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Full Paper

C_8H_6 Thermal Chemistry. 7-Methylenecyclohepta-1,3,5-dienyne (Heptafulvyne) by Flash Vacuum Thermolysis–Matrix Isolation. Chemical Activation in the Rearrangements of Phenylenedicarbenes and of Benzocyclobutadiene to Phenylacetylene

Arvid Kuhn,[A] *Daisuke Miura,*[A] *Hideo Tomioka,*[B] *and Curt Wentrup*[A,C]

[A]School of Chemistry and Molecular Biosciences, The University of Queensland,
Brisbane, Qld 4072, Australia.
[B]Mie University, Tsu, Mie 514-8507, Japan.
[C]Corresponding author. Email: wentrup@uq.edu.au

Methylenecycloheptadienyne **11** (heptafulvyne) is obtained very cleanly by flash vacuum thermolysis (FVT) of the diazobenzocyclobutene precursor **8** at 400°C followed by isolation as a neat solid at 77 K or in an Ar matrix at 7–10 K. Compound **11** is a yellow solid, stable till ~−100°C in the neat state. The diazo compound itself (**2**) is observable by IR spectroscopy following mild decomposition of the tosylhydrazone salt **1** at 115°C. FVT of **8** at 200°C also generates diazo compound **2** as observed by IR spectroscopy and on-line mass spectrometry. FVT of **8** at 600–800°C causes rearrangement of **11** to phenylacetylene **12** and benzocyclobutadiene **13**. Mechanisms for the rearrangements are proposed. Facile rearrangement of benzocyclobutadiene to phenylacetylene is ascribed to chemical activation, which is also seen to be involved in the rearrangement of *p*-, *m*-, and *o*-phenylenebiscarbenes **25**–**27** to phenylacetylene **12**.

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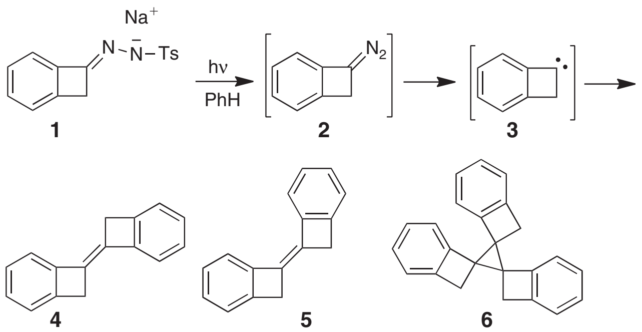
Introduction

Two dimers **4** and **5** and a trimer **6** of the unobserved benzocyclobutenylidene **3** have been isolated in a combined yield of 65 % from photolysis of a suspension of the tosylhydrazone salt **1** in benzene (Scheme 1).[1]

Addition of benzocyclobutenylidene **3** to benzene takes place in this reaction as well, and this has also been observed in the thermal decomposition of **1** in benzene.[2]

Thermolysis of the tosylhydrazone salt **7** generated diazo compound **2**, which was observable by its IR absorption at 2042 cm^{-1} in an Ar matrix. Photolyses of the three precursors **2**, **8**, and **9** in Ar matrices led to the formation of the novel methylenecycloheptadienyne **11** (heptafulvyne), possibly formed in a vinylidene–acetylene rearrangement of the valence isomer **10** (Scheme 2).[3] Neither **3** nor **10** were observable. Preparative flash thermolysis of **9** at 500°C with NMR spectroscopic analysis of the stable products afforded a low yield of a mixture of phenylacetylene **12** and the dimer **14** of benzocyclobutadiene **13** in a ~7 : 1 ratio.[2]

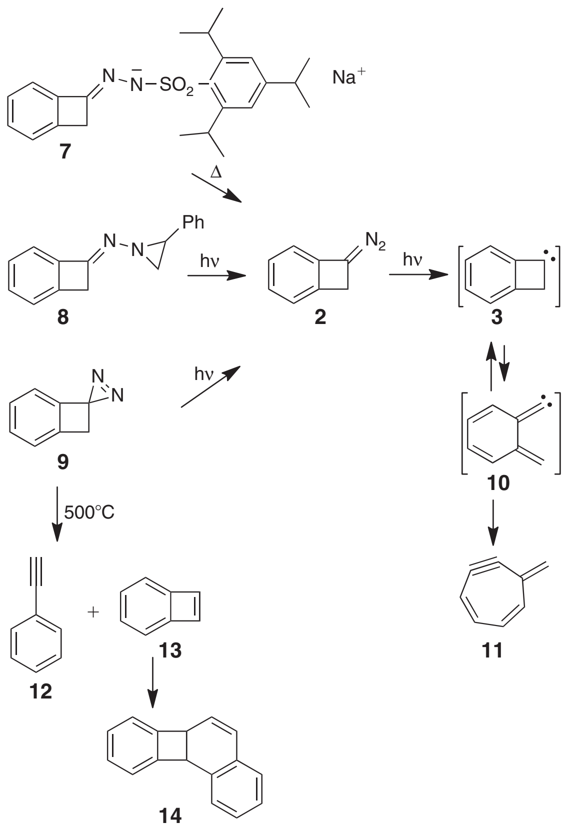
In an endeavour to shed more light on this chemistry, we have investigated the flash vacuum thermolysis (FVT) of **1** and **8** with Ar matrix isolation of the products.



Scheme 1. Dimers and trimer formed on photolysis of **1** as a suspension in benzene.[1]

Results

Gentle decomposition of the solid tosylhydrazone salt **1** at 115°C in high vacuum (5×10^{-4} hPa) with deposition of the material at 77 K gave diazo compound **2** absorbing at 2041, 1589, 1584, 1430 cm^{-1} (2047, 1599, 1595, 1443 cm^{-1} by photolysis of **9**[3]). The same diazo absorption was also obtained by first depositing a sample of solid aziridine **8** at 77 K and then photolyzing it with a high-pressure Hg/Xe lamp. Compounds **4**, **5**, and **6** were not obtained under these conditions, but FVT of **8** at 200–400°C with deposition of the neat product at 77 K afforded a weak band at 2098 cm^{-1} in the IR spectrum, assigned to **11**. This compound was stable to ~−100°C on subsequent warm-up. This was the first observation of **11** in a purely thermal reaction.



Scheme 2. Formation of methylenecycloheptadienyne **11** by matrix photolysis.[3]

Further FVT reactions of **8** were carried out at 400, 600, and 800°C with isolation of the products in Ar matrices at ~7 K. Apart from the necessary by-product styrene (**15**), the IR spectrum of the products of the 400°C reaction showed clear absorptions assigned to the cycloheptadienyne **11**,[3] which is formed very cleanly (Fig. 1; Scheme 3). The acetylenic $C{\equiv}C$ stretch appears at 2102 cm^{-1}, and other absorptions at 1570, 848, 731, 618, and 609 cm^{-1} are in good agreement with previous observations. FVT at 600 and 800°C showed formation of styrene **15**, disappearance of **11**, and formation of two new products, which were identified by comparison with literature data: phenylacetylene **12** and benzocyclobutadiene **13** (Fig. 2). The intensities of bands attributable to **11** decrease as those of **12** and **13** increase. Compound **11** has largely disappeared at 600, and completely at 800°C (Fig. 2).

The bands attributable to phenylacetylene **12** at 2122, 1490, 1446, 1218, 1028, 912, 758, and 648 cm^{-1} were assigned by comparison with data reported by Jørgensen et al.[4] and King and So.[5] Benzocyclobutadiene **13** absorbed at 1430, 1400, 1280, 1240, 898, 735, and 690 cm^{-1} in accord with a spectrum reported by Chapman.[6]

A correlation between observed and calculated IR spectra of **11** (Fig. 3) is in excellent agreement with the previous observations of McMahon and co-workers.[3] Comparison with the calculated IR spectra (B3LYP/6–31G*) of several other potential rearrangement products **16**–**20** is shown in Fig. S1 (Supplementary Material). Their relative energies calculated at the B3LYP/6–31G* level are shown in Chart 1. Energies and structures of **17** and several other C_8H_6 isomers have been calculated previously at the MNDO level.[7] The unstable *Z*,*Z*-isomer of octadienediyne **19** has been observed to rearrange to

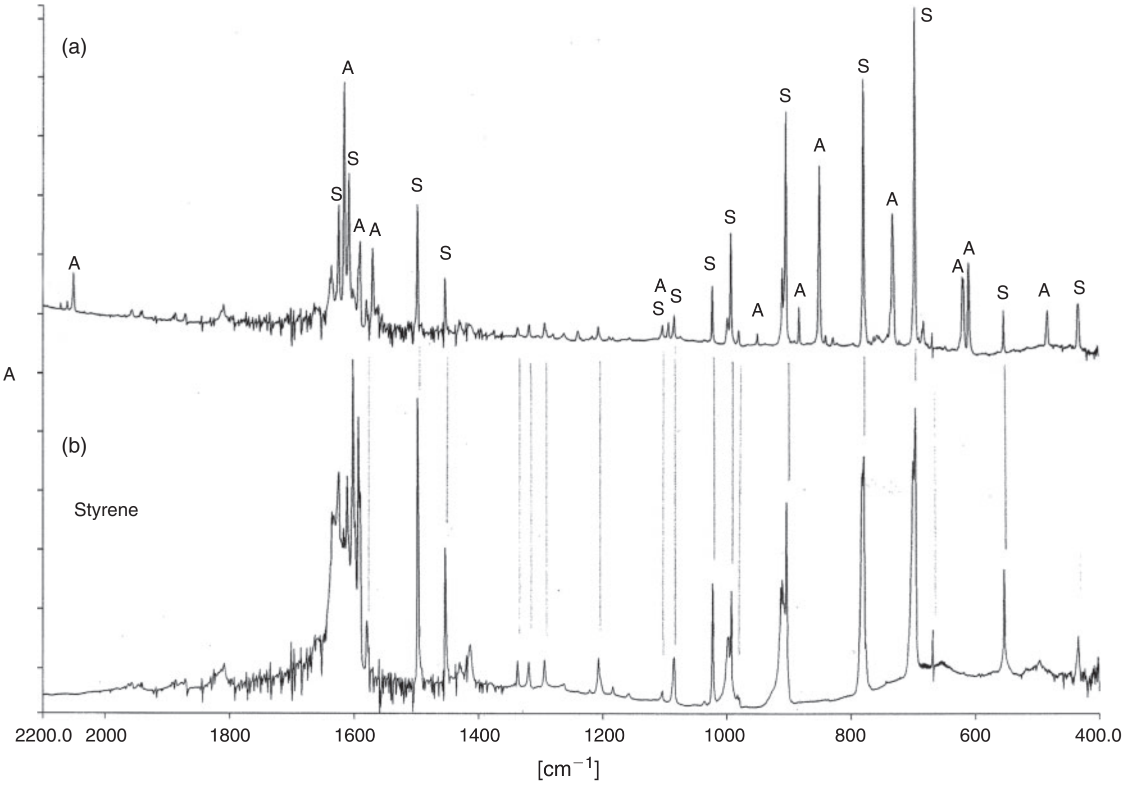


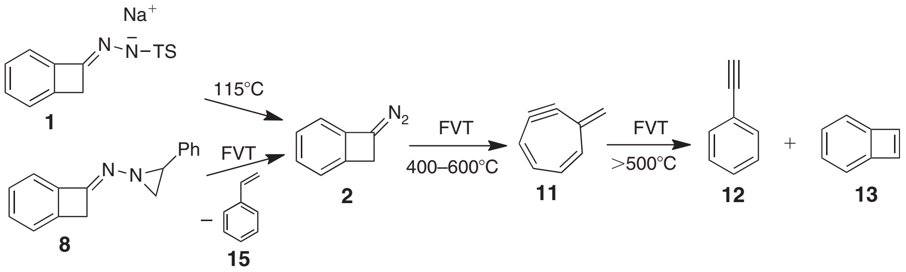
Fig. 1. IR spectra (Ar matrices, ~7 K; Ar/substance ratio ~1000 : 1). (a) The product of FVT of **8** at 400°C. A = methylenecycloheptadienyne **11**. S = styrene. (b) Pure styrene **15**.

cycloocta-1,2,4,6,7-pentaene **18** and then to benzocyclobutadiene **13** at room temperature.[8] The calculated IR spectra of **16**–**20** (Fig. S1) do not match the experimental IR spectrum ascribed to **11** (Figs. 1–3).

Parallel to the FVT/matrix isolation–IR investigation, the FVT reactions of **8** were also monitored by direct on-line mass spectrometry. At a FVT temperature of 200–300°C, peaks at *m/z* 130 and 102 are observed, corresponding to $\mathbf{2}^{+\bullet}$ and $[\mathbf{2}^{+\bullet} - N_2]$ (Fig. S2 in the Supplementary Material). At 400°C the spectrum changes completely, the peak at *m/z* 130 disappears, and a peak at *m/z* 28 increases (N_2), and two major signals were recorded at *m/z* 104 (styrene) and *m/z* 102 (Fig. S3 in the Supplementary Material). The latter corresponds to **11**, **12**, and/or **13**, and on the basis of the IR investigation reported above, it is assumed the mass spectrum is attributable largely to **11** at this temperature. The mass spectrum is very similar to that of phenylacetylene **12**, but minor differences in relative abundances and in particular a strong peak at *m/z* 101 $[M^{+\bullet} - H]$ in the collisional activation mass spectrum are compatible with $\mathbf{11}^{+\bullet}$ being the carrier (Figs S4 and S5 in the Supplementary Material). The most abundant fragment peak in the collisional activation spectra of both **11** and **12** is *m/z* 76 (C_6H_4), which corresponds to the benzyne molecular ion or an ion formed by ring opening of the benzyne ion.[11]

FVT of **8** at 500°C, isolation of the material at 77 K, warm-up and extraction with hexane followed by gas chromatography–mass spectrometry (GC-MS) analysis of the product afforded a small amount of benzocyclobutadiene dimer **14**. The two dimers **4** and **5** and the trimer **6** synthesized by Frimer et al.[1] (Scheme 1) were resynthesized from **1**, and their mass spectra were shown to be different from that of **14** (Fig. S6 in the Supplementary Material). Thus, it appears that benzocyclobutenylidene **3** survives in sufficient amount to dimerize and trimerize when generated by photolysis in benzene at 0–10°C; but it does not survive the FVT conditions used by us or by McMahon and co-workers.[3]

Interestingly, Dürr et al. reported the formation of low yields of Frimer's dimers **4** and **5** on 'flash pyrolysis' of the Li salt corresponding to **1** at 350°C.[12] However, the reaction conditions used by these workers involve dropping the solid salt into a heated and evacuated pyrex flask at 0.05–0.1 hPa. This results in



Scheme 3. Thermal formation and rearrangement of **11** on flash vacuum thermolysis (FVT).

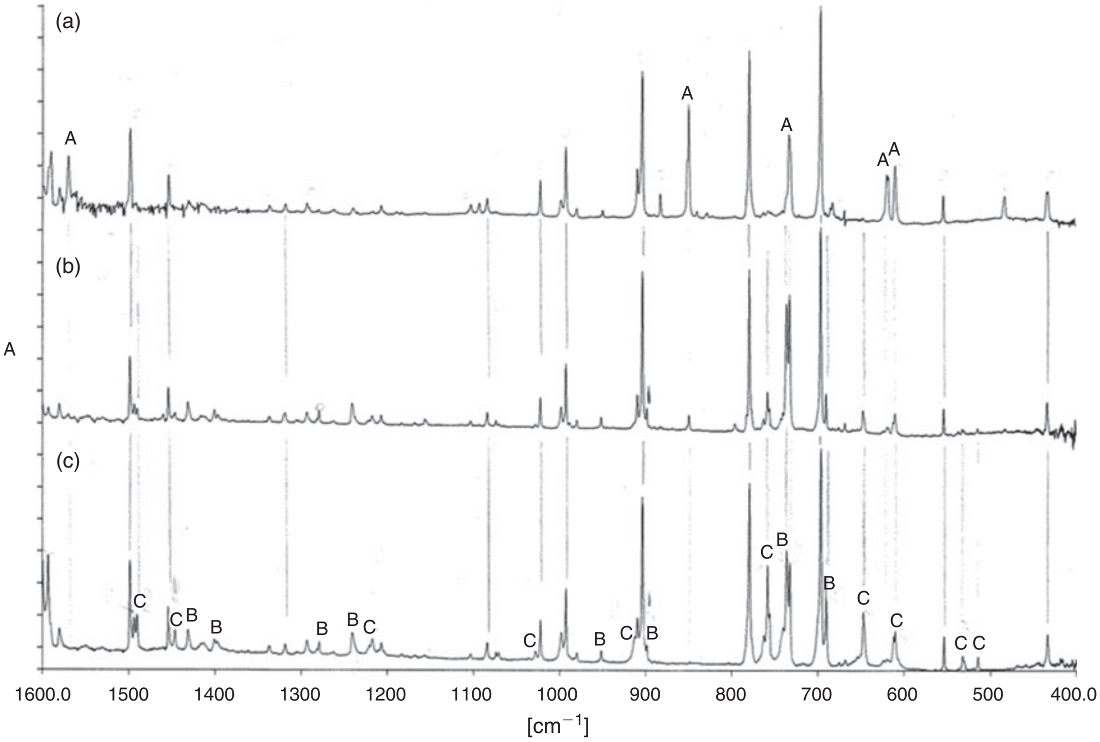


Fig. 2. Products of flash vacuum thermolysis (FVT) of **8** at (a) 400, (b) 600, and (c) 800°C. A = methylenecycloheptadienyne **11**. B = benzocyclobutadiene **13**. C = phenylacetylene **12**. The acetylenic band at 2102 cm^{-1} (Fig. 1) also disappears at 600–800°C. Unmarked bands are attributable to styrene **15** (compare Fig. 1).

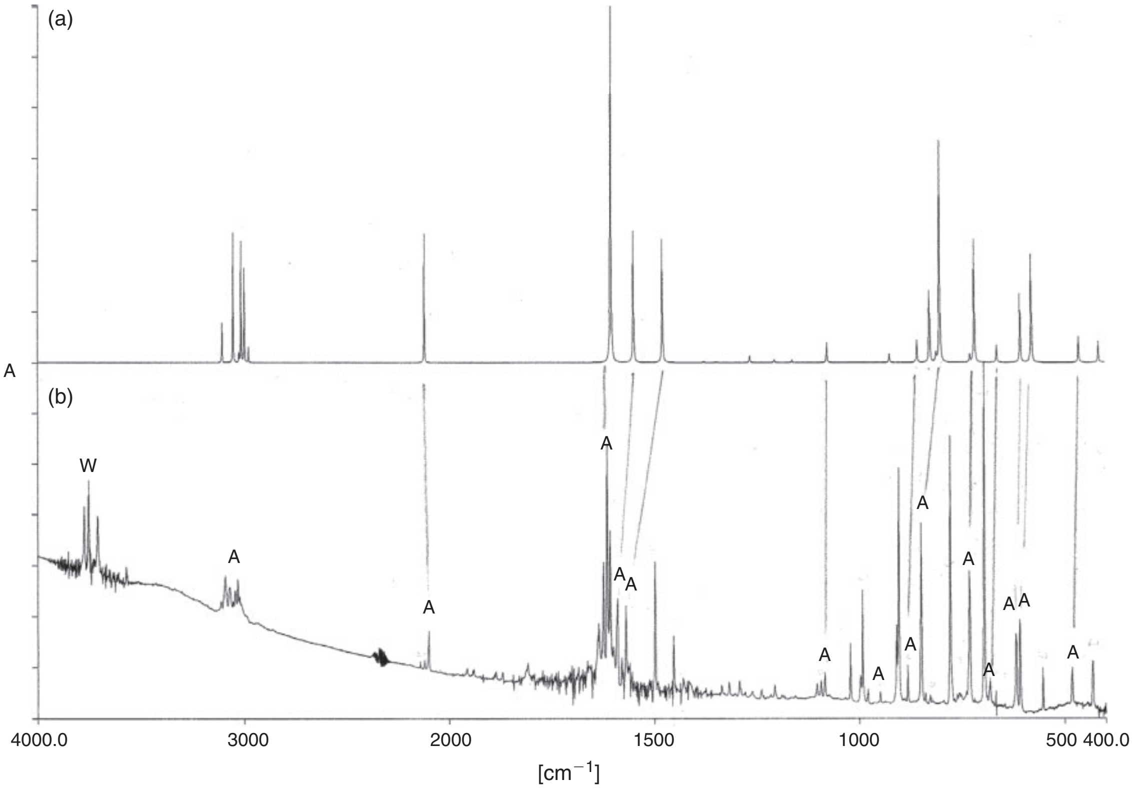


Fig. 3. (a) Calculated IR spectrum of **11** (B3LYP/6–31G*; wavenumbers scaled by 0.95). (b) Experimental spectrum from the flash vacuum thermolysis (FVT) of **8** at 400°C. A = **11**, W = water.

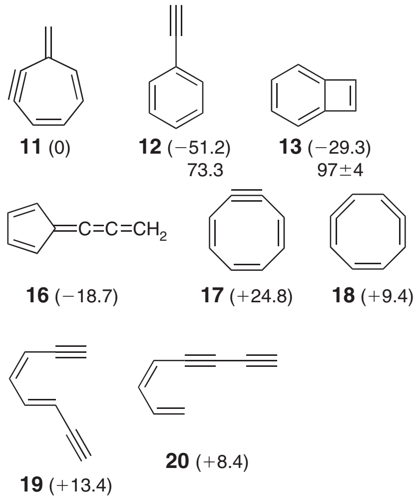
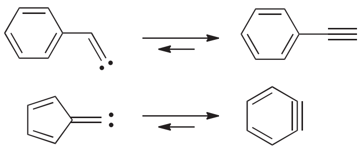


Chart 1. Energies of C_8H_6 isomers **11**, **12**, and **13** and potential structures **16**–**20**. Values in parentheses are relative energies in kcal mol^{-1} at the B3LYP/6–31G* level. Other values in plain font for **12** and **13** are experimental enthalpies of formation in kcal mol^{-1}.[9,10]

an immediate pressure rise due to pyrolysis in the solid state. These conditions cannot be compared with conventional low-pressure FVT. It thus appears that concentrations of benzocyclobutenylidene (**3**) sufficiently high for its dimerization are produced from the solid salt, either by photolysis or thermolysis of a suspension, and by pyrolysis of the bulk material. It is worth noting that reaction between the tosylhydrazone salt and benzocyclobutenylidene as well as benzocyclobutenone azine was recorded by Frimer et al.[1]



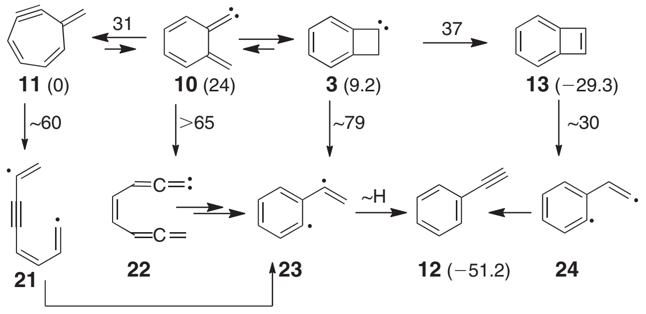
Scheme 4. Roger Brown rearrangements.

Discussion

The rearrangement **10** → **11** is formally a vinylidene–acetylene rearrangement, i.e. a Roger Brown rearrangement.[13] The corresponding phenyl group shift from phenylvinylidene to phenylacetylene (Scheme 4) has a calculated barrier of ~10 kcal mol^{-1}; i.e. it is very rapid under FVT conditions, and it is exothermic by ~47 kcal mol^{-1} (both H and phenyl can undergo the 1,2-migration).[14] The rearrangement of fulven-6-ylidene to *o*-benzyne (Scheme 4) is even faster, with a calculated barrier of only ~2 kcal mol^{-1}.[15]

Our matrix–IR investigation shows that the cycloheptadienyne **11** is formed in high yield on FVT at 400°C, but it rearranges to phenylacetylene **12** and benzocyclobutadiene **13** at higher temperatures.

The calculated activation barrier of ~31 kcal mol^{-1} [3] suggests the possibility of a thermal reversion of **11** to carbene **10**, which is endothermic by ~24 kcal mol^{-1}. A negligible barrier then permits the cyclization of **10** to **3** (exothermic by 15 kcal mol^{-1}). A 1,2-H shift in **3** leading to benzocyclobutadiene **13** has a calculated barrier[3] of ~28 kcal mol^{-1} (Scheme 5). Therefore, the highest barrier for the formation of **13** lies ~37 kcal mol^{-1} above **11**. The low pressure FVT conditions do not favour dimerization of the elusive carbene **3**; hence Frimer's products **4**, **5**, and **6** are not obtained. But the



Scheme 5. Potential mechanisms for the thermal rearrangements of **11** to benzocyclobutadiene **13** and phenylacetylene **12**. Ground state energies in kcal mol^{-1} relative to **11** calculated at the B3LYP/6–31G* level. Transition state energies estimated (see text).

benzocyclobutadiene **13** formed in the gas-phase will survive to the cold trap and dimerize to **14** on subsequent warm-up.

Compounds **11**, **10**, **3**, and **13** can all in principle rearrange to phenylacetylene **12** via ring opening (Scheme 5). Breaking of the C1–C7 bond in **11** would lead to the diradical **21**. Cyclization to the benzenoid diradical **23** followed by a single H-shift leads to phenylacetylene **12**. Ring opening of **10** to the allenylidene **22** may be able to provide another route to **23**. Benzocyclobutenylidene **3** can ring open directly to **23**. Normal vinylic C–C bond dissociation energies are ~90 kcal mol^{-1}. The strain energy of cycloheptyne is calculated as 31 kcal mol^{-1}.[16] This would still suggest a high energy requirement of the order of 60 kcal mol^{-1} for ring opening **11** → **21**, thereby making this path unlikely. The ring opening of cyclobutane to 1,4-butanediyl has a barrier of 57 kcal mol^{-1},[16] and a similar or higher barrier can be expected for a direct ring opening of **3** to **23**. This ring opening can also be estimated as an aryl–C bond breakage (~100 kcal mol^{-1}) minus the release of ~30 kcal mol^{-1} of cyclobutene strain energy) = ~70 kcal mol^{-1}.[16] Adding the calculated energy of **3** (9.2 kcal mol^{-1}) places **23** ~79 kcal mol^{-1} above **11**. Such a reaction is not likely under the reaction conditions. The ring opening **10** → **22** is expected to be endothermic by at least 50 kcal mol^{-1}.[17] For comparison, the parent 6π electrocyclic, endothermic ring opening of cyclohexadiene to *Z*-hexatriene has an activation energy of ~45 kcal mol^{-1}.[18] Adding the calculated energy of **10** (24 kcal mol^{-1})[3] places **22** at least 65 kcal mol^{-1} above **11**. Thus, at any rate, reaction **10** → **22** is not likely to be competitive. Finally, a C–C bond cleavage **13** → **24** is expected to have a barrier of ~60 kcal mol^{-1} (the C–C bond dissociation energy, ~100 kcal mol^{-1}, minus the strain energy of benzocyclobutadiene (**13**),[8] 40 kcal mol^{-1}).[19] The low enthalpy of formation of benzocyclobutadiene (**13**) then places this transition state at ~30 kcal mol^{-1} relative to **11**, and this therefore becomes the most favourable path to **12**. In summary, thermochemical arguments indicate that the rearrangement **11** → **13** will have an overall activation barrier of ~37 kcal mol^{-1} relative to **11**. Such activation energies are readily accessed under modest FVT conditions (above 400°C). It must be kept in mind that benzocyclobutadiene **13** formed from **11** in a low pressure FVT reaction will be chemically activated[20] by ~66 kcal mol^{-1} (37 + 29 kcal mol^{-1}; Scheme 5), which will facilitate the passage over the 60 kcal mol^{-1} barrier to **12** (Fig. 4).[21]

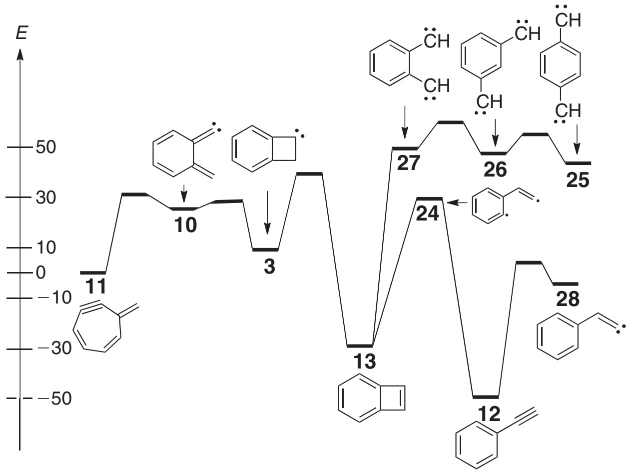
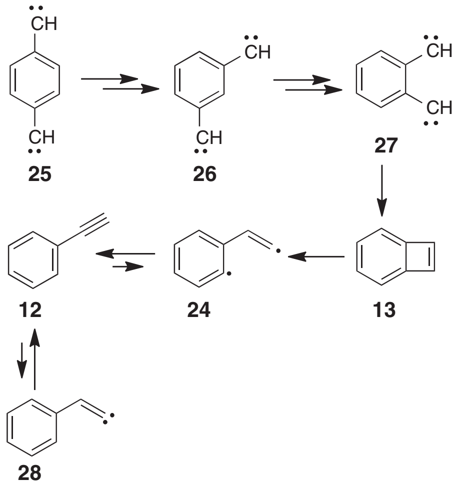


Fig. 4. Schematic energy profiles for the reactions in Schemes 5 and 6. Energies (*E*) in kcal mol^{-1} relative to heptafulvyne **11**. The energies of **11**, **10**, and **3** are at the G2(MP2,SVP) level from Ref. [3]. The energies of **12** and **13** are based on the experimental enthalpies of formation.[9,10] The energies of **24**–**27** are thermochemical estimates.[19] The barriers to ring expansion–ring contraction in the phenylenebiscarbenes are assumed to be similar to those in phenylcarbenes (13–15 kcal mol^{-1}).[23] The barrier **12** → **28** is based on B3LYP/6–31G* calculations on related molecules by Mackie and Johnson.[14]



Scheme 6. *p*-Phenylenebiscarbene → *m*-phenylenebiscarbene → *o*-phenylenebiscarbene → benzocyclobutadiene → phenylacetylene → phenylvinylidene rearrangement.

The rearrangement of benzocyclobutadiene **13** to phenylacetylene **12** under FVT conditions has been proposed previously based on a double ^{13}C-labelling experiment on another C_8H_6 isomer, benzene-1,4-biscarbene **25** (Scheme 6).[22] The distribution or the ^{13}C-labels in phenylacetylene **12** was in accord with the carbene–carbene rarrangements to **26** and **27** via ring expansion–ring contraction, cyclization to benzocyclobutadiene **13**, isomerization to phenylacetylene **12**, and finally the Roger Brown rearrangement interconverting the two acetylenic carbons in **12** via phenylvinylidene **28** (both H and phenyl can undergo the 1,2-migration). Here too, the rearrangement **27** → **13** will be massively exothermic – by ~80 kcal mol^{-1} [19] thereby allowing a chemically activated isomerization **13** → **12**.

Conclusion

Mild thermolysis of the tosylhydrazone salt **1** (150°C) yields diazobenzocyclobutene **2**, which is also obtained by elimination of styrene from **8** under mild FVT conditions. FVT of **8** at 400°C results in clean formation of the methylenecycloheptadienyne **11** (heptafulvyne). FVT at higher temperatures (600–800°C) causes rearrangement of **11** to benzocyclobutadiene **13** and phenylacetylene **12**. The facile rearrangement of **13** to **12** in the rearrangement of **11**, and the occurrence of a phenylacetylene–phenylvinylidene interconversion (**12** → **28**) in the rearrangement of *p*-, *m*-, and *o*-phenylenebiscarbenes **25**–**27** are ascribed to chemically activated benzocyclobutadiene **13**.

Experimental

General procedures for FVT and matrix isolation[24] and descriptions, drawings, and images of the FVT apparatus[24c] have been published. The FVT apparatus consisted of a 10 cm long, 0.7 cm internal diameter, electrically heated quartz tube suspended in a vacuum chamber directly flanged to the cryostat cold head, with a wall-free flight path of ~3 cm between the exit of the quartz tube and the cold KBr target at $\sim10^{-5}$ hPa. Ar matrices were deposited onto KBr disks at ~22 K, and IR spectra were recorded at 7–10 K with a resolution of 1 cm^{-1}. Ar was ultra high purity. For isolation of FVT products at 77 K the same pyrolysis apparatus was flanged to a liquid N_2-cooled cryostat. GC-MS data were obtained using a Zebron capillary GC column ZB-5 (30 m length). Mass spectra were recorded on Kratos MS25RFA or Waters AutoSpec 6F mass spectrometers in electron ionization mode at 70 eV. Both instruments had an FVT oven directly attached to the ion source.[11,25,26] For the AutoSpec 6F of EBEEBE geometry typical ion source conditions were 8 kV accelerating voltage and 200 mA trap current. The solid samples were introduced with a direct insertion probe.

Materials

Compounds **1** and **8** and benzocyclobutadiene dimers and trimer **4**, **5**, and **6** were prepared according to literature methods.[1,3]

Supplementary Material

Figs S1 (calculated IR spectra of **11** and **16**–**20**), S2–S3 (mass spectra from the FVT of **8** at 200 and 400°C, S4-S5 (collisional activation mass spectra of fragment ion *m/z* 102 from phenylacetylene and from the FVT of **8**), and S6 (mass spectra of **4**, **5**, and **14**) and computed vibrational data are available on the Journal's website.

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