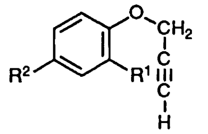
# Claisen Rearrangements and Cyclisations in Phenyl Propargyl Ethers under Electron Impact Conditions

**Devalla V. Ramana** * **and Marimanikuppam S. Sudha**
*Department of Chemistry, Indian Institute of Technology, Madras 600 036, India*

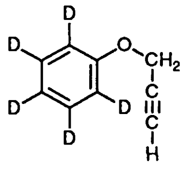
An interesting Claisen rearrangement has been observed in phenyl propargyl ether, yielding significant amounts of the [M − CO] ion under electron impact conditions. The other competing pathway is the loss of a hydrogen radical from $M^{\cdot+}$ furnishing the most abundant ion in its mass spectrum. Expulsion of a hydrogen radical from the propargylic carbon leads to the propargylic cation species, while ejection of the *ortho* hydrogen gives rise to a benzopyrylium cation structure. Substituents on the phenyl ring do not favour the Claisen rearrangement, whereas ejection of the substituents producing benzopyrylium cations gains importance. The mechanisms and ion structures proposed are supported by high-resolution data, B/E and $B^2/E$ linked-scan spectra, Collision Activated Decomposition (CAD)-B/E linked-scan spectra and deuterium isotope labelling.

Claisen rearrangements in the gas phase have gained importance in recent years, as in solution.[1,2] Phenyl allenyl ethers[3] lose CO by a Claisen rearrangement pathway from their molecular ions giving rise to intense [M − CO] ions under electron impact conditions. Such a rearrangement in phenyl allyl ether[4] and *N*-allylaniline[5] under positive CI conditions has been well documented. A Claisen rearrangement has also been noticed under EI conditions in *N*-allylaniline[6] leading to the expulsion of HCN to the extent of 1%. The anionic Claisen rearrangement leading to interesting fragment ions has been reported under negative CI conditions in deprotonated allyl phenyl acetate,[7] allyl phenyl ether[8] and allyl vinyl ether.[9] The thermal[10] and catalysed[1] Claisen rearrangement of phenyl propargyl ether is well established and under positive CI conditions its [M + H] ion loses CO, for which a Claisen rearrangement is proposed.[4]

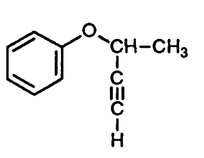
Hence, it was considered interesting to study the behaviour of phenyl propargyl ethers (compounds **1**–**10**) under positive ion EI conditions.



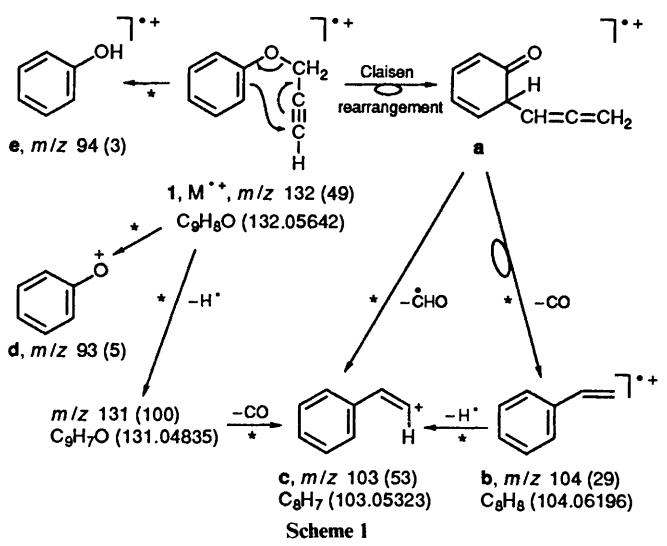
| | R1 | R2 |
|---|---|---|
| **1** | H | H |
| **2** | OCH3 | H |
| **3** | H | OCH3 |
| **4** | CH3 | H |
| **5** | H | CH3 |
| **6** | Cl | H |
| **7** | H | Cl |
| **8** | H | NO2 |



**9**



**10**



Scheme 1

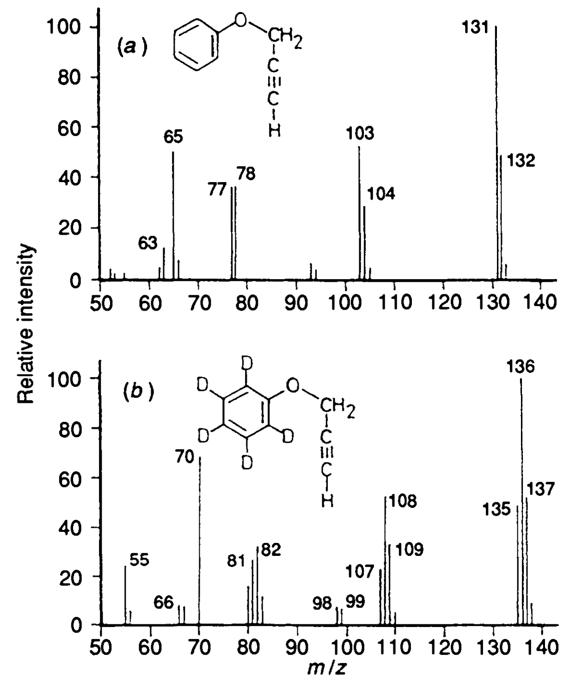


Fig. 1 EI mass spectra at 70 eV of (*a*) compound **1** (*b*) compound **9**

## Results and Discussion

The most interesting fragment ion in the mass spectrum of phenyl propargyl ether (**1**) is the ion **b** at *m*/*z* 104 (Scheme 1, Table 1 and Fig. 1). The exact mass of the ion **b** is found to be 104.061 96 which corresponds to an elemental composition of $C_8H_8$. This fact reveals that **b** is formed by the expulsion of CO from the molecular ion of **1**. The proposed direct formation of the ion **b** from $M^{\cdot+}$ of **1** is supported by the B/E linked-scan spectrum of $M^{\cdot+}$ at *m*/*z* 132 (Table 2) and $B^2/E$ linked-scan spectrum of ion **b** (Table 2).

Table 1 Partial mass spectra of compounds **1**–**10**

| | Relative abundances of | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Compound | $M^{\bullet +}$ | $[M - H]^+$ | $[M - R]^+$ | **b** | **c** | **d** | **e** | Other ions |
| **1** | 49(132)[a] | 100(131) | 100(131) | 29(104) | 53(103) | 5(93) | 3(94) | |
| **2** | 60(162) | 2(161) | 3(131) | 4(134) | — | 100(123) | 10(124) | 74(95) |
| **3** | 26(162) | — | 1(131) | 1(134) | — | 100(123) | 9(124) | 29(95) |
| **4** | 94(146) | 85(145) | 90(131) | 15(118) | 59(117) | 65(107) | 9(108) | 17(103), 50(79), 100(77) |
| **5** | 96(146) | 80(145) | 86(131) | 15(118) | 47(117) | 70(107) | 9(108) | 19(103), 58(79), 100(77) |
| **6** | 37(166) | 10(165) | 100(131) | 5(138) | 20(137) | 14(127) | 4(128) | 39(103), 63(99) |
| **7** | 39(166) | 12(165) | 100(131) | 4(138) | 11(137) | 34(127) | 10(128) | 43(103), 60(99) |
| **8** | 46(177) | 28(176) | 100(131) | 2(149) | 10(148) | — | 1(139) | 9(161), 38(160), 88(130) |
| **9** | 53(137) | 100(136) | 49(135) | 33(109) | 53(108) | 7(98) | 6(99) | |
| **10** | 25(146) | 10(145) | 10(145) | 5(118) | 13(117) | 3(93) | 100(94) | 32(131), 8(103) |

[a] The figures in parentheses indicate the *m*/*z* values of the ions.

Table 2 B/E and $B^2$/E linked-scan spectral data of compound **1**

| | B/E | | $B^2$/E |
|---|---|---|---|
| Parent ion *m*/*z* | *m*/*z* values of daughter ions with abundances in parentheses | Daughter ion *m*/*z* | *m*/*z* values of parent ions with abundances in parentheses |
| $M^{\bullet +}$, 132 | 131(100), 104(31), 103(36), 94(4), 93(10) | 104 | 132(100) |
| 131 | 130(100), 103(54), 77(4) | 103 | 132(20), 131(100), 104(25) |
| 104 | 103(22), 78(100), 77(94) | | |

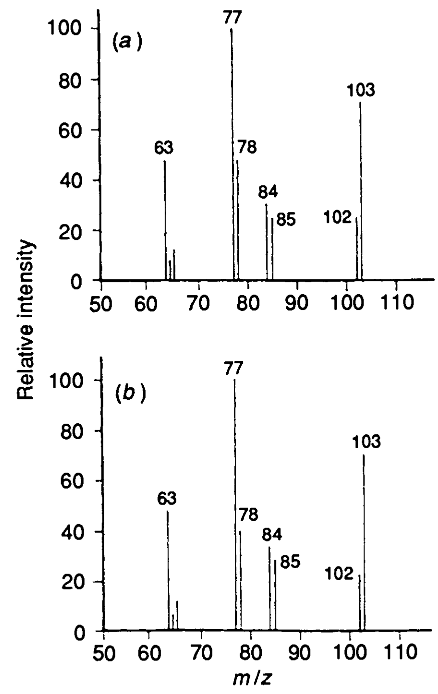
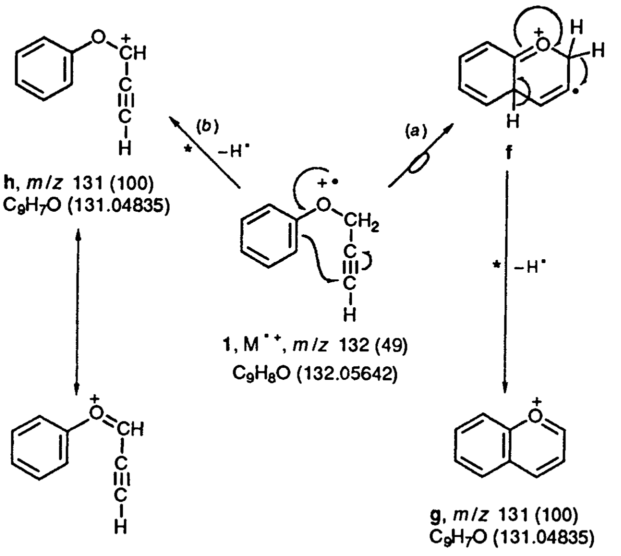


Fig. 2 CAD-B/E linked-scan spectra of (*a*) *m*/*z* 104 of phenyl propargyl ether (**1**) and (*b*) $M^{\bullet +}$, *m*/*z* 104 of styrene

A Claisen rearrangement in the molecular ion of **1** is envisaged for the formation of ion **b** (Scheme 1). The $M^{\bullet +}$ of **1** leads, after Claisen rearrangement, to the allenic species **a** which ejects a molecule of carbon monoxide followed by skeletal rearrangement yielding the ion **b**. The styrene radical cation structure, proposed for **b**, is confirmed with the help of Collision Activated Decomposition (CAD)-B/E linked-scan spectra of **b** and the $M^{\bullet +}$ of styrene, taken as the reference compound, which are found to be identical (Fig. 2). The abundant ion **c** at *m*/*z* 103 is formed by the loss of a hydrogen radical from **b**. Ion **c** is also formed from the molecular ion by the direct expulsion of ĊHO (Scheme 1).



Scheme 2

The base peak in the mass spectrum of **1** is at *m*/*z* 131 (Table 1 and Fig. 1) which corresponds to the expulsion of a hydrogen radical from $M^{\bullet +}$ as shown by its accurate mass measurement and linked-scan spectra (Table 2). The hydrogen radical lost from $M^{\bullet +}$ can originate from either the propargylic carbon or the *ortho* position of the ring (Scheme 2). The mass spectrum of the $[^2H_5]$-compound **9** (Fig. 1) reveals that the loss of H:D from the $M^{\bullet +}$ is in the ratio 2:1 after isotopic correction. This suggests that the loss of propargylic hydrogen is twice that of the *ortho* hydrogen. The expulsion of a hydrogen radical from the *ortho* position [path (*a*)] would lead to the ion **g** having a benzopyrylium cation structure, as has been observed in the case of phenyl allenyl ethers,[3] while the ejection of H• from the propargylic carbon [path (*b*)] would lead to the ion **h**.

The CAD-B/E linked-scan spectrum of the ion at *m*/*z* 131 from **1** is compared with those from phenyl α-methylpropargyl ether (**10**), 2*H*-1-benzopyran (**11**) and compound **6** (Fig. 3). It

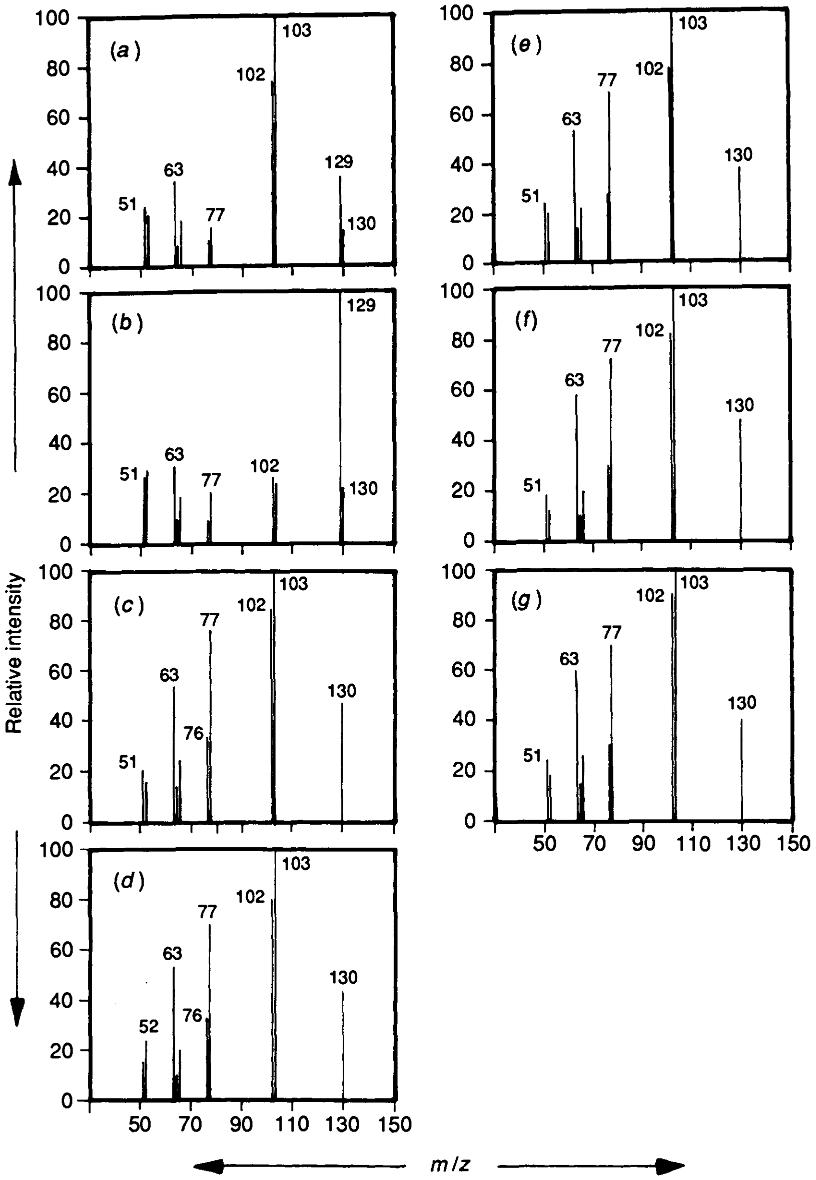
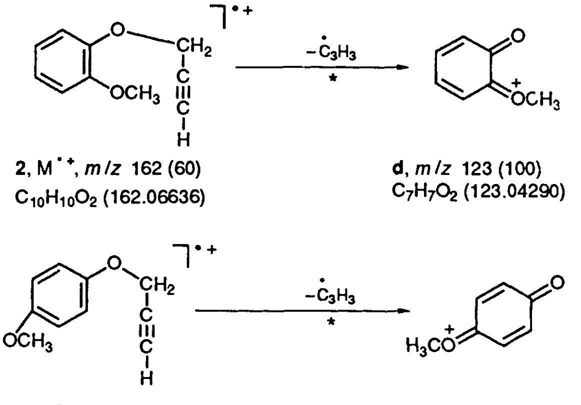


Fig. 3 CAD-B/E linked-scan spectra of ions at (*a*) *m*/*z* 131 of **1**, (*b*) *m*/*z* 131 of **10**, (*c*) *m*/*z* of **11**, (*d*) *m*/*z* 131 of **6**, (*e*) *m*/*z* 131 of **5**, (*f*) *m*/*z* 131 of **7** and (*g*) *m*/*z* 131 of **8**

can be noticed that the CAD-B/E linked-scan spectrum of the ion at *m*/*z* 131 from **6** is exactly identical with that from **11**, whereas the CAD spectrum of the ion at *m*/*z* 131 from **10** is distinctly different when compared to that from **11**. Furthermore, the CAD-B/E linked-scan spectrum of the ion at *m*/*z* 131 from **1** resembles those from compounds **10** and **11**. It is clear from these observations that the ion at *m*/*z* 131 from **1** is a mixture of two species, namely, the ion **g** having a benzopyrylium cation structure and the ion **h**, a propargylic cation species. It can further be inferred from the CAD spectra of the ion at *m*/*z* 131 from **10** and **11** that the propargylic cation species does not cyclise to the benzopyrylium cation structure. Hence it can be concluded that the cyclisation must be occurring in the $M^{\cdot+}$ of **1** yielding **f** which then loses $H^{\cdot}$ [path (*a*), Scheme 2], rather than cyclisation after the expulsion of hydrogen radical from the propargylic carbon to yield **g**. This hypothesis can also be confirmed from the fact that the $^{2}[H_5]$-compound **9** will not be losing $D^{\cdot}$ from its $M^{\cdot+}$ if the cyclisation occurs after the initial ejection of the propargylic hydrogen.

Compounds **2** and **3** undergo simple cleavage to yield the ions at *m*/*z* 123 (Table 1) having quinonoid structures as the most abundant ions (Scheme 3) in their mass spectra. The Claisen rearrangement and cyclisation occur to a very minor extent in these compounds. In contrast, compounds **4** and **5** undergo Claisen rearrangement yielding ions at *m*/*z* 118 (Table 1) of



**2**, $M^{\cdot+}$, *m*/*z* 162 (60)
$C_{10}H_{10}O_2$ (162.06636)

**d**, *m*/*z* 123 (100)
$C_7H_7O_2$ (123.04290)

**3**, $M^{\cdot+}$, *m*/*z* 162 (26)
$C_{10}H_{10}O_2$ (162.06636)

**d**, *m*/*z* 123 (100)
$C_7H_7O_2$ (123.04287)

**Scheme 3**

reasonable abundance while loss of H$^{\bullet}$ is a major fragmentation pathway. The hydrogen radical can be lost in these compounds either from the propargylic carbon or from the methyl substituent to give ring expanded tropylium cation structures. Interestingly, compounds **6**, **7** and **8** favour cyclisation by the expulsion of the substituents leading to fragment **g** at *m*/*z* 131 as the most intense ions in their mass spectra. The ejection of the substituents in the *p*-isomers (compounds **5**, **7** and **8**) for the formation of the cyclised ion **g** [confirmed by the CAD-B/E linked-scan spectra, Fig. 3 (*e*), (*f*) and (*g*)] may involve substituent scrambling.

All the fragmentation pathways shown in Schemes 1 and 2 are also noticed in other compounds studied. These are supported by the accurate mass measurements, B/E and B$^2$/E linked-scan spectra.

The mass spectra of **1** and **4** taken at 70 eV under cold conditions (inlet temperature 50 °C and source temperature 20 °C) were identical to those taken under normal conditions. Also, compound **1** was recovered unchanged after pyrolysis at 120 °C and at 20 mmHg pressure for 30 min. These experiments confirm that the loss of CO through the Claisen rearrangement in these compounds is only due to electron impact and is not a thermal process.

## Conclusion

It can be seen from this study that the substituents on the phenyl ring tend to facilitate cyclisation reaction by expelling the substituents from the molecular ions, while the Claisen rearrangement is not a predominant process. Surprisingly, no *ortho* interaction is noticed in compounds **2** and **4** between the *ortho* substituent and the triple bond, whereas in the case of *o*-nitrophenyl propargyl ether,[11] the principal fragment ion is derived by the transfer of an oxygen from the nitro group to the acetylenic moiety.

## Experimental

All the compounds studied in this work have been described in the literature. Compounds **1**–**10** were prepared according to the procedure of I. Iwai and J. Ide[12] but using DMF as the solvent at room temperature.[13] The compounds were purified by column chromatography with hexane as the eluent. The structures were confirmed by IR and $^1$H NMR data. Mass spectra were recorded on a Finnigan MAT 8230 double focussing mass spectrometer. The mass spectra were run at 70 eV with an emission current of 100 μA and an accelerating voltage of 3 kV. All the compounds were introduced into the mass spectrometer through either the reference inlet at 110 °C or the direct insertion probe at 25 °C. Accurate mass measurements were carried out at a resolution of 8000 (10% valley) and PFK was used as the reference. The CAD-B/E linked-scan spectra, in the first field free region were investigated using helium as the collision gas with a Finnigan MAT 8230 mass spectrometer at an ionisation energy of 70 eV and an accelerating voltage of 3 kV.

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