyclo[3.2.2]nona-6,8-dien-3-ones showed a weak parent − 56 peak and a more intense parent − 57 peak, which could be due to concerted loss of oxyallyl (C_3H_4O) and regeneration of the arene.

Scheme II. Possible Mode of Cleavage of Bicyclic **3b′**



Bromine Containing and Other By-Products. The slow liberation of acid during the reaction has one further consequence in that not only arylated enol ethers are protonated, but also the reagents, *viz.*, 2-methoxyallyl bromide and its isomer, 1-bromo-2-methoxy-1-propene [Scheme III, (1)]. One can see that the oxonium salt so produced will be converted into bromoacetone (**5d**), which was observed, *e.g.*, on concentrating the filtered mother liquors, and into 1-bromo-2,2-dimethoxypropane (**5c**). Furthermore, there exists the possibility of forming electrophilic bromine compounds [reaction 3] which will give the observed dibrominated by-products **5a** and **5b**. To our surprise, an experiment using 2-methoxyallyl iodide[11] rather than the bromide was unsatisfactory, an intractable tar being formed. Conceivably, $IOCOCF_3$ is produced more readily than $BrOCOCF_3$ under these conditions and does more damage to the reagents and products.

Scheme III. Formation of Bromine Containing By-Products



How are the aldehydes—like benzaldehyde in the reaction with benzene—being formed? A likely source seems to be phenylacetone, and indeed commercial samples of this ketone were found to contain benzaldehyde. A possible oxidizing agent in our reaction mixture is Ag_2CO_3,[12] which is formed according to

$$2CF_3CO_2Ag + Na_2CO_3 = Ag_2CO_3 + 2CF_3CO_2Na$$

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[10] H. G. Smith and R. E. Rundle, *J. Amer. Chem. Soc.*, **80**, 5075 (1958).

[10a] Note Added in Proof. *Cf.* also the interesting proposal by M. J. Goldstein and S. A. Kline (*J. Amer. Chem. Soc.*, **95**, 935 (1973)) that a degenerate $C_{11}H_{11}^+$ cation of theirs is best described as a planar cyclopentadienyl anion, which is sandwiched by two mutually perpendicular dehydroallyl ligands.

[11] G. Greenwood and H. M. R. Hoffmann, *J. Org. Chem.*, **37**, 611 (1972).

[12] M. Fétizon, M. Golfier, and J. M. Louis, *Chem. Commun.*, 1102, 1118 (1969).

even without solvent, *i.e.*, by leaving a finely ground mixture of the two salts overnight. Ag_2CO_3 tends to be a sticky solid, and its formation, which is of course undesirable, can be suppressed by adding silver trifluoroacetate in small portions to the mixture of the other reagents as described above.

In discussing the formation of minor by-products it is worthy of mention that dihydroindanones, which would have to arise *via* a nonconcerted 3 + 2 cycloaddition of the 2-methoxyallyl cation to the arene, have *not* been detected in any of the reaction mixtures. Seen in this light the formation of bicyclo[3.2.2]nona-6,8-dien-3-ones is the more remarkable[13] and can be construed as a piece of evidence for a concerted mode of formation. In fact, even the formation of 1-aryl-2-propanones could be formulated *via* the bicyclic oxonium ion and subsequent cleavage of the weakened σ bond (Scheme I) rather than *via* the conventional mechanism of electrophilic aromatic substitution involving the Wheland intermediate.

Conclusion

While the silver trifluoroacetate promoted reaction of 2-methoxyallyl bromide with arenes is rather complex in triggering various consecutive processes, it is clear that a considerable measure of control can be achieved. Since the reactions described are one-flask procedures and since all the starting materials are readily available, a range of provocative and hitherto unknown bicyclics has become easily accessible. It is of theoretical interest that the parent benzene molecule can be activated toward electrophilic attack with resultant loss of aromaticity in such mild conditions. In this respect, the reactions described in this paper are to our knowledge without precedent.

Experimental Section

Instruments. Routine spectra were recorded on a Varian T60 nmr, an AEI MS12 mass, and a Perkin-Elmer 257 ir spectrometer. Combined glc–ms was carried out on a Pye 104 gas chromatograph with a 10% PEG 20M column (5 ft × 0.25 in., 100–120 mesh Celite) attached to an AEI MS30 double beam mass spectrometer. A Varian Aerograph Series 712 (20 ft × 0.375 in. column, 20% Carbowax 20M on 40–60 mesh Supersorb) and a Griffin flame ionization chromatograph (20 ft × 0.25 in. column, 20% Carbowax 20M on 60–80 mesh Supersorb) were used for preparative and analytical glc, respectively.

Glc Retention Times. Retention times for the series of products from the four arenes (benzene, toluene, *p*-xylene, mesitylene) tended to be erratic when using benzene as internal standard. By measuring retention times relative to the appropriate 1-aryl-2-propanone which was formed as a major product in all four reactions, the reproducibility was improved in that data could be compared over a fair range of temperatures and gas flow rates. The retention times R_t' were helpful in the identification of the various products (see Figure 2 and Table V).

The efficiency of preparative gas–liquid chromatography was tested with standard solutions of 1-phenyl-2-propanone in benzene. Since losses of up to 50% of the ketone were noted with decigram quantities and complete losses with some of the smaller samples, the isolated yields given below should not be regarded as optimum.

Silver Trifluoroacetate Promoted Reaction of 2-Methoxyallyl Bromide with Benzene. 2-Methoxyallyl bromide (5 g, 33 mmol), which was prepared as described previously and contained isomeric 1-bromo-2-methoxypropene as well as a minor amount of 1-bromo-2,2-dimethoxypropane,[3,11] was dissolved in benzene (40 ml, 477 mmol), diluted with isopentane (100 ml), and mixed with finely ground Na_2CO_3 (2 g). The resulting suspension was stirred with a vibromixer (100 cps), while a mixture of silver trifluoroacetate (10 g, 46 mmol) and Na_2CO_3 (4 g) was added in small portions (0.25 g each) during 9 hr at 23°. After complete addition of the silver salt the reaction mixture was stirred for a further 16 hr in the dark and then worked up by carefully adding nitric acid (10%, 100 ml) (evolution of CO_2!), warming to remove the bulk of isopentane and extracting the resulting suspension with $CHCl_3$ (3 × 100 ml). The combined organic layer was briefly washed, dried, and concentrated to a yellow oil, which was subjected to preparative glc yielding 1-phenyl-2-propanone (**1c**) ($R_t \equiv 1.00$; 0.89 g, 20%), as a colorless oil and bicyclo[3.2.2]nona-6,8-dien-3-one (**1b**) (R_t = 1.25, 0.27 g, 6%): mp 56°, white crystalline solid;[4] ir (CCl_4) 1698 cm^{-1} (vs). When the products were worked up by careful fractional distillation (45° (0.03 mm)) bicyclo[3.2.2]nona-6,8-dien-3-one (**1b**) was obtained in 11% yield.

Table V. Normalized Retention Times R_t' of 1-Aryl-2-propanones[a]

1-Phenyl-2-propanone (**1c**)		$\equiv$1.00
1-*o*-Tolyl-2-propanone	(**2c**, **2c′**)	1.40
1-*p*-Tolyl-2-propanone		1.35[b]
1-*p*-Xylyl-2-propanone (**3c**)		1.69
1-Mesityl-2-propanone (**4c**)		2.48

[a] 20-ft Carbowax 20M column at 206°; standard 1-phenyl-2-propanone. [b] Barely resolved shoulder.

Nonaqueous Work-up of the Mother Liquor (B1). The reaction was carried out as before, but treatment with dilute nitric acid as the first step of the work-up was omitted. Instead, the crude reaction mixture was filtered and the residue washed thoroughly with isopentane (3 × 100 ml). The combined organic filtrates were concentrated to afford a yellow oil, which rapidly decomposed throwing down silver compounds and forming bromoacetone. Slow vacuum distillation of the resulting liquid at 25° (15 mm) removed volatile bromine compounds including bromoacetone; at 30° (0.05 mm) a fraction of a fairly stable colorless liquid was obtained which was subjected to combined analytical glc–ms and purified by preparative glc yielding 2-methoxy-1-phenyl-1-propene (**1e**) (R_t = 0.85) as a colorless liquid containing some **1c**; 1-phenyl-2-propanone (**1c**, R_t = 1.00) and finally bicyclo[3.2.2]nona-6,8-dien-3-one (**1b**), R_t = 1.25. The bicyclic so obtained contained another compound as indicated by the mass spectrum which showed the parent ion of **1b** at *m/e* 134 with diminished intensity and a peak at *m/e* 148. A small peak at *m/e* 149 appeared to correspond with the natural abundance of ^{13}C rather than the fragmentation ion of any bicyclic hemiketal (**1a** + H_2O). The appropriate glc peak was not resolved on Carbowax nor on a silicon oil SE-30 column, but on the former column the peak was marginally broader (R_t = 1.25–1.30) than that of authentic **1b** (R_t = 1.25) obtained after washing with dilute acid. An attempt to collect the unknown compound together with **1b** by preparative glc gave bicyclo[3.2.2]nona-6,8-dien-3-one (**1b**) as the major product.

Three further sensitive compounds were recognized by combined glc–ms. 2-Hydroxy-2-methoxy-1-phenylpropane (**1g**) (R_t = 0.92) showed the following mass spectrum: *m/e* 166 (1), 165 (2), 151 (1), 150 (4), 149 (28), 148 (18), 147 (4), 132 (6), 117 (18), 115 (12), 105 (18), 91 (28), 90 (10), 89 (100). Attempts to isolate the compound by preparative glc gave 2-methoxy-1-phenyl-1-propene (**1e**) and 1-phenyl-2-propanone (**1c**). 2-Methoxy-1-phenyl-1-propene (**1f**) (R_t = 0.58) [*m/e* 149 (8), 148 (84), 147 (22), 133 (24), 118 (10), 117 (54), 116 (56), 115 (54), 105 (66), 103 (16), 92 (12), 91 (100), 89 (10), 79 (14), 78 (12), 77 (20), 65 (28), 57 (40), 51 (10)] gave phenylacetone (**1c**) on attempted collection by preparative glc. By using a silicon oil SE-30 instead of a Carbowax column a third minor isomer of **1e** and **1f** was detected, which appeared to be 2-methoxy-3-phenyl-1-propene (**1d**). While its glc peak was ill-resolved and nearly coincided with that of 1,3-dibromo-2,2-dimethoxypropane (**5b**), its mass spectrum could be derived by subtraction: *m/e* 149 (18), 148 (94), 147 (18), 146 (12), 134 (10), 133 (24), 118 (12), 117 (18), 116 (16), 115 (24), 106 (16), 105 (100), 104 (14), 103 (24), 92 (12), 91 (38), 90 (18), 89 (20), 79 (30), 78 (16), 77 (34).

The proportion of all products changed with time and depended

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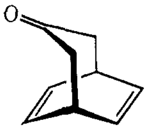
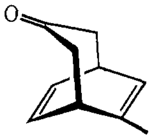
(13) To our knowledge, 1,4-cycloadditions to benzene have hitherto been described for electron-deficient acetylenes only and not for charged π components; see C. G. Krespan, B. C. McKusick, and T. L. Cairns, *J. Amer. Chem. Soc.*, **83,** 3428 (1961); R. G. Miller and M. Stiles, *ibid.*, **85,** 1798 (1963); E. Ciganek, *Tetrahedron Lett.*, 3321 (1967). Some polyalkylbenzenes give a minor amount of 1,4-substituted 1,4-cyclohexadiene on nitration in solvent acetic anhydride: A. Fischer and J. N. Ramsay, *J. Chem. Soc., Perkin Trans. 2*, 237 (1973) and references therein.

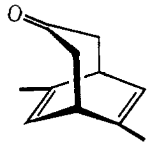
on the mode of isolation (see Table II), phenylacetone (**1c**) being favored thermodynamically (Scheme I).

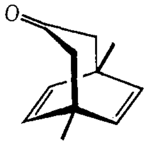
Fraction B2. The silver-containing residue from the isopentane washings was treated carefully with nitric acid (10%, 100 ml) and extracted with $CHCl_3$ (3 × 100 ml). The combined organic layer was briefly washed and dried, and the solvent was removed at reduced pressure leaving a yellow liquid which on purification by preparative glc afforded **1c** and bicyclo[3.2.2]nona-6,8-dien-3-one (**1b**) (see Table I).

Table VI. Proton Nmr Spectra (δ ppm, TMS, CCl_4) of Bicyclo[3.2.2]nona-6,8-dien-3-ones


1b


2b


3b


3b′

Proton type	**1b**	**2b**	**3b**	**3b′**
Olefinic	6.2–6.4 (m, 4 H)	5.7–5.9 (complex d, 1 H) 6.13–6.37 (m, 2 H)[a]	5.7–6.0 (complex d, 2 H)	5.92 (s, 4 H)
Bridgehead	3.1–3.4 (br m, 2 H)	2.7–3.2 (br, 2 H)	2.7–3.0 (br m, 2 H)	
Methylene	2.35 (d, J = 4 Hz, 4 H)	Obscured	2.28, 2.32 (4 H)	2.20 (s, 4 H)
Methyl		1.79 (d, $J \sim 1.7$ Hz, 3 H)	1.80 (d, J = 1.4 Hz, 6 H)	1.32 (s, 6 H)

[a] The signals due to H-7 and H-8, H-9 are very similar to those of the olefinic protons in **3b** and **1b**, respectively.

Table VII. ^{13}C Nmr Shifts (δ ppm, TMS, CCl_4) of Bicyclo[3.2.2]nona-6,8-dien-3-ones[a]

1b	**3b**	**3b′**	Assignment
209.3	210.5	209.3	C=O
	143.9		$=\overset{*}{C}-CH_3$
134.8	127.2	138.9	$=CH-$
46.9	45.4	53.3	CH_2
		36.5	$>\overset{*}{C}-CH_3$
32.9	38.3		$>C-H$
		26.1	$>C-\overset{*}{C}H_3$
	20.5		$=C-\overset{*}{C}H_3$

[a] Determined from proton decoupled spectra.

Table VIII. Mass Spectra of Bicyclo[3.2.2]nona-6,8-dien-3-ones

Compd	m/e
1b	135 (2), 134 (40), 133 (6), 116 (12), 115 (6), 105 (42), 93 (6), 92 (62), 91 (100), 78 (12), 77 (26), 65 (6), 43 (25)
3b	163 (1.6), 162 (14), 147 (1.6), 120 (20), 119 (100), 106 (6), 105 (38), 91 (10), 77 (6), 43 (4)
3b′	163 (4), 162 (34), 121 (4), 120 (30), 119 (100), 106 (10), 105 (52), 104 (4), 103 (4)

The Behavior of Bicyclo[3.2.2]nona-6,8-dien-3-one toward Acid. Bicyclo[3.2.2]nona-6,8-dien-3-one (**1b**) was dissolved in deuteriotrifluoroacetic acid in an nmr tube. The solution assumed a red coloration and within 30 min more than 50% of the bicyclic had disappeared. After 4 hr, cleavage of **1b** was complete, a clean conversion into 1-phenyl-2-propanone (**1c**) being observable. Under the same conditions 8-oxabicyclo[3.2.1]oct-6-en-3-one[3] took about 11 days to form 1-(2′-furanyl)-2-propanone, whereas 8-isopropylidenebicyclo[3.2.1]oct-6-en-3-one[3] required *ca.* 5 hr for the analogous cleavage.

Bicyclo[3.2.2]nona-6,8-dien-3-one(tricarbonyl)iron. Bicyclo[3.2.2]nona-6,8-dien-3-one and $Fe_2(CO)_9$ were stirred in benzene overnight at room temperature. Dry-column chromatography afforded bicyclo[3.2.2]nona-6,8-dien-3-one(tricarbonyl)iron as an orange colored solid: mass spectrum m/e 275 (2), 274 (16), 272 (1), 247 (4), 246 (30), 244 (2), 219 (6), 218 (50), 216 (4), 191 (12), 190 (100), 188 (12), 164 (6), 162 (4), 161 (4), 160 (36), 158 (4), 149 (2), 148 (8), 147 (6), 135 (4), 134 (32), 133 (2), 132 (4), 92 (18), 91 (50).

Table IX. Pmr Spectra (δ ppm, TMS, CCl_4) of Arylpropanones

1-Phenyl-2-propanone (**1c**)	7.15 (br s, 5 H), 3.52 (s, 2 H), 1.94 (s, 3 H)
1-Tolyl-2-propanone (*o* and *p*) (**2c**, **2c′**)	7.03 (br s, 4 H), 6.99 (br s, 4 H), 3.53 (s, 2 H), 3.46 (s, 2 H), 2.26 (s, 3 H), 2.17 (s, 3 H), 1.95 (s, 6 H)
1-*p*-Xylyl-2-propanone (**3c**)	6.85–6.92 (complex, 3 H), 3.47 (s, 2 H), 2.25 (s, 3 H), 2.15 (s, 3 H), 1.95 (s, 3 H)
1-Mesityl-2-propanone (**4c**)	6.73 (s, 2 H), 3.54 (s, 2 H), 2.20 (s, 3 H), 2.15 (s, 6 H), 1.93 (s, 3 H)

Table X. Mass Spectra of Arylpropanones

	m/e
1-Phenyl-2-propanone (**1c**)	135 (1), 134 (6), 92 (14), 91 (42), 65 (14), 43 (100)
1-Tolyl-2-propanone (*o* and *p*) (**2c**, **2c′**)	149 (14), 148 (36), 106 (46), 105 (100), 79 (16)
1-*p*-Xylyl-2-propanone (**3c**)	162 (16), 120 (16), 119 (100)
1-Mesityl-2-propanone (**4c**)	177 (2), 176 (18), 134 (12), 133 (100), 91 (10)

Table XI. Pmr Spectra (δ ppm, TMS, CCl_4) of 1-Aryl-2-methoxy-1-propenes

2-Methoxy-1-phenyl-1-propene (**1e**)	7.12 (br s, 5 H), 5.48 (s, 1 H), 3.62 (s, 3 H), 1.95 (s, 3 H)
2-Methoxy-1-*p*-xylyl-1-propene (**3e**)	6.79 (br s, 3 H), 5.37 (s, 1 H), 3.55 (s, 3 H), 2.23 (s, 3 H), 2.17 (s, 3 H), 1.77 (s, 3 H)
1-Mesityl-2-methoxy-1-propene (**4e**)	6.75 (br s, 2 H), 5.17 (s, 1 H), 3.62 (s, 3 H), 2.22 (s, 3 H), 2.15 (s, 6 H), 1.52 (s, 3 H)[a]

[a] The proton decoupled ^{13}C nmr spectrum of **4e** showed 10 singlets (δ ppm, TMS, CCl_4) at 155, 137, 135.5, 133, 128, 95.9, 54.4, 20.9, 20.5, 16.9 ppm.

Reaction with Toluene. The reaction was carried out as described for benzene and the products were worked up in two ways. Acidic work-up (fraction A) followed by preparative glc afforded 1-tolyl-2-propanone as a mixture of ortho and para isomer (R_t = 1.00, 0.52 g, 10.5%) and 6-methylbicyclo[3.2.2]nona-6,8-dien-3-one (**2b**, R_t = 0.96, 0.02 g, 0.5%). The preparative separation of the various components of the nonaqueous work-up was not attempted owing to the poor resolution of the products on the Carbowax column (see Table XIII) and the high solubility of silver trifluoroacetate in toluene (Table III).

Reaction with *p*-Xylene. Acidic work-up of the reaction mixture followed by preparative glc yielded 1-*p*-xylyl-2-propanone (**3c**) (0.54 g, 10%, R_t = 1.00) as well as 6,8-dimethylbicyclo[3.2.2]nona-6,8-dien-3-one (**3b**) (0.19 g, 3.5%, R_t = 0.85), ir (CCl_4) 1695 cm^{-1} (vs), and the symmetric 1,5-dimethylbicyclo[3.2.2]nona-6,8-dien-3-one (**3b′**) (0.05 g, 1%, R_t = 0.56), ir (CCl_4) 1690 cm^{-1} (vs).

Table XII. Mass Spectra of 1-Aryl-2-methoxy-1-propenes

2-Methoxy-1-phenyl-1-propene (**1e**)	149 (8), 148 (60), 133 (12), 115 (14), 106 (10), 105 (100), 91 (14), 90 (10), 89 (10), 79 (18), 77 (18)
2-Methoxy-1-tolyl-1-propene (*o* and *p*) (**2e**)	163 (18), 162 (100), 148 (10), 147 (34), 132 (12), 131 (24), 130 (20), 129 (20), 128 (14), 127 (10), 120 (12), 119 (58), 117 (12), 116 (12), 115 (24), 105 (20), 104 (16), 93 (10), 92 (10), 91 (28), 81 (10), 79 (10), 78 (12), 77 (18)
2-Methoxy-1-*p*-xylyl-1-propene (**3e**)	177 (12), 176 (100), 161 (32), 146 (12), 145 (16), 144 (14), 133 (48), 128 (10), 119 (12), 117 (14), 115 (12), 105 (14), 91 (16)
1-Mesityl-2-methoxy-1-propene (**4e**)	191 (16), 190 (100), 176 (10), 175 (64), 160 (32), 159 (36), 158 (86), 157 (14), 147 (40), 145 (12), 144 (10), 143 (44), 142 (12), 141 (12), 133 (20), 132 (18), 131.5 (metastable peak; calcd for *m*-CH_3OH: 131.4), 131 (12), 129 (18), 128 (26), 119 (16), 117 (22), 116 (16), 115 (34), 105 (12)

Table XIII. Products from the Reaction with Toluene

Mode of isolation	Retention time R_t	Composition %	Assignment	Formula no.
A	≡1.00	78	1-Tolyl-2-propanone (*o* and *p*)	**2c**, **2c'**
	0.96	18	6-Methylbicyclo[3.2.2]nona-6,8-dien-3-one	**2b**
	0.82	4	1-Methylbicyclo[3.2.2]nona-6,8-dien-3-one	**2b'**
B1	1.00	64	1-Tolyl-2-propanone (*o* and *p*)	**2c**, **2c'**
	0.93	17	6-Methylbicyclo[3.2.2]nona-6,8-dien-3-one[a]	**2b**
	0.83 0.81 0.78	7	2-Methoxy-1-tolyl-1-propene(s) 1-Methylbicyclo[3.2.2]nona-6,8-dien-3-one[a]	**2b'**
	0.61	12	2-Methoxy-1-tolyl-1-propene(s)	
	0.44	Trace	Tolualdehyde(s)	
B2	1.00	83		**2c**, **2c'**
	0.94	2	6-Methylbicyclo[3.2.2]nona-6,8-dien-3-one	**2b**
	0.81	15	1-Methylbicyclo[3.2.2]nona-6,8-dien-3-one	**2b'**

[a] The bicyclic dienone contained another compound of similar retention time which was presumably a bicyclic triene.

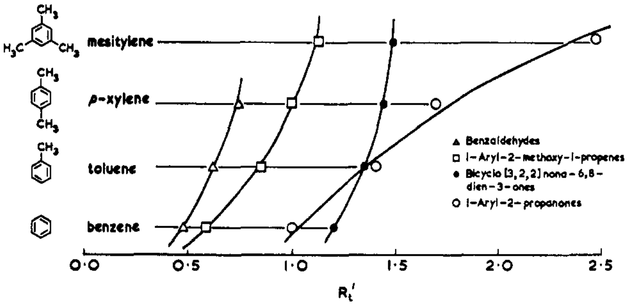


Figure 2. Normalized retention times R_t' of selected reaction products (20-ft Carbowax 20M column, 206°).

In the alternative mode of work-up (B1) the crude reaction mixture was filtered, concentrated, and distilled at high vacuum to yield a liquid which was subjected to preparative glc. The following compounds were isolated: **3c** (0.05 g, 0.9%), **3b** (0.17 g, 3.2%) which on the basis of combined glc-ms contained a second compound with a molecular ion *m/e* 176 (6,8-dimethyl-3-methoxybicyclo[3.2.2]nona-2,6,8-triene?); **3b'** (0.01 g, 0.2%) which was shown to contain a second compound with a molecular ion *m/e* 176 (1,5-dimethyl-3-methoxybicyclo[3.2.2]nona-2,6,8-triene?). Apparently, during preparative glc on the Carbowax column the two unidentified compounds were partly converted into the bicyclic dienones **3b** and **3b'**, respectively. The combined residues from the filtration and concentration of the mother liquor were treated carefully with dilute nitric acid and extracted with chloroform. On preparative glc **3c** (0.02 g, 0.3%), **3b** (0.10 g, 1.8%), and a fairly respectable quantity of **3b'** (0.27 g, 5%) were obtained (see Table IV).

Reaction with Mesitylene. The reaction was run as described for benzene, 35 g mesitylene being used. Work-up with dilute nitric acid followed by extraction with $CHCl_3$ and preparative glc gave 1-mesityl-2-propanone (**4c**) (0.51 g, 8.5%, R_t = 1.00), mp 55° after sublimation (*Anal.* Calcd for $C_{12}H_{16}O$: C, 81.7; H, 9.2. Found: C, 82.5; H, 9.4) and 1-mesityl-2-methoxy-1-propene (**4e**) (0.30 g, 5%, R_t = 0.45), mp 51° after sublimation (*Anal.* Calcd for $C_{13}H_{18}O$: C, 82.1; H, 9.5. Found: C, 82.3; H, 9.4). After a delayed work-up of 2 days the reaction mixture contained traces (<0.05%) of a third component (R_t = 0.57), which could be 1,6,8-trimethylbicyclo[3.2.2]nona-6,8-dien-3-one (**4b**) on comparison of its normalized retention time R_t' with that of other bicyclics (see Figure 2).

Table XIV. Mass Spectra of Bromine-Containing Compounds

	m/e
2-Methoxyallyl bromide	152 (100), 150 (100), 109 (74), 107 (74), 95 (54), 93 (54), 71 (60), 57 (54), 56 (58), 55 (60), 53 (58)
1-Bromo-2-methoxy-1-propene	153 (2), 152 (18), 151 (2), 150 (18), 71 (100), 56 (12)
1-Bromo-2,2-dimethoxypropane (**5c**)	169 (4), 167 (4), 153 (30), 151 (32), 89 (100), 72 (18), 71 (14)
1,1-Dibromo-2,2-dimethoxypropane (**5a**)	249 (1), 247 (2), 245 (1), 233 (4), 231 (10), 229 (6), 175 (0.5), 173 (1), 171 (0.5) (*m*-$CHBr_2$), 152 (10), 89 (100)
1,3-Dibromo-2,2-dimethoxypropane (**5b**)	233 (40), 231 (54), 229 (40), 179 (94), 177 (94), 151 (40), 149 (40), 148 (40), 137 (40), 135 (42), 133 (38), 123 (38), 121 (36), 105 (44), 103 (42), 101 (36), 89 (66), 88 (44), 87 (54), 86 (40), 82 (38), 80 (38), 73 (100), 72 (36), 71 (40)

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