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ANCHIMERIC ASSISTANCE IN ELECTRON-IMPACT REACTIONS: HOMOALLYLIC SYSTEMS†

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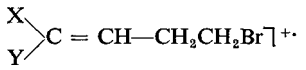
Abstract—A combination of a kinetic approach, thermochemical approach and atomic labeling techniques has been employed to demonstrate that several series of allylic and homoallylic bromides undergo Br· expulsion with the aid of remote π-electron density.

INTRODUCTION

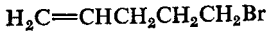
IN TWO previous publications, we presented evidence supporting phenyl participation in the expulsion of Br· from the molecular ion of β-phenyl-ethyl bromide[1] and oxygen participation in the expulsion of Br· from the molecular ion of β-bromoethyl benzoate.[2] Our conclusions were based primarily on metastable data, relative activation energies of competing processes, atomic labeling and substituent effects. Using some of the same techniques, we have now investigated the possibility of anchimeric assistance in the formation of $[M - Br]^+$ from some homoallylic bromide molecular ions of the type shown below.



(I)

Although Grützmacher has argued against anchimeric assistance (phenyl participation) in electron-impact reactions,[3] Cooks and co-workers have recently rebutted Grützmacher's argument while presenting their own evidence for participation in the fragmentation reactions of some 4-substituted azulenes.[4] Earlier Weininger, Mai and Thornton postulated homoallylic stabilization to explain the loss of carbon monoxide from the molecular ion of tetrahydrophthalic anhydride.[5]

Our present study represents the first attempt to apply the quasi-equilibrium theory of mass spectrometry along with thermochemical measurements to the investigation of participation by π-electrons associated with aliphatic carbon atoms. The systems investigated were ring-substituted 5-bromo-2-phenyl-2-pentenes (I, X = C_6H_5; Y = CH_3), 4-bromo-1-butene (I, X = Y = H) and its homolog 5-bromo-pentene (II) and some bicyclic unsaturated bromides, *exo*- and *endo*-5-bromo-2-norbornene (III). All of these systems appear to yield $[M - Br]^+$ ions with the aid of some remote π-electron density.



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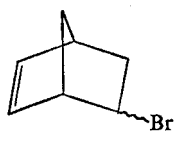

(III)

† Presented in part at the ASTM Committee E-14, 18th Annual Conference on Mass Spectrometry and Allied Topics, San Francisco, California, 14th to 18th June 1970.

‡ NASA Fellow 1966 to 69, NSF Cooperative Fellow 1969 to 1970.

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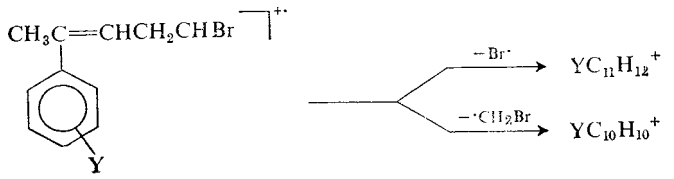
|| The Editor-in-Chief wishes to apologise for the delay in the publication of this paper.

RESULTS AND DISCUSSION

In this study, as in previous studies,[1,2] we have used the kinetic approach of Williams and Cooks,[6] which is based on the simplified form of the basic equation of the quasi-equilibrium theory, $k(E) = \nu[E - \varepsilon/E]^{s-1}$. This kinetic approach is based on the fact that a rearrangement ion will increase relative to a competing simple cleavage ion as the internal energy of the ion is decreased. We have also used the observations of Chupka[7] and McLafferty[8] that the metastable peak area for a rearrangement reaction will be greater than the metastable peak area for a competing simple cleavage because of the lower activation energy and slower rise in K vs. E for the rearrangement reaction. In addition thermochemical data were used in certain cases.

5-Bromo-2-phenyl-2-pentene (IV) and its ring substituted derivatives undergo two main reactions: 1) expulsion of bromine and 2) loss of $\cdot CH_2Br$ via a simple cleavage reaction.



(IV)

We have utilized the competing simple cleavage reaction (loss of $\cdot CH_2Br$) as an internal average rate standard and our kinetic results expressed as $(M - Br^+)/[(M - Br^+) + (M - CH_2Br^+)]$ are given in Table 1.

TABLE 1. $(M - Br^+)/[(M - Br^+) + (M - CH_2Br^+)]$ RATIO FROM RING SUBSTITUTED 5-BROMO-2-PHENYL-2-PENTENE AS A FUNCTION OF IONIZING ENERGY $(M - Br^+)/[(M - Br^+) + (M - CH_2Br^+)]$

Substituent	30 eV	20 eV	19 eV	18 eV	17 eV	16 eV	15 eV	14 eV	13 eV
m-CH_3O	0·807	0·834	0·840	0·849	0·863	0·894	0·927	0·948	1·000
m-NO_2	0·694	0·700	0·688	0·709	0·704	0·714	0·723	0·752	0·804
p-CF_3	0·583	0·629	0·650	0·661	0·682	0·738	0·797	0·839	0·870
m-CF_3	0·559	0·617	0·635	0·652	0·692	0·725	0·785	0·835	0·855
m-F	0·563	0·610	0·621	0·639	0·667	0·700	0·764	0·807	0·841
m-Cl	0·573	0·597	0·614	0·627	0·650	0·695	0·722	0·784	0·835
m-CH_3	0·513	0·556	0·572	0·583	0·610	0·637	0·695	0·741	0·795
H	0·501	0·539	0·551	0·564	0·590	0·625	0·667	0·725	0·767
p-Cl	0·450	0·483	0·493	0·509	0·522	0·550	0·603	0·685	0·764
p-CH_3	0·428	0·470	0·481	0·500	0·524	0·562	0·616	0·680	0·770
p-F	0·432	0·459	0·473	0·490	0·509	0·543	0·589	0·643	0·680
p-OCH_3	0·311	0·335	0·341	0·352	0·361	0·382	0·411	0·483	0·630

In all cases the loss of bromine increased relative to the loss of $\cdot CH_2Br$ as the ionizing energy is decreased. These kinetic data are entirely consistent with the loss of bromine having a lower frequency factor than the loss of $\cdot CH_2Br$ because of the loss of bromine involving a 'rearrangement-like' transition state.† In addition these data indicate that the loss of bromine has a lower activation energy than does the loss of $\cdot CH_2Br$.

Table 2 shows the ratio of metastable peak areas for the two competing reactions.

† The increase in loss of bromine on decreasing the ionizing energy from 30 eV to 13 eV is at least as large as the increase in the $[M - C_2H_2O]^{+\cdot}/[M - CH_3CO]^+$ ratio in acetanilides and phenyl acetates where the $[M - C_2H_2O]^{+\cdot}$ ion definitely arises through a rearrangement process.[9]

TABLE 2. RATIO OF METASTABLE PEAK AREAS IN RING SUBSTITUTED 5-BROMO-2-PHENYL-2-PENTENES AT 30 eV

Substituent	m_1^*/m_2^*[a]
H	3·25
p-OCH_3	0·9
m-OCH_3	7·65
p-CF_3	7·87
m-CF_3	7·60
p-CH_3	2·66
m-CH_3	4·33
p-F	3·33
m-F	9·0
p-Cl	4·67
m-Cl	1·85
m-NO_2	2·4

[a] $m_1^* = (M - Br)^2/(M)$; $m_2^* = (M - CH_2Br)^2/(M)$.

These data, except for the *p*-methoxyl substituted case, are also consistent with that expected if the loss of bromine involves a lower frequency factor and slower rise in its *k vs. E* curve than does the loss of $\cdot CH_2Br$; i.e. the loss of Br· involves a rearrangement-like transition state.[7,8]

It is also somewhat surprising that the loss of bromine is the lowest energy process.† The unexpectedly lower activation energy for loss of bromine compared to the loss of $\cdot CH_2Br$ is completely consistent with the concept of anchimeric assistance lowering the activation energy for loss of bromine.

Any proposal as to the nature of the transition state leading to the $(M - Br)^+$ ion and thus of the structure of the ion itself, should be consistent with the effect of substituents on the rates of reaction.

If the transition states involved resemble a ring-substituted cinnamyl cation (1),

† That the AP of the $(M - CH_2Br)^+$ ion would be predicted to be less than the AP of the $(M - Br)^+$ ion arises from the following considerations.[10a,10b,11]

$$IP(C_3H_5\cdot) = 8{\cdot}1 \text{ eV} \qquad IP(C_6H_5CH_2\cdot) = 7{\cdot}7 \text{ eV}$$

$$CH_2 = CH{-}CH_2{-}CH_3 \rightarrow C_3H_5\cdot + \cdot CH_3 = 2{\cdot}8 \text{ eV}$$

$$\text{S.E. } \cdot CH_2Br \text{ relative to } \cdot CH_3 = 0{\cdot}9 \text{ eV}$$

Therefore,

$$CH_2 = CH{-}CH_2{-}CH_2Br \rightarrow C_3H_5\cdot + \cdot CH_2Br = 1{\cdot}9 \text{ eV}$$

$$IP(CH_3CH_2CH_2CH_2\cdot) = 8{\cdot}4 \text{ eV}$$

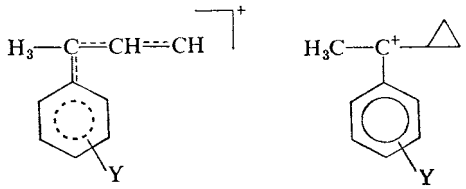
$$D(CH_3CH_2{-}Br) = 3{\cdot}4 \text{ eV}$$

If no long range interactions are operative the loss of bromine should be comparable to loss of Br· from a primary alkyl bromide.

$$AP(R_1^+) = IP(R_1\cdot) + D(R_1 - R_2)$$

Inserting the above figures into this equation leads to a calculated AP for loss of $\cdot CH_2Br$ = 10·0 eV and for loss of ·Br = 11·8 eV. Any additional lowering of the IP of the allyl radical by substitution with a phenyl group would, of course, increase the difference.

for the loss of $\cdot CH_2Br$ and the α-cyclopropyl-α-methylbenzyl cation (2), for the loss of ·Br, the substituent effect would be similar to that observed for the loss of bromine from β-phenylethyl bromides since 1 and 2 are homologs of the transition states in the β-phenylethyl bromides.



(1) (2)

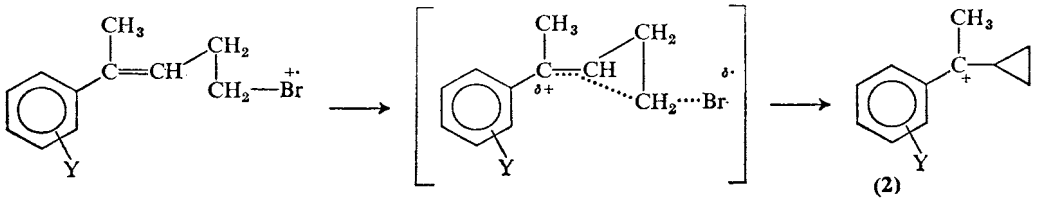
Since it is known that an adjacent cyclopropyl group stabilizes a neighboring cationic center to a greater extent than does either an adjacent double bond[12] or an adjacent aromatic ring,[13] a substituent should have a greater stabilizing or destabilizing effect on the $[M - CH_2Br]^+$ ion than on the $[M - Br]^+$ ion. Thus, one would expect that *meta* substituents would have little effect on the relative abundances of the $[M - Br]^+$ ions and $[M - CH_2Br]^+$ ions since they are not in direct conjugation with the reaction center. Electron withdrawers in the *para* position should destabilize 1 to a greater extent than 2 and therefore exhibit a greater $[M - Br]^+$ abundance. On the other hand, electron donors in the *para* position should enhance the simple cleavage ion relative to the $[M - Br]^+$ ion.

Table 3 compares the substituent effects on IV with those on β-phenylethyl bromide at 15 eV. Table 3 shows that the β-phenylethyl bromides exhibit the expected behavior, but IV exhibits significantly different substituent effects; namely, *meta* electron donors significantly enhance the loss of bromine relative to the loss of $\cdot CH_2Br$. In fact, the order for stabilizing the $[M - Br]^+$ ion by *meta* electron donors is the same as that for stabilization of the $[M - CH_2Br]^+$ ion by *para* substituents, i.e. $OCH_3 > F > Cl > CH_3$.

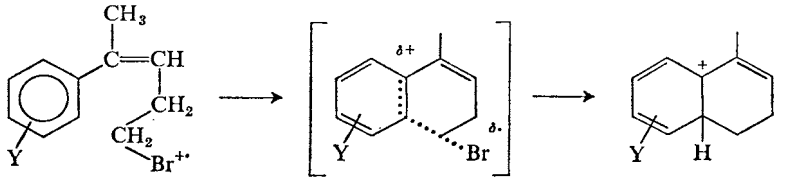
TABLE 3. SUBSTITUENT EFFECTS ON THE LOSS OF BROMINE FROM SUBSTITUTED β-PHENYLETHYL BROMIDES AND SUBSTITUTED 5-BROMO-2-PHENYL-2-PENTENE AT 15 eV

5-Bromo-2-phenyl-2-pentene		β-Phenylethyl bromide	
Substituent	$\frac{(M - Br^+)}{(M - Br^+) + (M - CH_2Br^+)}$	Substituent	$\frac{(M - Br^+)}{(M - Br^+) + (M - CH_2Br^+)}$
m-OCH_3	0·93	*p*-NO_2	0·75
m-NO_2	0·72	*m*-NO_2	0·68
p-CF_3	0·80	*m*-CF_3	0·56
m-CF_3	0·79	*m*-F	0·48
m-F	0·76	H	0·45
m-Cl	0·72	*m*-OCH_3	0·45
m-CH_3	0·70	*m*-Cl	0·44
H	0·67	*m*-CH_3	0·38
p-CH_3	0·62	*p*-Cl	0·28
p-Cl	0·60	*p*-CH_3	0·27
p-F	0·59	*p*-F	0·27
p-OCH_3	0·41	*p*-OCH_3	0·17

The anomalous substituent effects can be best explained by invoking two mechanisms for the expulsion of bromine: (1) homoallylic participation as in Scheme 1 for electron withdrawers and (2) aromatic participation as in Scheme 2.

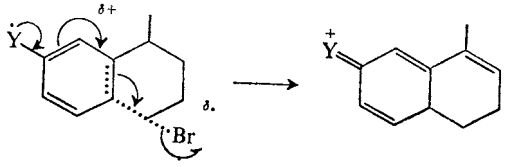


SCHEME 1



SCHEME 2 (3)

Electron donors in the *meta* position would be expected to stabilize the transition state leading to 3 since they are in direct conjugation with the developing positive charge.



(3)
(contributing structure)

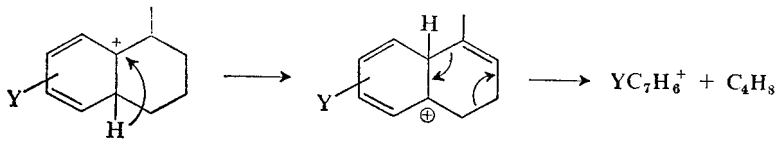
These structures also are consistent with the secondary fragmentations observed for the $(M - Br)^+$ ions. The $(M - Br)^+$ ions, except for the nitro-substituted one,† undergo a secondary fragmentation to yield $\cdot YC_7H_6^+$ and formation of $\cdot YC_8H_8^+$ is also observed as a minor process. The $(M - Br)^+$ ion from IV, Y = CF_3, undergoes loss of C_2H_4 to a greater extent than it undergoes formation of $YC_7H_6^+$ while the reverse is true for other substituents.

The secondary decomposition of IV (Y = CF_3) by expulsion of C_2H_4 is consistent with a product of structure 2 since cyclopropyl systems have been observed to expel C_2H_4.[14]

Intervention of a product ion like 3 also explains the unexpectedly large abundance

† The *m*-nitro substituted compound loses NO_2 from both the $(M - Br)^+$ and $(M - CH_2Br)^+$ ion.

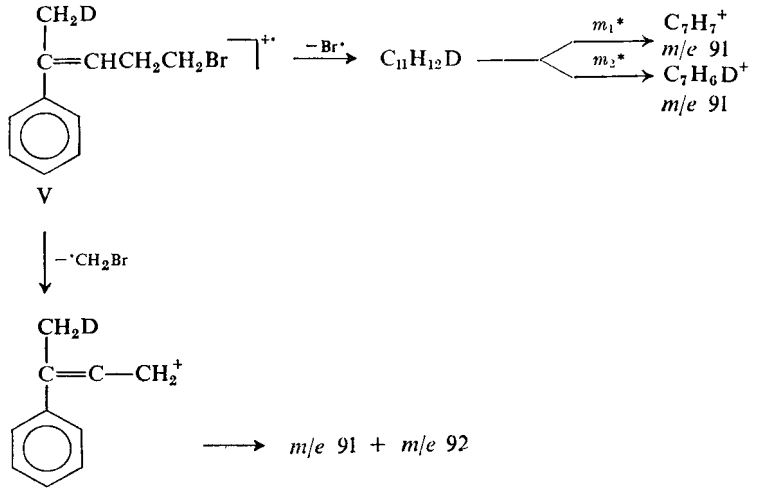
of $YC_7H_6^+$ relative to $YC_8H_8^+$, since the cyclic nature of this ion provides a route for this process as indicated in Scheme 3.



(3) SCHEME 3

If such a mechanism is operative for the formation of $YC_7H_6^+$, it is easy to visualize that all of the hydrogens may eventually become scrambled. If the product is best represented by 2, it is unlikely that all of the hydrogens would become equivalent since the aromatic ring would be disrupted.

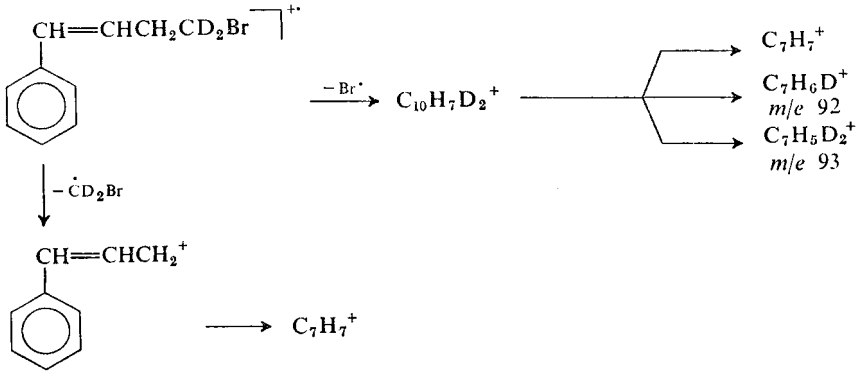
To investigate this possibility 5-bromo-2-phenyl-2-pentene-1-d_1 (V), was synthesized. Since both the $[M - Br]^+$ and $[M - CH_2Br]^+$ ions undergo secondary decomposition to *m/e* 91, the ratio of *m/e* 92 to *m/e* 91 cannot be used to investigate the degree of scrambling in the $[M - Br]^+$ ion. Since the metastable peaks for the transitions are obscured by normal peaks in this region, an IKE spectrum was obtained.† The observed ratio for m_2^*/m_1^* (Scheme 4) was 1·15:1 which is in excellent agreement with a calculated ratio of 1·16:1 for complete scrambling and inconsistent with the calculated ratio of 0·33:1 for only side chain hydrogen scrambling.



SCHEME 4

Although it is impossible to determine the amount of scrambling in the fast reaction, a very similar compound, 4-bromo-1-phenyl-1-butene-4,4-d_2 (VI, Scheme 5), shows a nearly statistical ratio of $\frac{93}{92}$ ions in the 30 eV spectrum, i.e. an observed ratio of 0·72 *vs.* a calculated ratio of 0·75.

† Performed at Purdue University by Dr Richard Caprioli.

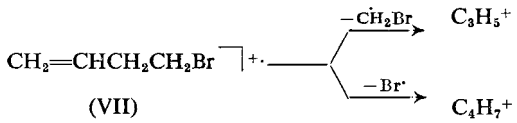


SCHEME 5

Thus the kinetic data, labeling data and substituent effects are consistent with the proposal that the loss of bromine from substituted 5-bromo-2-phenyl-2-pentenes involves anchimeric assistance and that with substituents on the aromatic ring capable of electron donation the transition state for loss of bromine resembles a bicyclic ion such as 3, while with substituents on the aromatic ring which strongly destabilize a positive charge the loss of bromine proceeds via the cyclopropyl carbinyl-like transition state 1.

Since this investigation of the possibility of homoallylic participation was not conclusive, we turned our attention towards a non-arylated system, 4-bromo-1-butene (VII).

Upon electron-impact 4-bromo-1-butene undergoes two competing fragmentations: 1) the expulsion of bromine and 2) the loss of $\cdot CH_2Br$.



(VII)

The kinetic data for loss of bromine from 4-bromo-1-butene utilizing the competing loss of $\cdot CH_2Br$ as an internal average rate standard are presented in Table 4.

TABLE 4. EFFECT OF IONIZING ENERGY ON THE RELATIVE ABUNDANCES OF $(M - Br)^+$ AND $(M - CH_2Br)^+$ IONS FROM 4-BROMO-1-BUTENE $(M - Br^+)/[(M - Br^+) + (M - CH_2Br^+)]$

30 eV	20 eV	19 eV	18 eV	17 eV	16 eV	15 eV
0·881	0·931	0·935	0·944	0·964	0·973	1·000

As the ionizing energy is lowered the abundance of the $(M - Br)^+$ ion increases relative to the abundance of the $(M - CH_2Br)^+$ ion. These data are consistent with the expulsion of bromine involving a lower-frequency factor because of the reaction proceeding through a 'rearrangement-like' transition state. On the other hand, it can also be argued that the lower frequency factor is due only to the difference in stretching vibrations of the bonds in question. Further evidence for anchimeric assistance can be obtained from the thermochemical data in Table 5, however. The activation energy for loss of bromine, 0·7 eV, is 0·3 eV lower than that found for the loss of bromine from propyl bromide, 1·0 eV.[15] This lower activation energy is

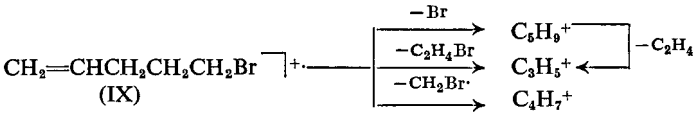
TABLE 5. APPEARANCE POTENTIALS AND IONIZATION POTENTIALS AND ACTIVATION ENERGIES OF SELECTED CLEAVAGES

Compound	Ion	AP (eV)	IP (eV)	E_a (eV)
4-Bromo-1-butene	$C_4H_7Br^{+\cdot}$		9·9	
4-Bromo-1-butene	$C_4H_7^+$	10·6		0·7
4-Bromo-1-butene	$C_3H_5^+$	12·6		2·7
5-Bromo-1-pentene	$C_5H_9Br^{+\cdot}$		9·6	
5-Bromo-1-pentene	$C_5H_6^+$	10·2		0·6
5-Bromo-1-pentene	$C_3H_5^+$	12·2		2·6

consistent with anchimeric assistance in the loss of bromine. In addition one would *a priori* expect the loss of bromine to have a higher AP than the loss of $\cdot CH_2Br$.†

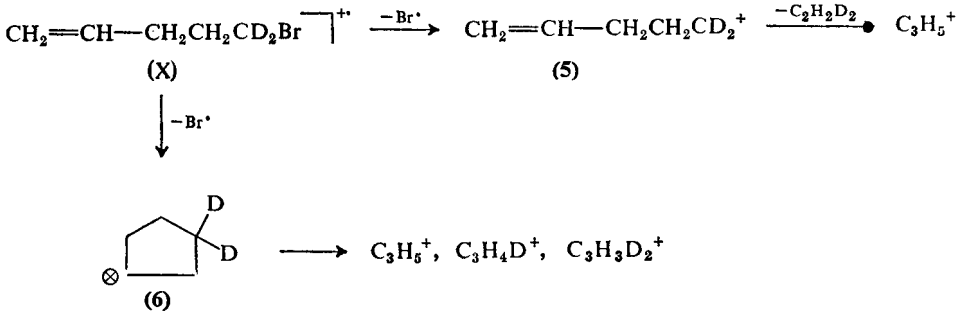
We propose that the transition state for loss of bromine resembles the cyclopropyl carbinyl cation (4).

To see if π-electrons associated with aliphatic carbon atoms can participate in the loss of a more remote halogen, we investigated the loss of bromine from 5-bromo-1-pentene (IX). IX undergoes three major reactions: 1) loss of $\cdot(CH_2)_2Br$ and 2) loss of $\cdot CH_2Br$ and 3) loss of bromine. In addition, the $[M - Br]^+$ ion undergoes a secondary loss of C_2H_4 to yield the $[M - C_2H_4Br]^+$ ion.



Again from thermochemical considerations the loss of $\cdot CH_2CH_2Br$ is expected to have a lower AP than the loss of Br.‡ In addition the activation energy for loss of bromine is 0·4 eV lower than that found for the loss of bromine from C_3H_7Br, 1·0 eV. These data are completely consistent with anchimeric assistance in the loss of bromine.

Evidence for the cyclic nature of the $[M - Br]^+$ ion comes from the labeled compound 5-bromo-1-pentene-5,5-d_2 (X). If the $[M - Br]^+$ ion is acyclic, e.g. 5, all of the deuterium should be lost in the expulsion of ethylene. If, on the other hand, it is cyclic, e.g. 6, fairly extensive scrambling could occur prior to loss of ethylene and C_2H_4, C_2H_3D and $C_2H_2D_2$ would be lost.

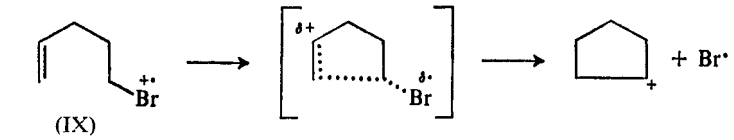


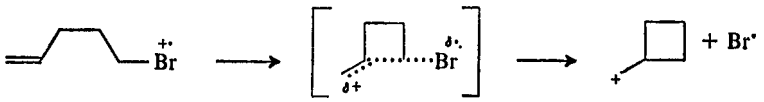
† See footnote p. 237.

‡ See footnote p. 237. The $\cdot CH_2CH_2Br$ radical should be 0·4 eV more stable than the $\cdot CH_5$ radical.[18]

Since there are two mechanisms for the formation of the $C_3H_5^+$ ion, we looked at the metastables for the loss of C_2H_4 (m_1*), C_2H_3D (m_2*) and $C_2H_2D_2$ (m_3*). The observed ratio of m_1*:m_2*:m_3* at 30 eV of 52:100:31 is only consistent with statistical scrambling of all hydrogens and deuteriums which gives a calculated m_1*:m_2*:m_3* ratio of 50:100:30.

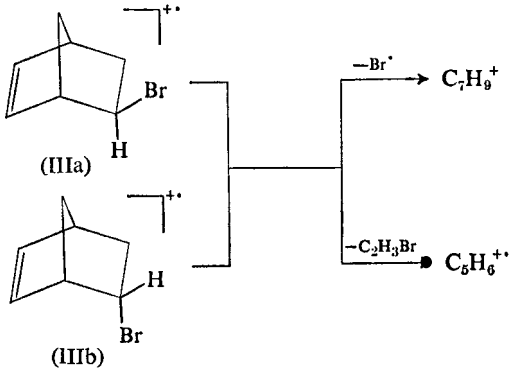
Thus the thermochemical and deuterium scrambling data are entirely consistent with the expulsion of bromine from IX involving a cyclic transition state leading to a cyclic product which decomposes from the same structure. We favor **6** rather than **7** as the structure of the $[M - Br]^+$ ion since formation of a five-membered ring is more favorable than a four-membered ring and the formation of **7** leads to a primary cation rather than a secondary cation.





Since physical organic chemists are almost required to make some study in the norbornyl system, we investigated the possibility of anchimeric assistance in the expulsion of bromine from *exo*- and *endo*-5-bromo-2-norbornene (IIIa and IIIb).

IIIa and IIIb undergo two competing reactions upon electron-impact: 1) the expulsion of bromine and 2) loss of the elements of vinyl bromide in a *retro*-Diels-Alder reaction.



The kinetic data for loss of bromine from IIa and IIb utilizing the competitive *retro*-Diels-Alder reaction as an internal average rate standard are presented in Table 6.

In both cases the abundance of the $[M - Br]^+$ ion increases slightly relative to the $[M - C_2H_3Br]^+$ ion abundance as the ionizing energy is decreased. Since the *retro*-Diels-Alder reaction involves bond formation in addition to bond cleavage in the

TABLE 6. EFFECT OF IONIZING ENERGY ON THE ABUNDANCE OF THE $(M - Br)^+$ ION RELATIVE TO THE $(M - C_2H_3Br)^{+\cdot}$ ION FROM *Exo*- AND *Endo*-5-BROMO-2-NORBORNENE $(M - Br^+)/[(M - Br^+ + (M - C_2H_3Br^+)]$

Isomer	30 eV	20 eV	19 eV	18 eV	17 eV	16 eV	15 eV	14 eV	13 eV
Exo	0·46	0·51	0·51	0·51	0·53	0·57	0·56	0·58	0·59
Endo	0·056	0·065	0·065	0·074	0·074	0·065	0·076	0·078	0·091

transition state, the frequency factor is lower than for simple cleavage reactions. The slight increase in the abundance of the $(M - Br)^+$ ion indicates that the loss of bromine involves a lower frequency factor than does the *retro*-Diels-Alder reaction. This behavior is consistent with the loss of bromine involving a 'rearrangement-like' transition state.

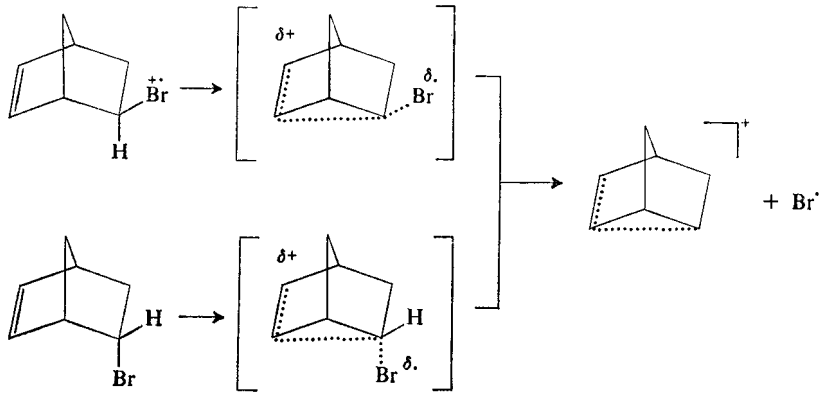
As further evidence for anchimeric assistance in the expulsion of bromine we have obtained the thermochemical data in Table 7. Using the relationships in the footnote

TABLE 7. APPEARANCE AND IONIZATION POTENTIALS AND ACTIVATION ENERGIES IN *Exo*- AND *Endo*-5-BROMO-2-NORBORNENE

Isomer	Ion	AP (eV)	IP (eV)	E_a (eV)
Exo	$C_7H_9Br^{+\cdot}$		9·2	
Exo	$C_7H_9^+$	10·2		1·0
Exo	$C_5H_6^{+\cdot}$	10·0		0·8
Endo	$C_7H_9Br^{+\cdot}$		9·2	
Endo	$C_7H_9^+$	10·1		0·9
Endo	$C_5H_6^{+\cdot}$	10·0		0·8

on p. 237 and assuming that a secondary alkyl bromide is a good model for IIIa and IIIb when there is no interaction between the olefinic bond and the carbon–bromine bond, we calculated that the AP for loss of bromine is at least 11·1 eV. The AP for the $(M - Br)^+$ ion is also probably lower (though within experimental error) than the AP for the $(M - Br)^+$ ion of the saturated 2-norbornylbromide where sigma participation has been postulated.[17]

The evidence is consistent with anchimeric assistance in the transition state for expulsion of bromine and formation of the delocalized norbornenyl cation (8), in both species.



Since the activation energy for the *retro*-Diels-Alder reaction is identical for both isomers and the activation energies for expulsion of bromine differ by only 2 kcal/mole, the significant difference in the average rates of expulsion of bromine from the two isomers should be a function of the frequency factor. The olefin and bromine in the *exo*-isomer are ideally situated sterically for participation. In the *endo*-isomer the olefin is not ideally situated for backside attack in the expulsion of bromine, however, and the molecule has to undergo severe twisting before the olefin is in position to participate. This will decrease the frequency factor and, thus, the average rate.

The thermochemical data we have obtained also lend support to the suggestion by Cooks[4] that some charge density must reside on the leaving group prior to expulsion of that leaving group. The difference in the ionization potentials of olefins and halo compounds is very similar to the activation energy in the acyclic compounds, e.g. 0·55 eV difference between the IP of 1-butene and 1-bromobutane vs. an 0·7 eV activation energy for loss of bromine from 4-bromo-1-butene and an 0·6 eV difference in the IP's of bromopentane and 1-pentene vs. an 0·6 eV activation energy for loss of bromine in 5-bromo-1-pentene.[18] Steele and co-workers observed that the molecular ions of *exo*- and *endo*-5-chloro-2-norbornene exhibited an insignificant loss of chlorine.[19] This is consistent with the higher ionization potential of chlorine vs. bromine. In the chloro compounds very little charge density is ever present on the chlorine moiety and thus the expulsion of chlorine is an insignificant reaction. The increased activation energy for loss of chlorine relative to loss of bromine (1·95 eV vs. 0·95 eV)† compares very well with the difference of 1·17 eV in IP's of atomic chlorine vs. atomic bromine and is significantly greater than the 0·2 eV expected on the basis of carbon-halogen bond strengths from $D(R\text{-}CH_2\text{-}X)^{+\cdot}$. A referee has pointed out that this difference may be due to a difference in the amount of anchimeric assistance in the two cases. There is no reason to assume this *a priori*, however.

These data indicate that, at least in these systems, once the leaving group begins to bear charge, it is expelled by the participating group with little or no activation energy.

EXPERIMENTAL

The mass spectra were obtained with a Varian MAT CH-5 mass spectrometer. The samples were introduced by means of a direct probe (solids) or an all glass heated (150°) inlet system (liquids and appearance potential measurements). In all cases a trap current of 20 microamps was employed. Appearance potentials were measured by the method of Lossing *et al.*[27]

Preparation of methyltriphenylphosphonium bromide[20] A solution of triphenylphosphine (55 g, 0·21 mol) and methyl bromide (16·5 ml, 0·29 mol) in benzene (45 ml) in a sealed bottle was left to stand for 48 hrs. After opening, the solution was filtered and the filtrate collected m.p. 230 to 231°, lit: 232 to 233°.[16]

Preparation of 1-*cyclopropyl-m-nitrostyrene.*[21] To a solution of *n*-butyllithium (0·02 mol) in ether (240 ml) was added methyltriphenylphosphonium bromide (7·14 g, 0·02 mol) under nitrogen and let stir for 4 hrs. The solution was added with cooling to cyclopropyl *m*-nitrophenyl ketone (0·02 mol) in ether (30 ml). After the addition was complete, benzene (200 ml) was added and the ether was distilled. The solution was heated at 60° for 4 hrs and water was added. The benzene layer was separated and washed successively with dilute hydrochloric acid, water, sodium bicarbonate solution and water and dried over magnesium sulfate. The benzene was removed at reduced pressures and the residue distilled. The fraction distilling at 78° at 0·01 mm Hg was collected.

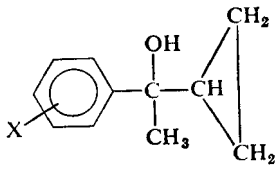
n.m.r.: 7·05(m, 4); 5·15(s, 1); 4·83(s, 1); 0·25 to 1·65(m, 5).

† The IP of the chloronorbornenes, 9·1 eV, compares well with our IP of 9·2 eV for the bromonorbornenes indicating that the initial site of ionization is the olefin in both.

Preparation of 1-*cyclopropylstyrene.*[22] Methyltriphenylphosphonium bromide (3·57 g, 0·1 mol) was added to a solution of *n*-butyllithium (0·1 mol) in anhydrous ether (200 ml). The solution was stirred for 4 hrs and cyclopropyl phenyl ketone (14·6 g, 0·1 mol) was added. The solution was heated at reflux for 24 hrs, stirred 16 hrs and water (200 ml) was added. The ether layer was separated and dried over magnesium sulfate. The ether was removed at reduced pressure and the residue distilled at water aspirator pressure at 91° (lit: $b._{25}$ 107°).[22]

Preparation of substituted α-cyclopropyl-α-methylbenzyl alcohols—general procedure. To the Grignard reagent prepared from substituted bromobenzene (0·08 mol) was added cyclopropyl methyl ketone (6·8 g, 0·08 mol) in ether (15 ml). After stirring ½ hr, we added dilute hydrochloric acid. The ether layer was separated, washed with water and dried over magnesium sulfate. The ether was removed at reduced pressure and the residue distilled. The conditions for distillation are listed in Table 8. Prepared in this manner were *m*- and *p*-methoxy, *m*-methyl, *m*-chloro, *m*-fluoro and *m*- and *p*-trifluoromethyl substituted α-cyclopropyl-α-methylbenzyl alcohols. The other alcohols used were commercially available.

TABLE 8. BOILING POINTS OF SUBSTITUTED α-CYCLOPROPYL-α-METHYLBENZYL ALCOHOLS



X	Pressure (mm Hg)	b.p.°
p-OCH_3	3·0	128
m-CH_3	2·7	104 to 106
m-Cl	3·2	122 to 123
m-F	1·8	90
m-OCH_3	3·0	126 to 128
m-CF_3	2·0	90
p-CF_3	3·4	102

n.m.r.: *p*-CF_3 (s, 4)7·4; (s, 1)2·4; (s, 3)1·25; (m, 1)0·85 to 1·2; (m, 4)0·15 to 0·4: *m*-CF_3 (m, 4)7·0 to 7·7; (s, 1)2·45; (s, 3)1·22; (m, 1)0·85 to 1·2; (m, 4)0·15 to 0·4: *m*-OCH_3 (m, 3)6·9 to 7·2; (m, 1)6·5 to 6·7; (s, 3)3·65; (s, 1)2·3; (s, 3)1·35; (m, 1)0·86 to 1·3; (m, 4)0·20 to 5: *m*-F (m, 4)6·5 to 7·3; (s, 1)2·33; (s, 3)1·33; (m, 1)0·85 to 1·3; (m, 4)0·2 to 0·5: *m*-Cl (m, 4)7·0 to 7·6; (s, 1)7·22; (s, 3)1·33; (m, 1)0·85 to 1·3; (m, 4)0·25 to 0·55: *m*-CH_3 (m, 4)6·7 to 7·3; (s, 3)2·2; (s, 1)2·0; (s, 3)1·3; (m, 1)0·85 to 1·3; (m, 4): 0·15 to 0·45: *p*-OCH_3 (d, 2)7·35; (d, 2)6·7; (s, 3)3·6; (s, 1)2·12; (s, 3)1·32; (m, 1)0·8 to 1·3; (m, 4)0·15 to 0·45.

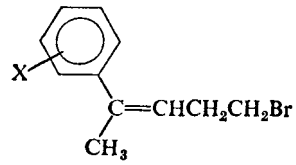
Preparation of substituted 5-bromo-2-phenyl-2-pentenes—general procedure.[23] The substituted α-cyclopropyl-α-methylbenzyl alcohol (2·5 g) was added at 0° to 48% hydrobromic acid (10 ml) and the resulting solution was stirred for ½ hr. The solution was extracted with petroleum ether. The organic layer was washed with water, sodium bicarbonate solution and water and dried over magnesium sulfate. The solvent was evaporated and the product purified by gas chromatography (see Table 9 for products and conditions). These compounds are thermally unstable and slowly decompose with time.

n.m.r.: *p*-F (m, 4)6·5 to 7·3; (m, 1)5·4; (t, 2)3·13; (m, 2)2·4; (s, 3)1·7: *m*-F (m, 4)6·5 to 8·2; (m, 1)5·6; (t, 2)3·2; (m, 2)2·55; (s, 3)1·8: *m*-OCH_3 (m, 4)6·4 to 7·2; (m, 1)5·55; (s, 3)3·5; (t, 2)3·15; (m, 2)2·45; (s, 3)1·75: *m*-CH_3 (m, 4)6·6 to 7·2; (m, 1)5·45; (t, 2)3·1; (m, 2)2·4; (s, 3)2·1; (s, 3)1·75: *m*-Cl (m, 4)7·0 to 7·3; (m, 1)5·55; (t, 2)3·25; (m, 2)2·55; (s, 3)1·8: *p*-CH_3 (q, 4)6·9; (m, 1)5·45; (t, 2)3·1; (m, 2)2·4; (s, 3)2·05; (s, 3)1·73: *p*-OCH_3 (d, 2)7·17; (d, 2)6·68; (m, 1)5·52; (s, 3)3·55; (t, 2)3·25(m, 2)2·55; (s, 3)1·82: *p*-Cl (s, 4)7·1; (m, 1)5·55; (t, 2)3·25; (m, 2)2·55; (s, 3)1·8: *m*-CF_3 (m, 4)7·1 to 7·5; (m, 1)5·6; (t, 2)3·2; (m, 2)2·53; (s, 3)1·82.

Preparation of 5-bromo-2-(m-nitrophenyl)-2-pentene. A solution of 1-cyclopropyl-*m*-nitrostyrene (0·45 g, 0·0024 mol) and 48% hydrobromic acid (0·47 g) in acetone (12 ml) was stirred for 48 hrs. Water was added and the acetone removed at reduced pressure. Ether was added and the ether layer was separated and dried over magnesium sulfate. The ether was removed and the product purified by gas chromatography (see Table 9).

n.m.r.: *m*-NO_2 (m, 4)7·2 to 8·3; (m, 1)5·85; (t, 2)3·45; (m, 2)2·8; (s, 3)2·07.

TABLE 9. PURIFICATION OF SUBSTITUTED 5-BROMO-2-PHENYL-2-PENTENES BY GAS CHROMATOGRAPHY



X	Column	Temperature (°)	Flow rate (ml/min)	Retention time (min)
m-NO_2	3% SE-30 5′ × ¼″	216	30	7·5
p-F	20% SE-30 5′ × ¼″	220	30	5·5
p-Cl	20% SE-30 5′ × ¼″	220	30	10·3
p-CH_3	20% SE-30 5′ × ¼″	220	30	7·5
m-Cl	20% SE-30 5′ × ¼″	220	30	10·0
m-CH_3	20% SE-30 5′ × ¼″	220	30	7·2
m-F	20% SE-30 5′ × ¼″	220	30	5·2
m-OCH_3	20% SE-30 5′ × ¼″	220	30	10·7
p-OCH_3	20% SE-30 5′ × ¼″	225	30	12·3
p-CF_3	20% SE-30 5′ × ¼″	225	30	6·3
m-CF_3	20% SE-30 5′ × ¼″	225	30	5·3
H	20% SE-30 5′ × ¼″	220	30	5·7

Preparation of alkenyl bromides—general procedure. To a solution of hydroxyalkene (5·0 g) in ether (25 ml) at 0° was slowly added phosphorous tribromide (2·4 ml). The solution was heated at reflux for 16 hrs and water was added. The ether layer was separated and washed with water, sodium bicarbonate and water. The ether layer was dried over magnesium sulfate and the ether was removed at reduced pressure. Prepared in this manner were 4-bromo-1-butene which was collected by gas chromatography on a 20% SE-30 5′ × ¼″ column at 98° and a flow rate of 30 ml/min at a retention time of 3·1 min and 5-bromo-1-pentene which was collected by gas chromatography on 20% SE-30 5′ × ¼″ column at 98° and a flow rate of 30 ml/min at a retention time of 5·9 min.

Preparation of diethyl allylmalonate.[24] To a refluxing solution of sodio malonic ester prepared from sodium (10·9 g, 0·47 g.at.) in absolute ethanol (110 ml) and diethyl malonate (75 g, 0·47 mol) was added 3-bromopropene (57 g, 0·47 mol). The solution was heated at reflux for ½ hr and diluted with water. The resulting aqueous solution was extracted with ether and the ether layer was washed with water and dried over magnesium sulfate. The ether was removed at reduced pressure. The residue was distilled and the fraction boiling at 118 to 128° at water aspirator pressure was collected (lit: b_{20} 116 to 124°).[24]

Preparation of allylacetic acid.[24] Diethyl allyl malonate (50 g, 0·25 mol) was stirred at room temperature in a solution of 85% potassium hydroxide (68 g) in water (77 g) for 2·5 hrs. The ethanol formed was evaporated and the solution was extracted with ether. The aqueous layer was acidified and extracted with ether. The ether layer was dried over magnesium sulfate and the ether removed at reduced pressure. The resulting solid was recrystallized from benzene/Skellysolve (C). The melting point was 101 to 102°, lit: 102°,[24] yield 10 g. The acid was decarboxylated at 180° and distilled at water aspirator pressure, b. 92°, lit: $b_{.17\ to\ 18}$ 91 to 92°,[24] yield 6·0 g.

Preparation of 5-bromo-1-pentene-5,5-d_2. Allylacetic acid (1 g, 0·01 mol) in ether (20 ml) was added to lithium aluminum deuteride (0·42 g, 0·01 mol) in ether (20 ml). The solution was heated at reflux for 1 hr and let stir for 2 days. Dilute hydrobromic acid was added. The ether layer was separated and washed with water, sodium bicarbonate and water and dried over magnesium sulfate.

The solvent was removed at reduced pressure. Ether (30 ml) was added to the residue and phosphorous tribromide (1 ml) was added. The solution was heated at reflux overnight and water was added. The ether layer was separated and washed with water; sodium bicarbonate and water. The solvent was removed at reduced pressure. The product was purified by gas chromatography (5·9 min retention time on a 20% SE-30 5′ × ¼″ column with a flow rate of 30 ml/min and a column temperature of 98°).

Preparation of 5-bromo-2-phenyl-2-pentene-1-d_1. A mixture of 1-cyclopropylstyrene (0·72 g, 0·005 mol), 48% deuterium bromide in D_2O (0·85 g) and ether (25 ml) was stirred 11 hrs. The ether layer was decanted and dried over calcium chloride. The product was purified by gas chromatography (13·5 min retention time on a 15% Carbowax 20 M 5′ × ¼″ column at 200° and a flow rate of 60 ml/min).

Preparation of exo- and endo-5-bromo-2-norbornene.[25] Dicyclopentadiene (30 g, 0·25 mol) was heated to reflux (160°) in a flask equipped with a Friedrich condenser and cyclopentadiene was collected by distillation. Cyclopentadiene (13·2 g, 0·2 mol) and vinyl bromide (32·2 g, 0·3 mol) were heated in a sealed glass tube at 170° for 20 hrs. The resulting liquid was distilled at water aspirator pressure and the fraction boiling at 69·5 to 70·5° was collected (lit: b_{15} 63 to 65·5°).[25] This material was a 40:60 mixture of *exo-* and *endo*-isomers which were separated by gas chromatography (on a 5′ × ¼″ 15% Carbowax 20 M column at 102° and a flow rate of 30 ml/min. The *exo*-isomer had a retention time of 21·6 min and the *endo*-isomer had a retention time of 27·8 min).

Preparation of 4-phenylbutenoic acid.[26] A solution of malonic acid (25 g, 0·24 mol) and phenyl acetaldehyde (30 g, 0·25 mol) and diethylamine (10 drops) in absolute ethanol (65 ml) was heated at reflux for 6 hrs. The solution was poured into excess 2N sodium carbonate, extracted with ether and the aqueous layer was acidified. The resulting acid was recrystallized from water and Skellysolve (B) to yield 10 g of product m.p. 82·5 to 85°, lit: m.p. 84 to 85°.[26]

Preparation of 4-bromo-1-phenyl-1-butene-1,1-d_2. A solution of 4-phenyl-3-butenoic acid (0·81 g, 0·005 mol) in ether (10 ml) was added to a solution of lithium aluminum deuteride (0·21 g) in ether (10 ml) and the resulting solution was stirred for 16 hrs. Dilute hydrobromic acid was added and the ether layer separated and dried over magnesium sulfate. The solvent was removed at reduced pressure. Ether (25 ml) was added and the solution was treated with phosphorous tribromide (1 ml). After heating at reflux for 16 hrs we added water. The ether layer was separated and washed with a sodium bicarbonate solution and the ether removed at reduced pressure. The product was collected on a 20% SE-30 5′ × ¼″ column at 208° with a flow rate of 30 ml/min and a retention time of 7·3 min.

n.m.r.: (s, 5)7·22; (m, 1)6·0 to 6·4; (t, 2)3·25; (m, 2)2·55.

All NMR data indicated were taken on crude reaction mixtures which were sometimes contaminated with starting material. In these cases the contaminating peaks are not given.

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