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# SKELETAL REARRANGEMENT OF ALLYL ACETATES AFTER PROTONATION BY CHEMICAL IONIZATION*

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**Abstract**—In the methane chemical ionization mass spectra of allyl phenylacetate and allyl phenoxyacetate the major reaction paths (>40% Σ) involve skeletal rearrangements, which have no analogy in the corresponding, simpler electron-impact spectra. Substituent and deuterium labeling studies suggest a mechanism involving intramolecular substitution of the phenyl ring by the allyl group. Abstraction of hydrogen from the *ortho* position of the phenyl ring or from the rearranged allyl group is followed by expulsion of water and carbon monoxide.

## INTRODUCTION

THE PREDOMINANT characteristics of chemical ionization (CI) mass spectrometry[1–3] are the formation and high stability of protonated molecular ions, and the relative simplicity of subsequent fragmentation reactions. These features are closely related to the mild conditions of the initial ionization process and it is therefore not surprising that skeletal rearrangements following chemical ionization are uncommon, in contrast to their rather frequent occurrence in electron ionization (EI) mass spectrometry.[4] Examples in which skeletal rearrangement induced by chemical ionization was suggested include the work of Field on bicyclo[2.2.2]octane,[5] bicyclo[2.2.2]-octene[6] and norbornadiene[7] using methane reagent gas, in which the products of rearrangement accounted for up to 18% of the total ion current. Tsang and Harrison have studied the formation of rearranged $[CH_2OH]^+$ derived from protonated acetone using the more energetic reagent gas hydrogen.[8]

We report here the results of a study of the CI mass spectra of allyl phenylacetate and allyl phenoxyacetate and their analogs, which produce skeletal rearrangements that account for 40 to 50% of total ion current. These reactions are of interest because of the mechanistic implications which are involved and also because they represent unusual examples in which the CI spectra are more complex than the analogous spectra resulting from electron-impact.

## RESULTS AND DISCUSSION

The methane CI spectrum of allyl phenylacetate is represented in Fig. 1 and the corresponding EI spectrum is shown in Fig. 2. The principal process represented in Fig. 1 corresponds to sequential loss of $H_2O$ (*m**, *m/e* 142·8) and then CO (*m**, *m/e* 108·1) from the protonated molecular ion, which requires skeletal rearrangement. A less intense metastable peak at *m/e* 97·0 corresponds to the sum of both processes $[MH - (H_2O + CO)]^+$. The CI spectrum of allyl phenoxyacetate (Fig. 3) exhibits the analogous sequence of peaks, which also differ substantially from the simpler EI spectrum. In the latter spectrum, simple C—C bond cleavage alpha to the carbonyl group leads to products of *m/e* 107, or *m/e* 91 in Fig. 2, as expected.

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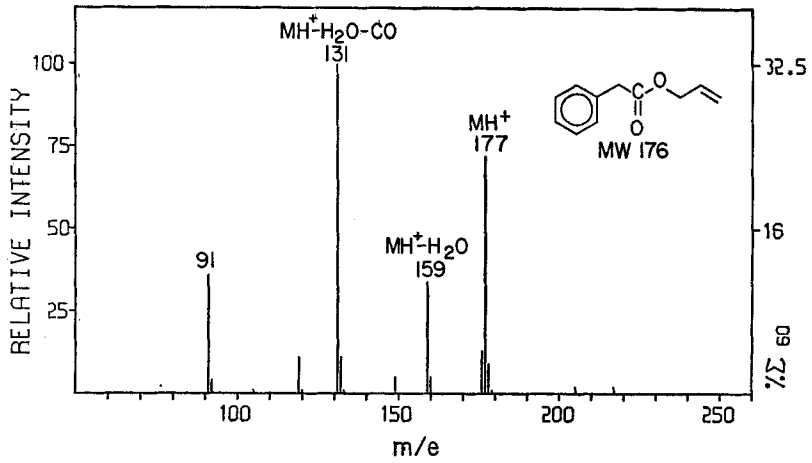



FIG. 1. CI mass spectrum of allyl phenylacetate, (methane reagent gas).

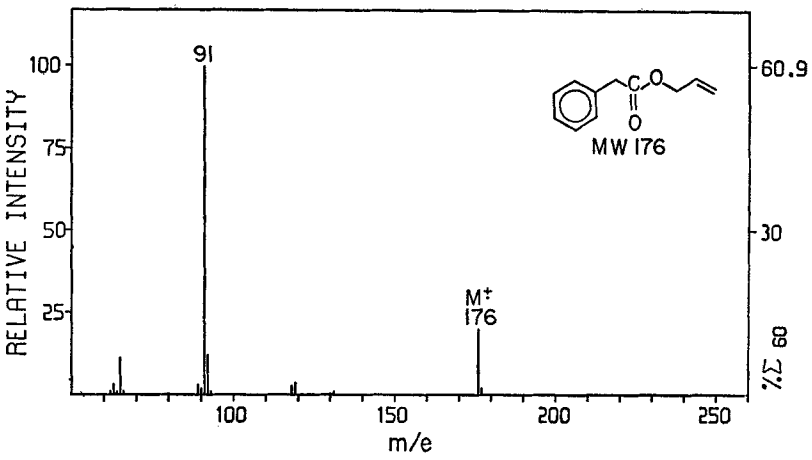



FIG. 2. EI mass spectrum of allyl phenylacetate (70 eV).

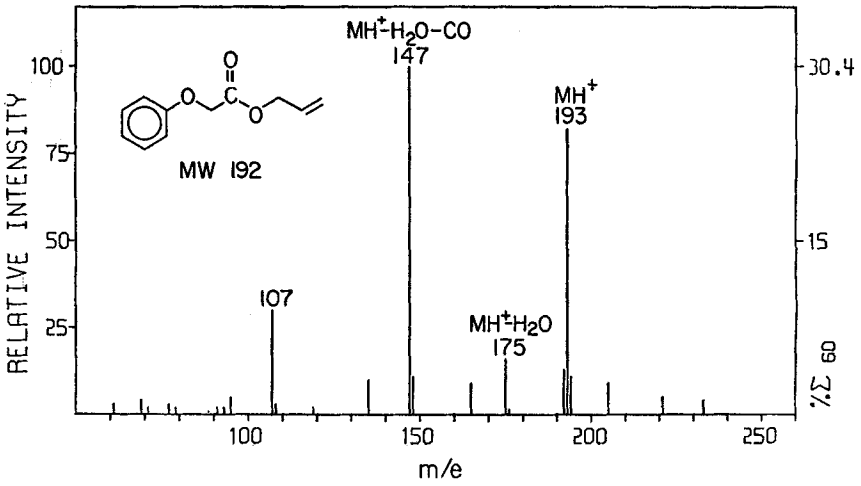
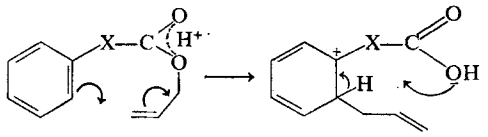


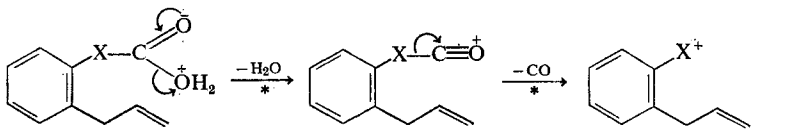

FIG. 3. CI mass spectrum of allyl phenoxyacetate (methane reagent gas).

The possibility of thermal rearrangement prior to protonation was excluded as a contributor to the formation of *m/e* 131 and 159 in Fig. 1, because of the absence of analogous peaks in the EI spectrum (Fig. 2), which is constant over a range of temperatures up to at least 250 °C.

Expulsion of $H_2O$ and CO was initially interpreted in terms of allyl migration to the phenyl ring in the protonated molecular ion:



$[MH]^+$ (X = $CH_2$, $OCH_2$)



$[MH - H_2O]^+$ $[MH - H_2O - CO]^+$

SCHEME 1

*Ortho*-allylation of phenols in solution is well known,[9,10] and the high stability of the C-allylation product is illustrated by the Claisen rearrangement of phenyl allyl ether to *o*-allylphenol. Therefore, after initial attack, abstraction of the *o*-hydrogen by the carboxyl group would lead to a highly favorable re-aromatization, thus completing an intramolecular electrophilic substitution.

The above mechanism was tested by deuterium labeling in the *ortho* positions of allyl phenoxyacetate, using the 2′,4′,6′-trideuterio compound. The resulting spectrum, shown in Fig. 4, reveals that approximately half of the water is lost in the first step as HDO, as indicated by *m/e* 177, 178 and the daughter products *m/e* 149, 150.

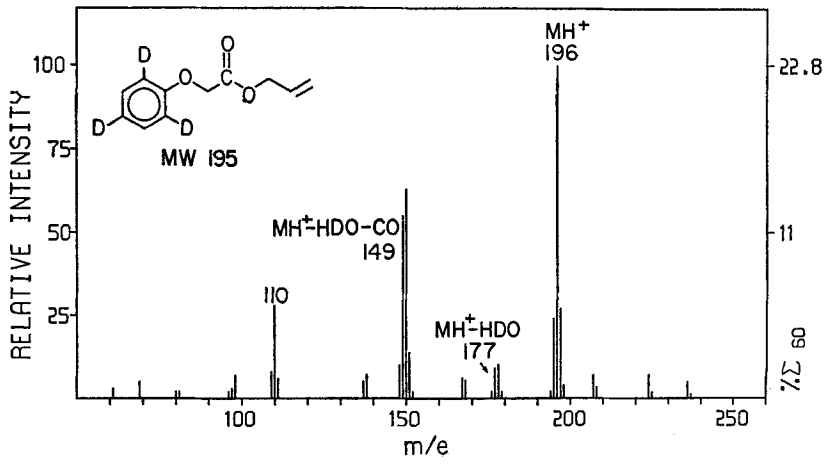



FIG. 4. CI mass spectrum of allyl 2′,4′,6′-trideuteriophenoxyacetate (methane reagent gas).

Additional evidence for *o*-allylation was gained from a comparison of the CI spectra of the isomeric allyl 3′,4′- and 2′,6′-dichlorophenylacetates. The former compound produced the rearranged ions as required ([MH − $H_2O$]$^+$, 19% Rel. int.*; [MH − $H_2O$ − CO]$^+$, 41% Rel. int.*), while the latter model in which both *ortho* positions are blocked, showed only conventional ester fragmentation,[11] i.e. loss of allyl alcohol followed by carbon monoxide.

The remaining 50% of hydrogen which was unaccounted for in the expulsion of water and which is not derived from reagent gas can in principle come from either of the two remaining sources: the benzylic position alpha to the ring or the allyl group. Although benzylic activation may *a priori* be considered a reasonable factor in implicating the benzylic hydrogens, the results of deuterium labeling show that this is not the case. In the spectrum of allyl phenyl-2,2-dideuterioacetate (Fig. 5), less than 5%† of the labeled hydrogen is involved, as shown by *m/e* 160 [MH − HDO]$^+$ and 132 (160-CO) regions of the spectrum.

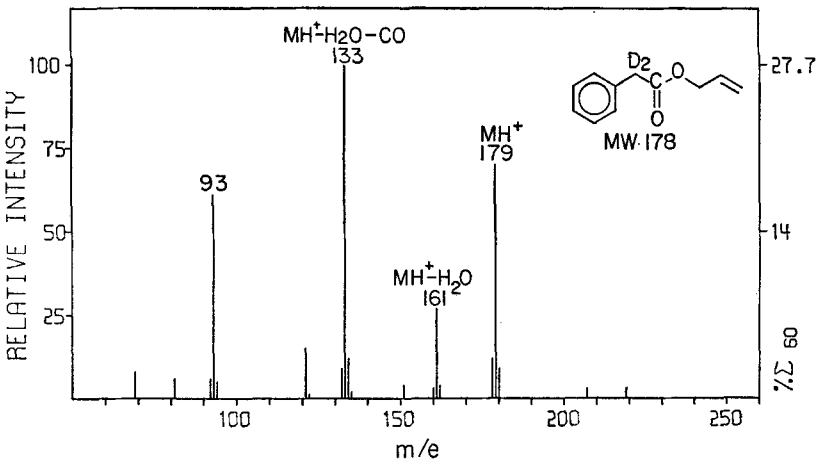
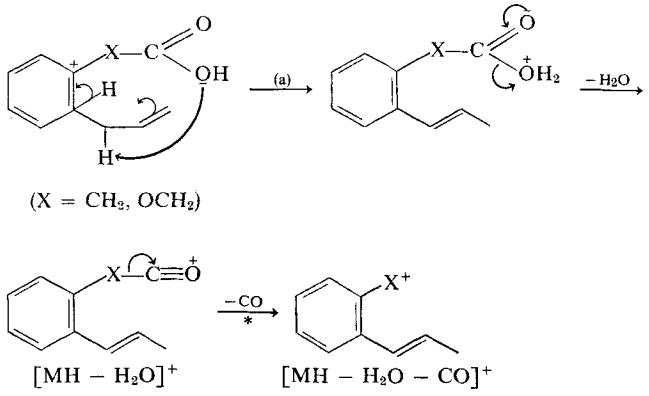



FIG. 5. CI mass spectrum of allyl phenyl-2,2-dideuterioacetate (methane reagent gas).

The second major pathway therefore proceeds by carboxyl abstraction of allylic hydrogen, which can rationally be interpreted in terms of double bond and proton migration (Scheme 2, step a), followed by expulsion of water and carbon monoxide. Therefore, in both the principal reaction pathways (Schemes 1 and 2), allylic *ortho* substitution in the phenyl ring is followed by competitive abstraction of hydrogen from either the ring or allyl function. A major driving force for the reaction is re-aromatization which precedes loss of water. It is of interest to note that the rearrangement does not occur with isobutane reagent gas because of the smaller amount of energy transferred during initial protonation. The failure of this reaction to occur under conditions of electron ionization (Fig. 2), is attributed to the absence of the reagent gas proton which is involved in the elimination of water, as well as differences associated with charge localization. The odd-electron molecular ion which bears

* $Cl^{35}$ isotopic ion species.

† After correction for presence of $d_1$ isotopic species, which was determined from the corresponding EI spectrum.




SCHEME 2

a charge located mainly in the phenyl ring generates a benzylic cleavage, presumably forming the tropylium ion, to the exclusion of any other significant fragmentation.

In view of the proposed mechanisms, it was of interest to examine the effects of substituents attached to the phenyl ring. The presence of a positive charge in the ring prior to expulsion of water (Schemes 1 and 2) should lead to suppression of the reaction sequence in the presence of electron withdrawing substituents. This effect is demonstrated by the spectrum of allyl 4′-bromophenylacetate (Fig. 6). The total ion current carried by $[MH - H_2O]^+$ and $[MH - H_2O - CO]^+$ is 27%, compared with 49% for the unsubstituted molecule (Fig. 1). A more extreme example is given by allyl 4′-nitrophenylacetate (Fig. 7), in which case the rearrangement is essentially inoperative.

By contrast, electron donating substituents such as methyl and methoxyl lead to rearranged products of about the same abundance as the unsubstituted model, but with sharply enhanced competition from benzylic (tropylium) ion formation. These effects are shown in the spectrum of allyl 4′-methylphenylacetate (Fig. 8) and similar results were obtained from the 4′-methoxy analog.

Although these results are mutually consistent and are readily interpreted in terms of the proposed mechanisms, they may be influenced to an unknown extent by

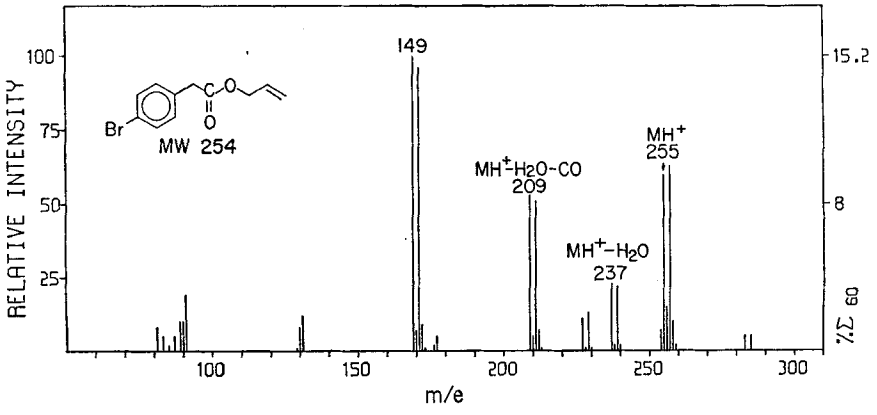



FIG. 6. CI mass spectrum of allyl 4′-bromophenylacetate (methane reagent gas).

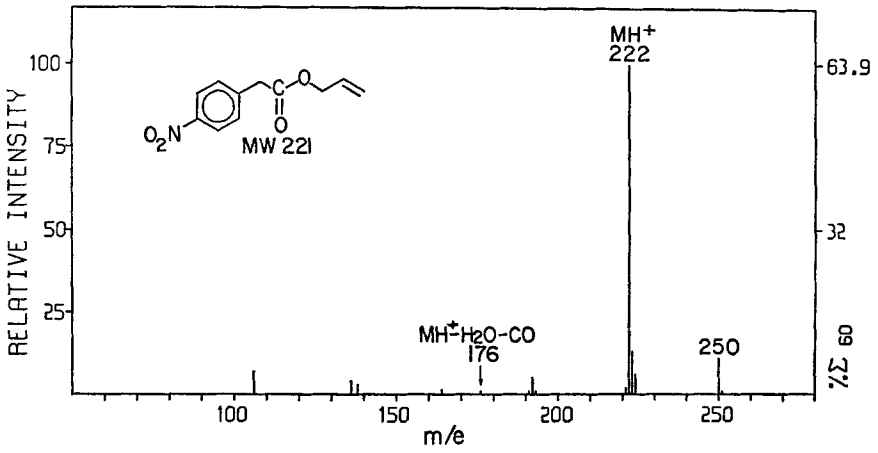



FIG. 7. CI mass spectrum of allyl 4′-nitrophenylacetate (methane reagent gas).

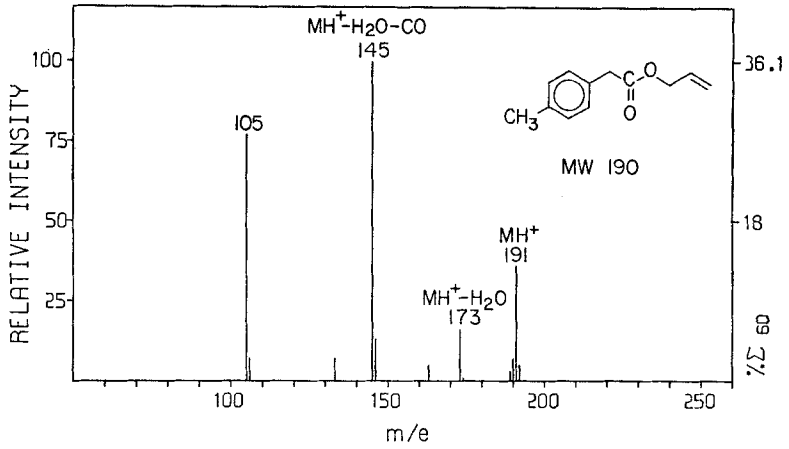



FIG. 8. CI mass spectrum of allyl 4′-methylphenylacetate (methane reagent gas).

differences in sites of protonation. For example, suppression of fragmentation of the nitro compound (Fig. 7) could in part result from protonation on the nitro group rather than at the ester function. Unfortunately, proton affinity data for these compounds or sufficiently closely related models are not available and so the extent of contributions from this effect cannot presently be determined.

## EXPERIMENTAL

CI mass spectra were acquired with a CEC 21-110B instrument modified for high pressure operation;[12] accelerating potential 8 kV, methane or isobutane reagent gas pressure 0·6 Torr. Samples were introduced by direct probe at minimum ion source temperatures required for vaporization, in the range 65 to 120 °C. The EI spectrum of allyl phenylacetate (Fig. 2) was determined with an LKB 9000 instrument with sample introduction by gas chromatograph (100 °C, 6 ft 1% SE-30); ionizing energy 70 eV, ion source temperature 250 °C).

All compounds were purified by gas-liquid chromatography (6 ft × ¼ in, 1% SE-30), using a modified Barber Colman 5000 instrument.

*Materials*

*Allyl phenylacetate* was prepared by standard procedure by reaction of phenylacetyl chloride with allyl alcohol.[13] *Allyl phenoxyacetate* was synthesized from sodium phenolate and allyl bromoacetate by a procedure analogous to the preparation of ethyl phenoxyacetate from ethyl bromoacetate.[14] *Allyl 2′,4′,6′-trideuteriophenoxyacetate* was prepared in the same manner using 2,4,6-trideuteriophenol (<1% $d_1$, 8% $d_2$, 92% $d_3$), which was obtained by an exchange reaction using $D_2O$/NaOD.[15] *Allyl phenyl-2,2-dideuterioacetate* (6% $d_1$, 94% $d_2$) was synthesized from phenyl-2,2-dideuterioacetic acid obtained from exchange in $D_2O$/NaOD.[16]

*Allyl 2′,6′-dichlorophenylacetate*, *allyl 3′,4′-dichlorophenylacetate*, *allyl 4′-nitrophenylacetate*, *allyl 4′-methylphenylacetate* and *allyl 4-methoxyphenylacetate* were synthesized by a standard procedure[17] by heating 2 to 3 mg of the corresponding substituted phenylacetic acid with 0·5 ml of allyl alcohol saturated with hydrogen chloride gas in a sealed tube for 5 h at 100 °C. All of the substituted phenylacetic acids were obtained commercially, with the exception of 2′,6′-dichlorophenylacetic acid, which was prepared by refluxing 10 g of 2′,6′-dichlorophenylacetonitrile with 6 g potassium hydroxide in 20 ml of ethylene glycol for 15 h: m.p. 156 to 157 °C (Lit.[18] 157 to 8 °C).

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