

Pyrolytic decomposition of simple acetylenic esters

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Dedicated to Nouria A. Al-Awadi on the occasion of her 55th birthday

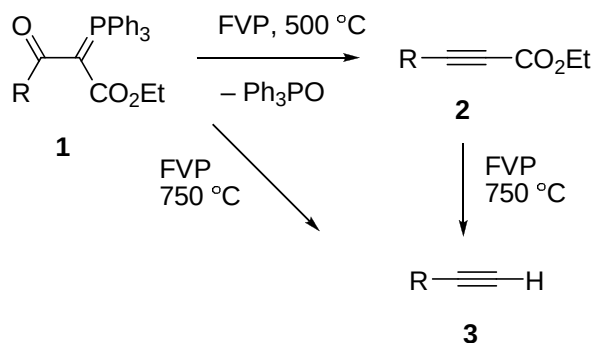
Abstract

The mechanism of thermal decomposition of nine acetylenic esters has been examined under conditions of flash vacuum pyrolysis. The products formed may be explained by a series of well-precedented steps involving such processes as ene reactions, alkyne to vinylidene rearrangements, carbene CH insertions, and fragmentation of 2,3-dihydrofuran-2-ones or 5,6-dihydropyran-2-ones with extrusion of CO and CO₂ respectively.

Keywords: Acetylenic ester, alkyne, carbene, fragmentation, pyrolysis

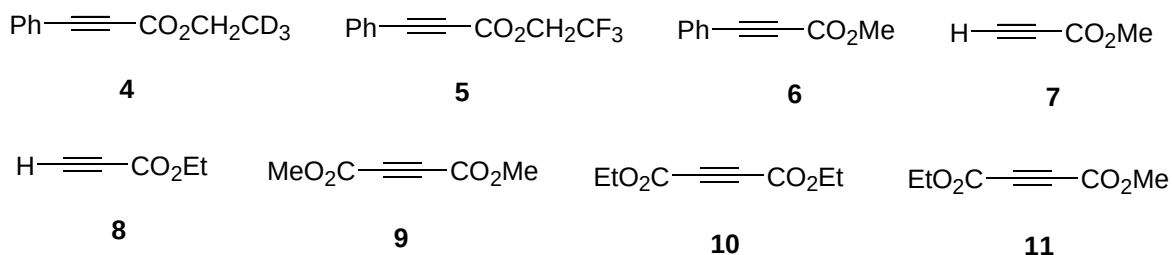
Introduction

Some time ago we reported that thermal decomposition of stabilised phosphonium ylides **1** bearing adjacent ketone and ethyl ester functions led to extrusion of Ph₃PO to give acetylenic esters **2** (Scheme 1).¹ This transformation was accomplished in high yield using flash vacuum pyrolysis (FVP) at 500 °C, but simply by raising the reaction temperature to 750 °C, complete loss of the ethyl ester function occurred to afford the alk-1-yne **3** in moderate yield. It was readily demonstrated that this was caused by secondary decomposition of esters **2** to give **3** in an apparently novel process.



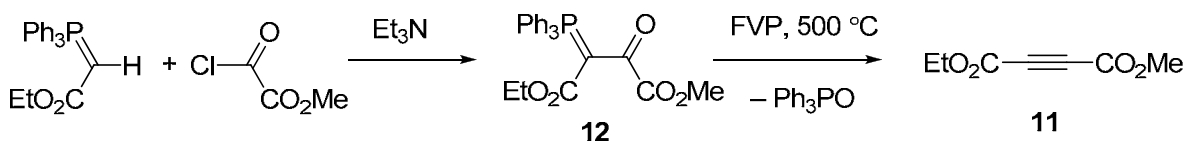
Scheme 1

A brief mechanistic study appeared to reveal a combination of different pathways leading to the alk-1-yne with, for example, the trideuterioethyl ester **4** giving a 4:1 mixture of labelled and non-labelled products, while the trifluoroethyl ester **5** also gave the alk-1-yne together with trifluoroacetaldehyde.¹ In this paper we present full details of these studies as well as an investigation of the pyrolytic decomposition of methyl phenylpropiolate **6**, methyl and ethyl propiolate **7** and **8**, dimethyl and diethyl acetylenedicarboxylate **9** and **10**, and ethyl methyl acetylenedicarboxylate **11**.



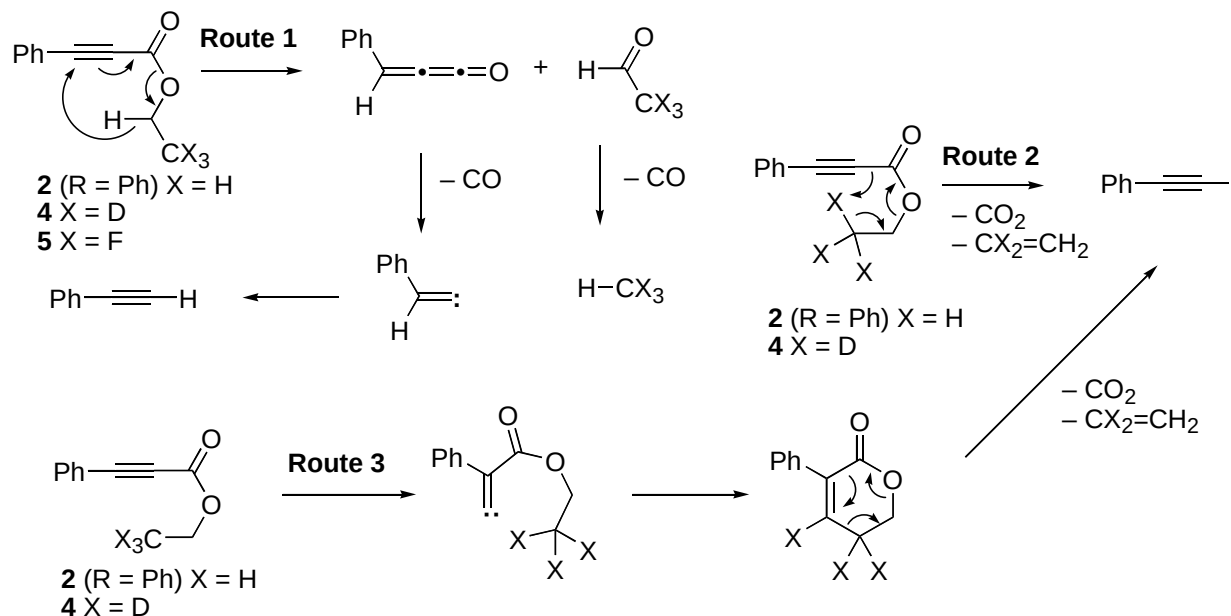
Results and Discussion

The acetylenic esters required for this study were either commercially available or readily prepared using standard methods. Phenylpropynoyl chloride was prepared from the corresponding acid and reacted with 2,2,2-trideuterioethanol or 2,2,2-trifluoroethanol to give esters **4** and **5** respectively. The preparation of **11** was most easily accomplished by pyrolytic extrusion of Ph_3PO (FVP, 500 °C) from the stabilised ylide **12** formed from ethoxycarbonylmethylenetriphenylphosphorane and methyl oxalyl chloride in the presence of triethylamine.²



As initially observed when the products **2** were formed by pyrolysis of ylides **1**, either increasing the ylide pyrolysis temperature to 750 °C or isolating **2** from pyrolysis at 500 °C and subsequently subjecting it to FVP at 750 °C gave the alk-1-yne **3**. Thus when **2** (R = Ph) was subjected to FVP at 750 °C, **3** (R = Ph) was formed in 70% isolated yield together with a low yield of ethene recognised by its ¹H NMR signal at 5.4 ppm which rapidly disappeared upon warming the solution to RT. Several mechanisms can be invoked to account for this reaction and the most important of these are shown in Scheme 2. Although these all account for formation of $\text{PhC}\equiv\text{CH}$, the ethoxycarbonyl group lost ends up either as methane and two molecules of CO (Route 1) or ethene and CO₂ (Routes 2 and 3). The process of Route 1 involving an ene reaction is similar to the formation of benzophenone and methyleneketene by FVP of diphenylmethyl propiolate,³ and also bears some resemblance to the process observed upon FVP of phenyl propiolate to give cyclohepta[b]furan-2(2*H*)-one.⁴ In the course of the former study, Brown and coworkers also observed minor products arising from formation of a carbene and its intramolecular CH insertion as shown in Route 3,⁵ and such isomerisation is a common feature of the pyrolysis chemistry of

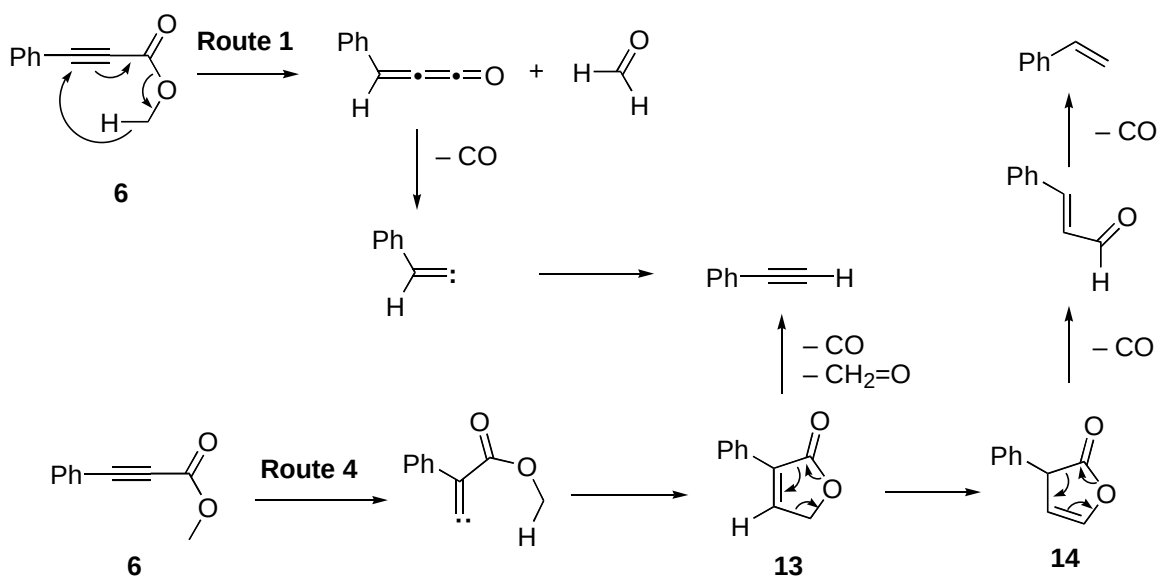
alkynes.⁶ In an attempt to shed more light on the processes involved, we examined the behaviour of the deuteriated and fluorinated analogues **4** and **5**.



Scheme 2. Possible routes for decomposition of acetylenic esters.

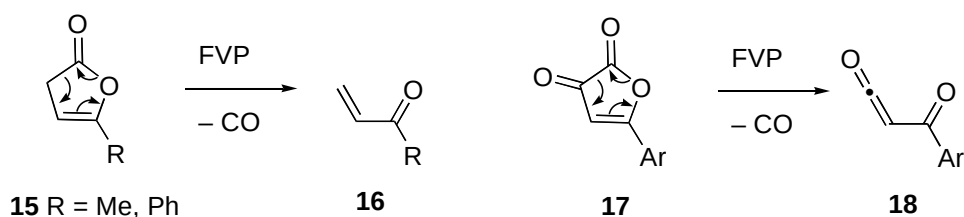
FVP of **4** at 750 °C gave almost the same yield as **2** (R = Ph) but the product consisted of a mixture of $\text{PhC}\equiv\text{CD}$ (60%) as expected from Route 2 or 3 and $\text{PhC}\equiv\text{CH}$ (15%) as expected from Route 1. In the case of **5**, Routes 2 or 3 which would involve breaking the strong C–F bond to give the little known 1-fluoroalkyne are obviously unfavourable and $\text{PhC}\equiv\text{CH}$ (55%) was formed together with a low yield of trifluoroacetaldehyde, a compound whose convenient preparation and isolation in pure form has just recently been described.⁷ It is thus clear that any assumption that loss of the ethoxycarbonyl group must be as ethene and CO_2 is invalid and this prompted us to examine the behaviour of the corresponding methyl ester **6**.

In this case, the FVP temperature had to be increased slightly and even at 780 °C there was still some unreacted starting material (13%). The main product was phenylacetylene (37%) accompanied by a little styrene (4%). As shown in Scheme 3, the mechanism of Route 1 is still viable and would now involve loss of formaldehyde and CO to give $\text{PhC}\equiv\text{CH}$, while a new pathway (Route 4) similar to Route 3 of Scheme 2 but now involving insertion of the carbene into CH would form a five-membered ring heterocycle, the 2,5-dihydrofuran-2-one (butenolide) **13**. Fragmentation of this can account for the major product, while isomerisation to the 2,3-dihydrofuran-2-one isomer **14** followed by the well preceded elimination of CO to give cinnamaldehyde and its further decarbonylation provides a route to styrene.

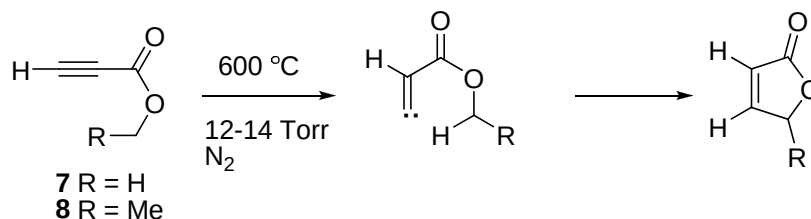


Scheme 3. Possible routes for decomposition of **6**.

Elimination of CO from the 5-methyl and 5-phenyl analogues **15** to give the vinyl ketones **16**,⁸ as well as from the 5-aryl-2,3-dihydrofuran-2,3-diones **17** to give benzoylketenes **18**⁹ have been observed under similar conditions.



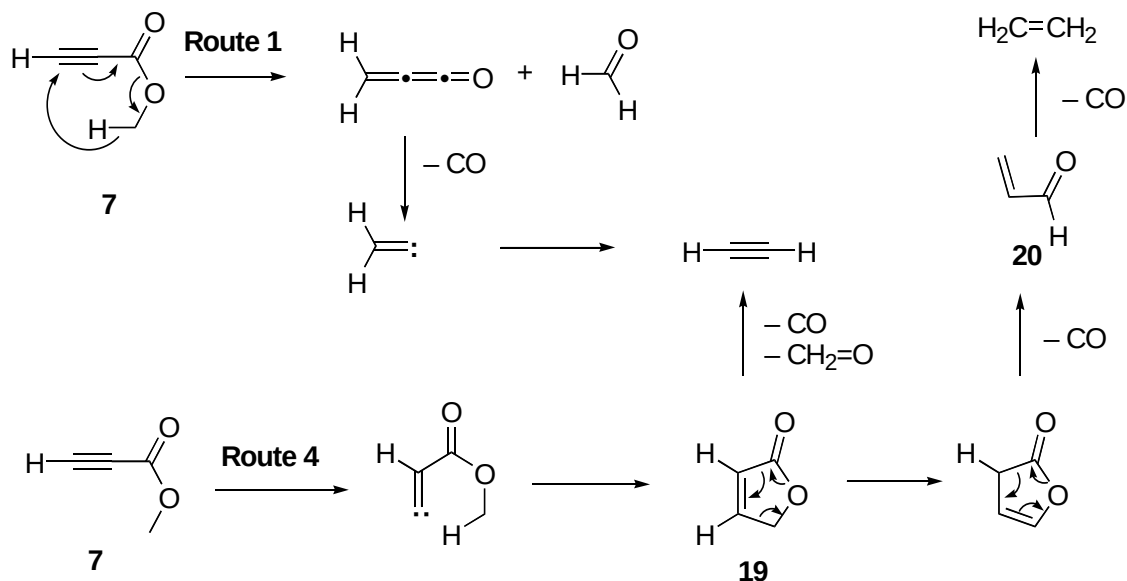
The behaviour of methyl and ethyl propiolate **7** and **8** has been reported under slightly different pyrolytic conditions of 600 °C at 12-14 Torr with a nitrogen carrier gas.¹⁰ This led to the formation of butenolides by the process analogous to Route 4 in Scheme 3 above (Scheme 4).



Scheme 4

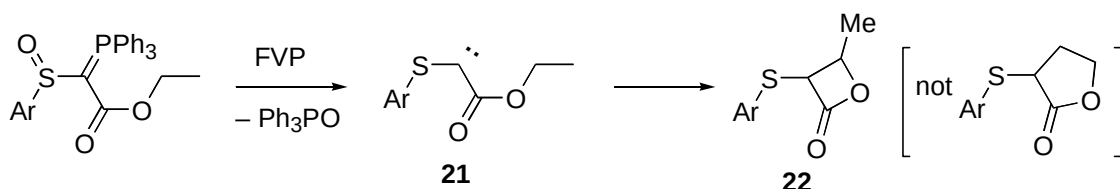
Under our conditions, which differ most especially in having a lower pressure and so favouring fragmentation processes, complete reaction of **7** required the higher temperature of 830 °C, and the main product trapped was acrolein **20** (15%) accompanied by low yields of formaldehyde and ethene. The formation of acrolein is attributed to loss of CO from the 2,3-dihydrofuran-2-one

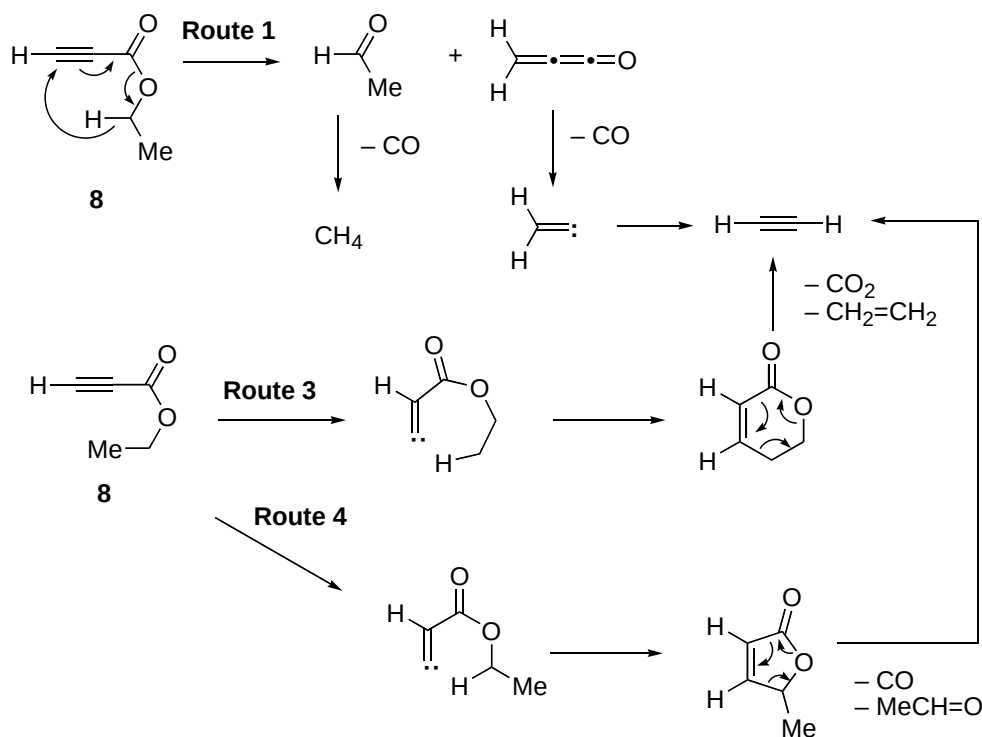
isomer of butenolide **19** and indeed FVP of **19** under the same conditions gave **20** (13%). This process is clearly analogous to the reaction proposed for **14** and the already reported decarbonylations of **15** and **17** mentioned above. The possible reaction pathways shown in Scheme 5 allow for formation of formaldehyde, CO and ethyne either by Route 1 or Route 4 but formation of ethene and particularly acrolein points to the carbene formation and CH insertion of Route 4 as the major pyrolytic process.



Scheme 5. Possible routes for decomposition of **7**.

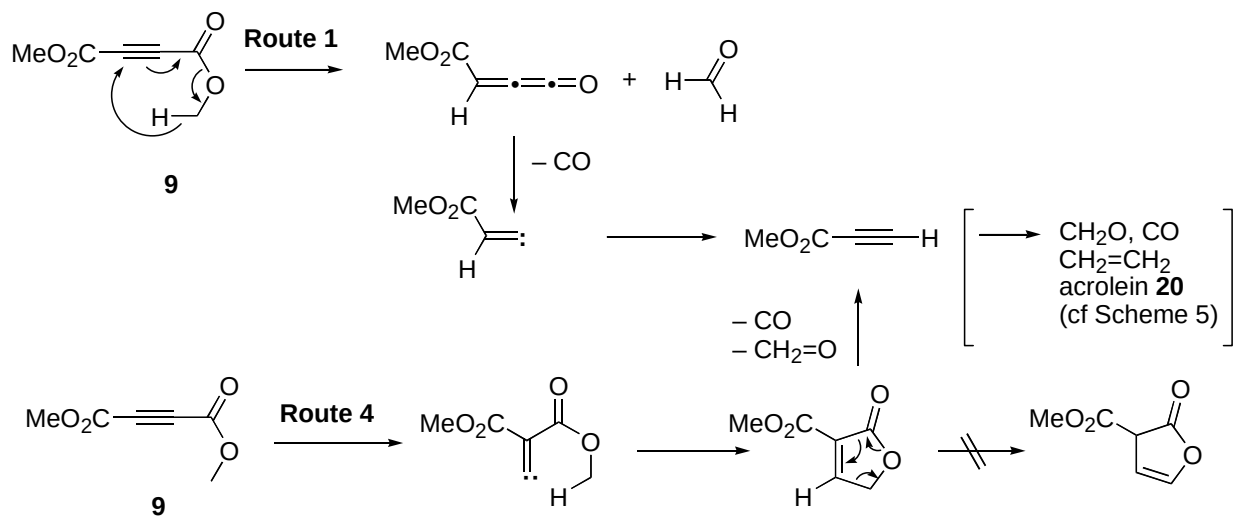
Ethyl propiolate **8** exhibited quite different behaviour. It decomposed completely at 750 °C to give mainly gaseous products which could only be trapped in low yield and included acetaldehyde, ethyne, ethene and methane. The formation of these may be accounted for by the processes of Scheme 6. It can be seen here that Routes 1, 3 and 4 are all feasible and lead to the observed final products. Whether the carbene formed by rearrangement of **8** is more likely to insert into the CH₃ C–H to give the dihydropyranone or into the CH₂ C–H to give the dihydrofuranone as observed by Dreiding and coworkers¹⁰ is unclear, although in a related case we have previously observed exclusive insertion of carbene **21** into the CH₂ C–H of an ethyl ester to give the smaller of two possible rings **22**.¹¹





Scheme 6. Possible routes for decomposition of **8**.

To complete this study we examined the pyrolysis behaviour of the readily available symmetrical acetylenic diesters **9** and **10** together with the mixed ethyl methyl ester **11**. The results in these cases served to reinforce the pattern of behaviour already observed and the major products were accounted for by combinations of the processes detailed above. FVP of DMAD **9** again required a somewhat higher temperature (830 °C) for complete reaction and gave acrolein as the major product in 68% yield, accompanied by small amounts of formaldehyde and ethene.

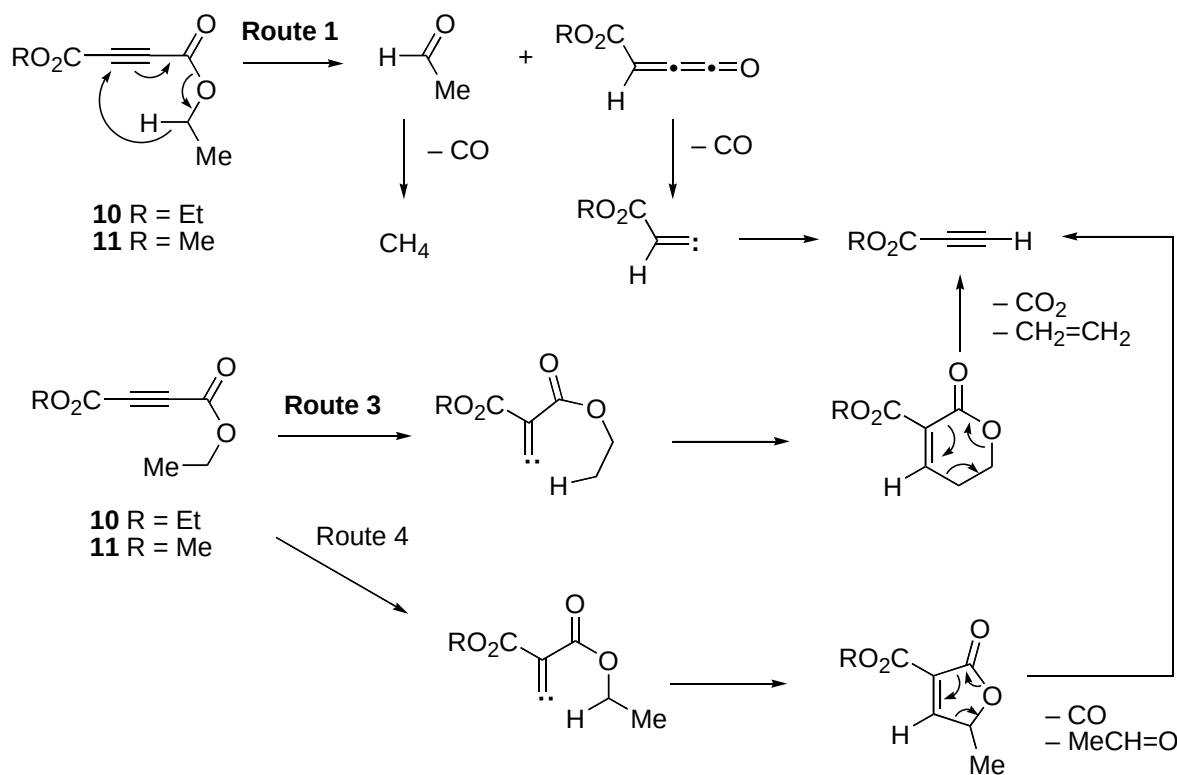


Scheme 7. Possible routes for decomposition of **9**.

As shown in Scheme 7, either Route 1 or Route 4 results in loss of one methoxycarbonyl group as formaldehyde and CO and the resulting methyl propiolate then simply fragments as already observed (Scheme 5) to give acrolein and thus ethene. The double-bond migration at the butenolide stage which would lead to loss of CO and formation of the unsaturated aldehydo ester, perhaps followed by decarbonylation to methyl acrylate was not observed and is perhaps less favourable with the conjugated double bond.

This pattern is essentially repeated with diethyl acetylenedicarboxylate **10**, which reacts completely upon FVP at 750 °C to give acetaldehyde, ethene and methane together with CO and CO₂. This is accounted for by loss of one ethoxycarbonyl group (Scheme 8) leading to ethyl propiolate **8** which then further degrades to the same fragments plus ethyne by the processes of Scheme 6.

Finally, the mixed diester **11** provided a direct comparison between the ease of fragmentation of ethyl and methyl ester groups. It reacted completely at 760 °C and as expected the ethyl ester was lost first (Scheme 8) leading to production of acetaldehyde and ethene but in this case also an isolable quantity of methyl propiolate **7**. This last product did however mainly break down under the conditions used according to Scheme 5 to give acrolein in 45% yield.



Scheme 8. Possible routes for decomposition of **10** and **11**.

Experimental Section

General Procedures. Infra red spectra were recorded for liquid films on a Perkin Elmer 1420 instrument. NMR spectra were obtained for ¹H at 300 MHz, for ²H at 46 MHz and for ¹³C at 75

MHz using a Bruker AM300 instrument and for ^{19}F at 75.3 MHz using a Bruker WP80 instrument. All spectra were run on solutions in CDCl_3 with internal Me_4Si as reference for ^1H and ^{13}C and internal CFCl_3 for ^{19}F , except ^2H spectra which were run in CHCl_3 with internal CDCl_3 (δ_{D} 7.30) as reference. Chemical shifts are reported in ppm to high frequency of the reference and coupling constants J are in Hz. Mass spectra were obtained on an A. E. I. MS-50 spectrometer using electron impact at 70 eV.

Methyl and ethyl propiolate **7** and **8**, and dimethyl and diethyl acetylenedicarboxylate **9** and **10** were commercial samples used without further purification, and methyl and ethyl phenylpropiolate **6** and **2** ($\text{R} = \text{Ph}$) were prepared by conversion of phenylpropionic acid into its chloride with thionyl chloride followed by reaction with methanol or ethanol.

2,2,2-Trideuterioethyl phenylpropiolate (4). This was prepared by stirring a mixture of phenylpropynoyl chloride (0.5 g, 3 mmol) and 2,2,2-trideuterioethanol (0.30 g, 6 mmol) at room temperature for 2 h followed by kugelrohr distillation to give a yellow liquid (0.52 g, 96%), bp (oven temp.) 145–150 °C at 18 Torr; $\nu_{\text{max}}/\text{cm}^{-1}$ 3040, 2950, 2882, 2203 (C–D), 1700, 1610, 1480, 1438, 1370, 1280, 1180, 990, 750 and 680; δ_{H} 7.7–7.3 (5 H, m) and 4.22 (2 H, br s); δ_{D} 1.32 (s).

2,2,2-Trifluoroethyl phenylpropiolate (5). A solution of phenylpropynoyl chloride (2.5 g, 15 mmol) and 2,2,2-trifluoroethanol (3.0 g, 30 mmol) in dry ether was heated under reflux for 3 h. Evaporation followed by kugelrohr distillation gave the product (3.2 g, 92%) as a colourless liquid, bp (oven temp.) 125–130 °C at 16 Torr (Found: C, 57.4; H, 3.05; M^+ , 228.0401. $\text{C}_{11}\text{H}_7\text{F}_3\text{O}_2$ requires C, 57.9; H, 3.1%; M^+ , 228.0398); $\nu_{\text{max}}/\text{cm}^{-1}$ 3050, 2960, 2212, 1720, 1608, 1486, 1442, 1405, 1300, 1265, 1160, 975, 840, 755, 740 and 686; δ_{H} 7.65–7.55 (2 H, m), 7.5–7.35 (3 H, m) and 4.59 (2 H, q, J 8); δ_{C} 152.2 (CO), 133.3 (2 C, Ph C-2), 131.3 (Ph C-4), 128.8 (2 C, Ph C-3), 122.7 (q, ^1J 277, CF_3), 119.0 (Ph C-1), 89.3 ($-\text{C}\equiv$), 79.2 ($-\text{C}\equiv$) and 61.2 (q, ^2J 37, CH_2); δ_{F} –74.2 (t, J 8); m/z 228 (M^+ , 25%), 209 (3), 165 (4), 129 (100), 102 (30) and 75 (27).

Ethyl methyl acetylenedicarboxylate (11). This was prepared, as previously reported,² by pyrolysis of 4-ethyl 1-methyl 2-oxo-3-triphenylphosphoranylidenebutanedioate **12** prepared by reaction of ethoxycarbonylmethylenetri-phenylphosphorane with methyl oxalyl chloride in the presence of triethylamine. FVP of this ylide (1.10 g, 500 °C, 2.2×10^{-2} Torr, inlet 120 °C) gave ethyl methyl acetylenedicarboxylate **11** as a colourless oil (346 mg, 88%); δ_{H} 4.29 (2 H, q, J 7), 3.48 (3 H, s) and 1.33 (3 H, t, J 7); δ_{C} 152.3, 151.7, 75.0, 74.2, 63.1, 53.5 and 13.9.

Flash vacuum pyrolysis of acetylenic esters

The apparatus used was as described previously.¹² All pyrolyses were conducted at pressures in the range 10^{-2} – 10^{-1} Torr. Under these conditions the contact time in the hot zone was estimated to be ≈ 10 ms. The conditions for each pyrolysis are quoted as (mass used, furnace temperature, mean pressure, inlet heating temperature). Products were identified by NMR comparison with authentic materials and the data are quoted only on the first occurrence. Yields were determined by calibration of the ^1H NMR spectra by adding an accurately weighed quantity of a solvent such as CH_2Cl_2 and comparing integrals, a procedure estimated to be accurate to $\pm 10\%$. It should be noted that in this particular study many of the products observed were highly volatile and, while dissolution in CDCl_3 while still frozen in the liquid nitrogen-cooled trap served to identify products such as methane (bp –162 °C), ethene (bp –104 °C), ethyne (bp –84 °C) and formaldehyde (bp –19

°C), the yields measured by the time a standard could be added and the spectrum run were consistently underestimated.

FVP of ethyl phenylpropiolate (2) (R = Ph). FVP of **2** (95 mg, 750 °C, 5×10^{-2} Torr, inlet 60 °C) gave phenylacetylene (70%); δ_{H} 7.55–7.45 (2 H, m), 7.4–7.3 (3 H, m) and 3.08 (1 H, s); δ_{C} 132.1 (2 C), 128.8, 128.3 (2 C), 122.1 (4ry), 83.7 (–C≡) and 77.2 (≡CH), and a small proportion of ethene; δ_{H} 5.40. The identity of the last signal was supported by the observation that its intensity rapidly diminished with time.

FVP of 2,2,2-trideuterioethyl phenylpropiolate (4). FVP of **4** (122 mg, 750 °C, 4×10^{-2} Torr, inlet 60 °C) gave phenylacetylene (15%) and phenyldeuterioacetylene, PhC≡CD (60%); δ_{H} 7.55–7.45 (2 H, m) and 7.4–7.3 (3 H, m); δ_{D} 3.14 (s); δ_{C} as above except for much reduced size of signal at 77.2 (≡CD)

FVP of 2,2,2-trifluoroethyl phenylpropiolate (5). FVP of **5** (115 mg, 750 °C, 5×10^{-2} Torr, inlet 60 °C) gave phenylacetylene (55%). Additional small signals indicated the presence of trifluoroacetaldehyde (2%); δ_{H} 9.45 (1 H, q, *J* 3), and its cyclic trimer, 2,4,6-tris(trifluoromethyl)-1,3,5-trioxane (4%); δ_{H} 5.16 (1 H, q, *J* 4).

FVP of methyl phenylpropiolate (6). FVP of **6** (140 mg, 780 °C, 3.4×10^{-2} Torr, inlet RT) gave phenylacetylene (37%), unchanged methyl phenylpropiolate **6** (13%), and styrene (4%); δ_{H} 7.67–7.25 (5 H, m), 6.68 (1 H, m), 5.73 (1 H, dd, *J* 20, 1) and 5.23 (1 H, dd, *J* 12, 1).

FVP of methyl propiolate (7). FVP of **7** (120 mg, 830 °C, 3.8×10^{-2} Torr, inlet cooled with solid CO₂/MeOH) gave acrolein (15%); δ_{H} 9.62–9.58 (1 H, m) and 6.55–6.32 (3 H, m); δ_{C} 194.5, 138.5 and 137.9, unchanged methyl propiolate **7** (trace), formaldehyde (monomer); δ_{H} 9.73 (1 H, s) and (polymer); δ_{H} 5.02–4.88 (m) [authentic formaldehyde polymerised in CDCl₃ to give δ_{H} 5.08–4.86 (m)] and ethene.

FVP of butenolide (2,5-dihydrofuran-2-one) (19). FVP of **19**, prepared by a literature route,¹³ (69 mg) at 830 °C gave a liquid consisting almost entirely of acrolein (13%).

FVP of ethyl propiolate (8). FVP of **8** (190 mg, 750 °C, 2×10^{-2} Torr, inlet RT) gave extremely volatile products in the cold trap consisting of acetaldehyde (2%); δ_{H} 9.79 (1 H, q, *J* 0.5) and 2.21 (3 H, d, *J* 0.5), ethene (0.5%), methane (0.4%); δ_{H} 0.23 and ethyne (2.1%); δ_{H} 1.80.

FVP of dimethyl acetylenedicarboxylate (9). FVP of **9** (90 mg, 830 °C, 4×10^{-2} Torr, inlet 70 °C) gave acrolein (68%), formaldehyde monomer and polymer, and ethene.

FVP of diethyl acetylenedicarboxylate (10). FVP of **10** (110 mg, 750 °C, 1.4×10^{-2} Torr, inlet 80 °C) gave extremely volatile products in the cold trap consisting of acetaldehyde (3.5%), ethene (2 %), and methane (0.5%) [all assuming two molecules produced per starting material] and ethyne (2.9%).

FVP of ethyl methyl acetylenedicarboxylate (11). FVP of **11** (42 mg, 760 °C, 1.4×10^{-2} Torr, inlet RT) gave acrolein (45%), and traces of methyl propiolate **7**, acetaldehyde and ethene.

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