

# A Simple and Inexpensive Method for the Detection of Carbon Monoxide Released from Thermal Cheletropic Decarbonylation Reactions

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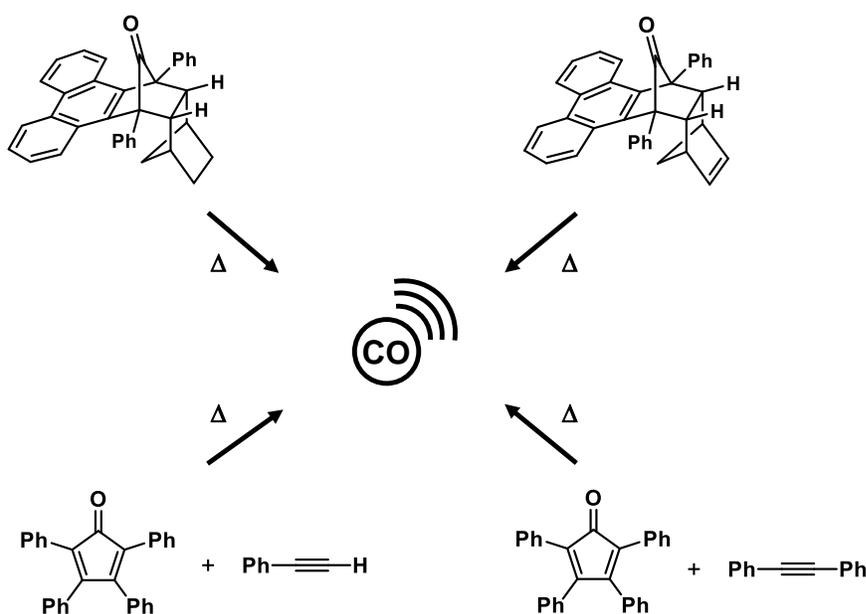
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## ABSTRACT

10 This work presents a simple protocol that demonstrates the use of an inexpensive household carbon monoxide detector as a useful tool to detect the release of carbon monoxide gas from thermal cheletropic decarbonylation reactions. The carbon monoxide detection method described has been employed in a short series of reactions used in a University teaching laboratory setting and full procedures for these are outlined. In each case, the procedure to isolate and identify the decarbonylation products has also  
15 been provided.

## GRAPHICAL ABSTRACT

Thermal cheletropic release of CO detected using a household alarm.



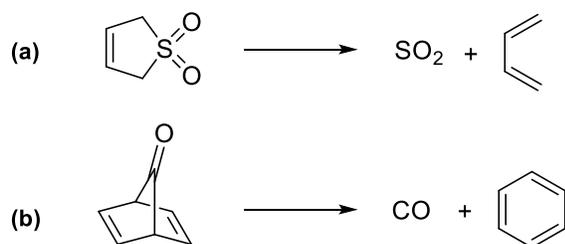
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20 **KEYWORDS**

Upper-Division Undergraduate, Laboratory Instruction, Organic Chemistry, Hands-On Learning / Manipulatives, Problem Solving / Decision Making, Aromatic Compounds, Gases, Laboratory Equipment / Apparatus, Qualitative Analysis, X-ray Crystallography

25 **INTRODUCTION**

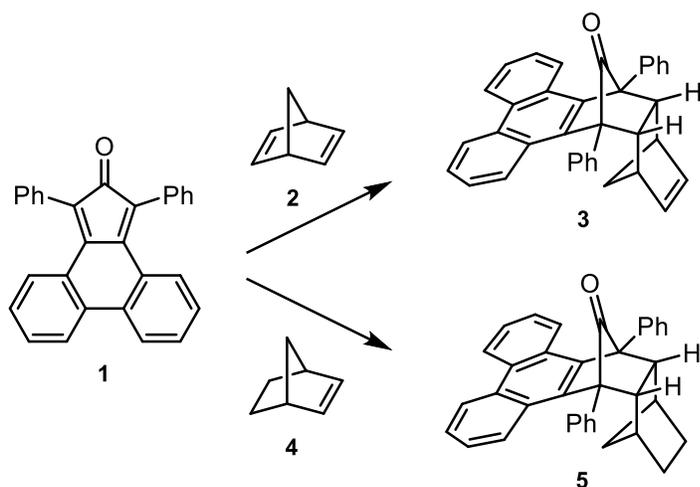
In their landmark paper in 1969, R. B Woodward and R. Hoffmann defined a cheletropic reaction as a process “in which two  $\sigma$  bonds which terminate at a single atom are made, or broken, in concert”.<sup>1</sup> Some examples of simple cheletropic reactions that illustrate release of sulfur dioxide and carbon monoxide are shown in scheme 1.<sup>1,2</sup> Reactions involving thermal cheletropic extrusion of sulfur dioxide and carbon monoxide are important in organic synthesis and feature in many chemistry teaching laboratory courses.<sup>1-3</sup> One of the best-known examples of a teaching laboratory activity that involves cheletropic extrusion of CO gas is the preparation of hexaphenylbenzene from tetracyclone and diphenylacetylene.<sup>3</sup> There are however other popular teaching examples involving the tetracyclone  
35 cycloadducts derived from dimethyl acetylenedicarboxylate (DMAD),<sup>3</sup> and benzyne.<sup>4</sup>



Scheme 1 – Example cheletropic reactions (a) release of sulfur dioxide from 3-sulfolene (b) release of carbon monoxide from norbornadiene-7-one.

40 A pericyclic sequence originally reported by E. A. Harrison<sup>5</sup> has featured successfully in our advanced organic chemistry laboratory course for many years. The key synthetic step in the sequence is a Diels-Alder reaction, followed by an example of cheletropic extrusion of carbon monoxide (this occurs during melting point analysis of the cycloaddition product). The original procedure focuses on the [ $\pi 4_s + \pi 2_s$ ] cycloaddition between phencyclone (**1**, 1,3-diphenyl-2-H-cyclopenta[1]phenanthrene-2-one) and

45 norbornadiene (**2**, bicyclo[2.2.1]hepta-2,5-diene) to afford bicyclo[2.2.1]heptene **3** (Scheme 2).  
Subsequently, we have extended the original experiment to include the cycloaddition of phencyclone (**1**)  
with norbornene (**4**, bicyclo[2.2.1]hept-2-ene) to form bicyclo[2.2.1]heptane **5** (Scheme 2). In addition to  
analysis by IR and  $^1\text{H}$  NMR spectroscopy, Harrison's paper states that on melting, compound **3** "exhibits  
the interesting (or mystifying) property of decomposing with (vigorous) gas evolution on heating".<sup>5</sup>  
50 However, the structure of the decomposition product is not disclosed in the paper and the gas evolved  
is not identified.



Scheme 2 – Diels-Alder reactions between phencyclone (**1**) and norbornenes **2** and **4** and to afford cycloadducts **3** and **5**.

55 A focus on the cheletropic reaction aspect of the original work has been of interest to us as an  
extension of this experiment, particularly the opportunity to identify the gas that is extruded. Reference  
to prior work by Mackenzie<sup>6</sup> confirms that the decomposition process described in Harrison's paper  
involves a thermal cheletropic decarbonylation reaction of cycloadduct **3** that releases CO gas.

## PEDAGOGICAL GOALS

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In this paper, we report a simple protocol that uses a household carbon monoxide detector as an  
inexpensive tool to detect the release of CO gas from a series of cheletropic decarbonylation reactions.  
The method described also allows the decomposition products obtained from cycloadducts **3** and **5** to  
be identified. Furthermore, we provide additional examples where the CO detection procedure can be

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65 applied in a well-known pericyclic sequence where tetracyclone is reacted at high temperature with  
diphenylacetylene to afford hexaphenylbenzene. The reactions involving cycloadducts of phencyclone  
are used in our advanced level organic laboratory courses, whereas the tetracyclone protocol is used in  
an optional 2<sup>nd</sup> year level course. In both cases, the goal of these practical tasks is to enable students to  
learn how to make, isolate and purify the reaction products. The students also learn how to characterize  
70 the products they have made using melting point analysis and appropriate spectroscopic techniques.  
Another goal is to relate mechanistic theory to experimental observations. Pre-laboratory reading or  
discussion with students (in small groups) about the mechanisms of the relevant reactions makes the  
students aware that release of carbon monoxide gas is also expected, and many will note bubbles of gas  
forming when they conduct their work. The new protocol reported here allows students to confirm that  
75 CO gas is formed using a simple and quick method, this provides a useful link between mechanistic  
understanding and the observations they make during their laboratory classes. The apparatus required  
is simple and allows students to assemble and use it themselves, alternatively small groups can watch  
an instructor demonstrate the process (Example laboratory manual descriptions have been provided in  
the Supporting Information document).

## 80 **OVERVIEW OF CARBON MONOXIDE DETECTION PROTOCOL**

As stated in the original paper,<sup>5</sup> the thermal decarbonylation of cycloadduct **3** can be conveniently  
observed using a melting point apparatus, we have also found the same is true for cycloadduct **5** (video  
footage of this has been provided in the Supporting Information document). However, the quantity of  
85 material used is very small, so it is difficult to detect the carbon monoxide released. The small amount  
of decomposed material formed when melting a sample in a melting point apparatus is also difficult to  
manipulate and characterize. We anticipated that the process could be scaled up so that the release of  
carbon monoxide gas from the reaction could be identified by using an inexpensive household carbon  
monoxide detector. We also reasoned that the increased amount of starting material would allow a useful  
90 amount of decomposed material to be isolated. In testing, it was found that heating 200-300 mg of  
cycloadducts **3** or **5** to their melting point in a test tube resulted in gas evolution and formation of an  
amber coloured liquid. Heating was stopped once gas evolution ceased, at this stage the liquid was

typically observed to cool to form a glassy solid. In order to detect the presence of carbon monoxide, a length of rubber tubing was connected to the open end of the test tube via a glass T-piece (which also had a balloon filled with nitrogen attached). The carbon monoxide detector was placed in a sealable polythene bag, and the end of the tubing was placed in the bag next to the detector. Once decomposition of the cycloadduct was complete (visible evolution of gas bubbles ceased), nitrogen gas was admitted to reaction vessel from the balloon to flush the carbon monoxide into the bag and be detected (see figure 1, further assembly details and a short film demonstration are provided in the Supporting Information document). There are various designs of carbon monoxide detector on the market, they have an audible alarm that sounds, although some devices also have a warning light and digital display to indicate that CO gas is present. Domestic detectors can typically indicate the presence of carbon monoxide at >10 ppm levels, so are sensitive enough to detect the gas released from the reactions being studied.<sup>7</sup> These devices are usually small enough to be portable, so it is convenient to place the reaction assembly in a fumehood and ensure the small quantity of CO gas produced can be ventilated safely.

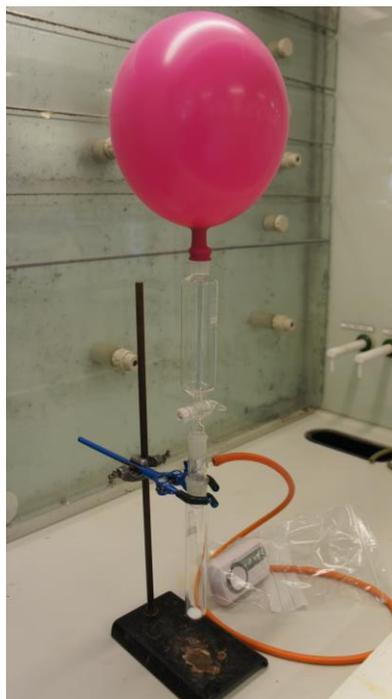
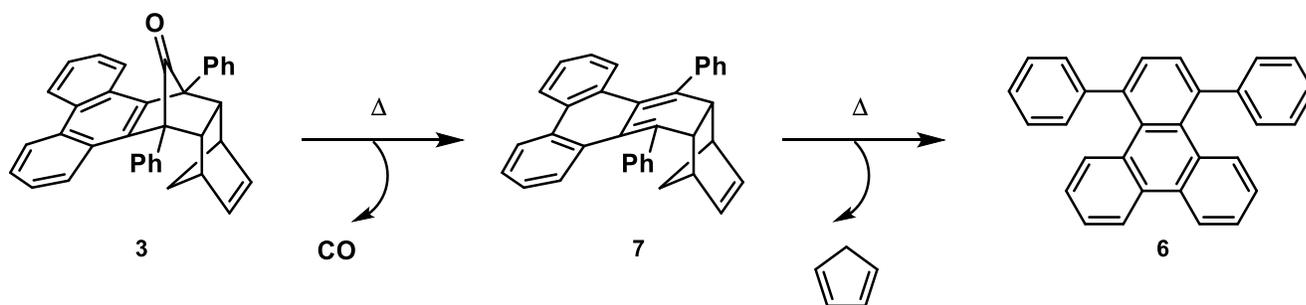


Figure 1 – Glassware assembly for thermal decomposition of cycloadducts **3** and **5** and connection to a domestic carbon monoxide alarm to detect the presence of CO gas released.

Example 1: Study of the Thermal Decomposition of Cycloadduct **3**

Cycloadduct **3** was heated as described in the general protocol above and CO gas was usually  
115 successfully detected after a few minutes of heating. The decomposition product was isolated by  
dissolving the residue in toluene, before addition of an equal volume of methanol. The solution was then  
stored overnight, any insoluble material being filtered off through a glass wool plug and the filtrate  
concentrated *in-vacuo* to afford the product. Satisfactory samples have also been obtained by allowing  
the residue from the thermal decomposition reaction to cool to room temperature. The resulting glassy  
120 material usually becomes a powdery solid after agitation with a small spatula for 1-2 minutes. The IR  
and  $^{13}\text{C}$  NMR spectrum of the product from both isolation methods confirmed that no C=O bond was  
present, and the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra confirmed that only aromatic signals were present. These  
observations are consistent with the formation of 1,4-diphenyltriphenylene (**6**) and this outcome is in  
accordance with the first report of this reaction by Mackenzie in 1960.<sup>6</sup> Thermal cheletropic  
125 decarbonylation of **3** might be expected to form compound **7** (Scheme 3), however Mackenzie's work  
demonstrated that a subsequent retro Diels-Alder reaction allows release of cyclopentadiene.  
Triphenylene **6** can readily be identified by melting point analysis, NMR spectroscopy and IR  
spectroscopy. The 1960 study pre-dates the widespread use of high field NMR techniques, so in that  
report, the loss of cyclopentadiene was confirmed by trapping and isolating the cycloadduct obtained on  
130 reaction with maleic anhydride.<sup>6</sup>

Scheme 3 – Thermal decomposition pathways of phencyclone cycloadduct **3**.

This activity is used in a year 3 laboratory course (as part of a 5-year degree), typically 30-40 students would attempt the experiment each year. Each student works individually through a set of allocated

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135 tasks and would be expected to complete this activity within an allocation of  $3 \times 3.5$  hour laboratory sessions. There are not enough carbon monoxide detectors available for the whole class to use individually, so instead, students can observe a demonstration of the cheletropic reaction with a preassembled apparatus equipped with a CO detector. The demonstration of CO detection is performed by an instructor who is familiar with the apparatus, as a result, the carbon monoxide detection protocol  
140 has been found to work without fail so far. After observing CO detection with their instructor, the students are able to repeat the decomposition procedure with the sample of cycloadduct **3** they prepared and obtain melting point and spectroscopic data for the decomposition product. Both cycloadduct **3** and triphenylene **6** are readily isolated after crystallisation and filtration (typical isolated yields being in the range 40-65%) and the reactions have proved to be reliable (very few students fail to obtain any  
145 products). The students on the course complete a parallel workshop focused on advanced spectroscopy and are therefore well prepared to interpret the NMR spectra obtained during this task.

#### Example 2: Study of the Thermal Decomposition of Cycloadduct **5**

Cycloadduct **5** is readily prepared in a very similar way to cycloadduct **3**, typical isolated yields after  
150 crystallisation and filtration are usually in the range 40-70%. Samples of compound **3** can be readily crystallised to afford material suitable to allow an X-ray crystal structure to be obtained (see figure 2). The crystal structure was not usually obtained and solved by students, instead, structural data could be made available to them as a handout *via* the course Virtual Learning Environment (VLE). It has been reported that the C=O and C–C bond distances in bridged cyclopentenones are useful indicators of the  
155 potential for cheletropic extrusion of CO gas.<sup>8</sup> The C–C bonds that are broken during the reaction are typically longer than those expected for the saturated analogue. Conversely, the C=O bond (that will become the CO triple bond) is shorter than would be anticipated for the corresponding cyclopentanone. The crystal structure allows the relevant bond distances in cycloadduct **5** to be measured and compared with those expected. In this case the C<sub>1</sub>–O<sub>1</sub> bond distance is 1.1953(16) Å and the C<sub>1</sub>–C<sub>2</sub> bond distance  
160 is 1.5486(19) Å, these data are consistent with the pattern reported in the literature. For comparison, the relevant C–C and C=O bond distances in bridged cyclopentanones are typically 1.519 Å and 1.207 Å respectively.<sup>8</sup> This information can provide some additional insight for students about the cheletropic

process that takes place on heating. When cycloadduct **5** was heated by an instructor as described in the general protocol above, carbon monoxide was routinely detected successfully once the evolution of gas subsided and the reaction flask was flushed with nitrogen. This version of the experiment has been used in the same laboratory setting as described in example 1, however, in this instance the students did not isolate and characterise the thermal decomposition product (the focus in this case was on detection of carbon monoxide released).

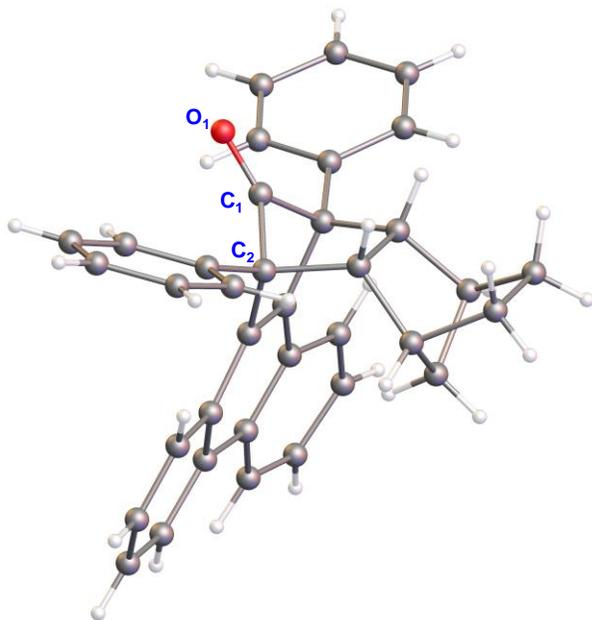
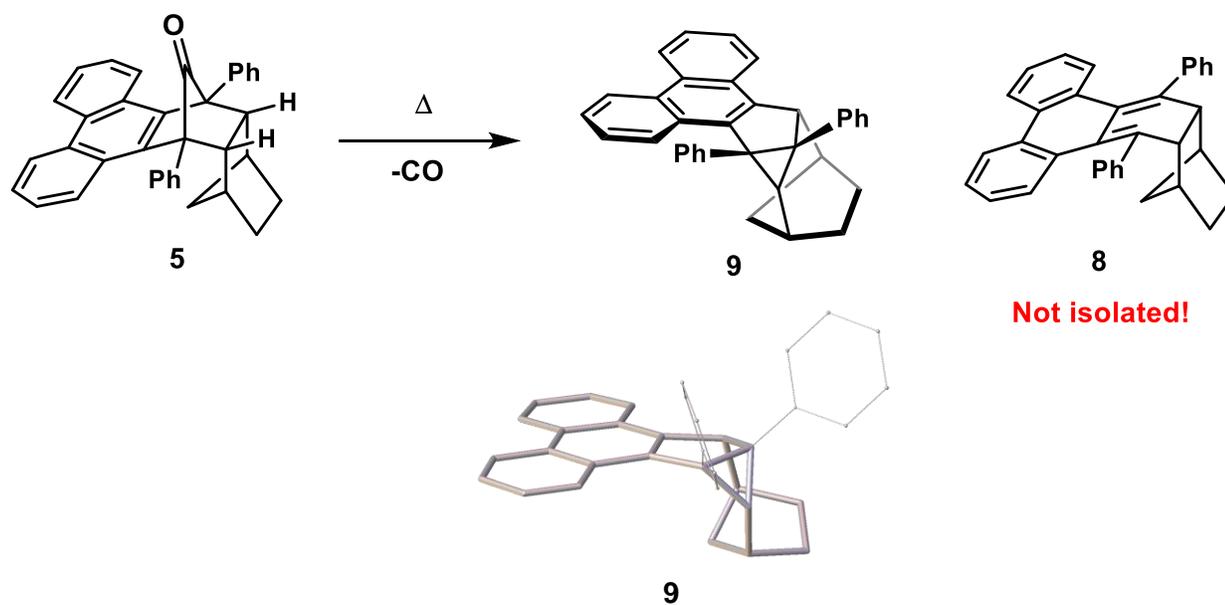


Figure 2 – X-ray crystal structure of cycloadduct **5** with key atoms for bond distance measurements highlighted.

In contrast with diene **7**, compound **8** is incapable of decomposition *via* a retro Diels-Alder reaction. Unexpectedly, the decarbonylation product has instead been found to be hydrocarbon **9** rather than compound **8**. The isolation and identification of compound **9** is not included in our existing practical task since the primary objective is to demonstrate the formation of carbon monoxide. However, the product can be isolated and the associated thermal decomposition process<sup>9</sup> could be of interest to very advanced students. The X-ray crystal structures allow the starting material and product to be easily visualised and could assist a discussion with students about potential mechanistic explanations for the formation of compound **9** from **5**.<sup>10,11</sup> The mechanism for this reaction has not been fully elucidated, however, a tentative sequence of steps has been formulated for the formation process. The isolation

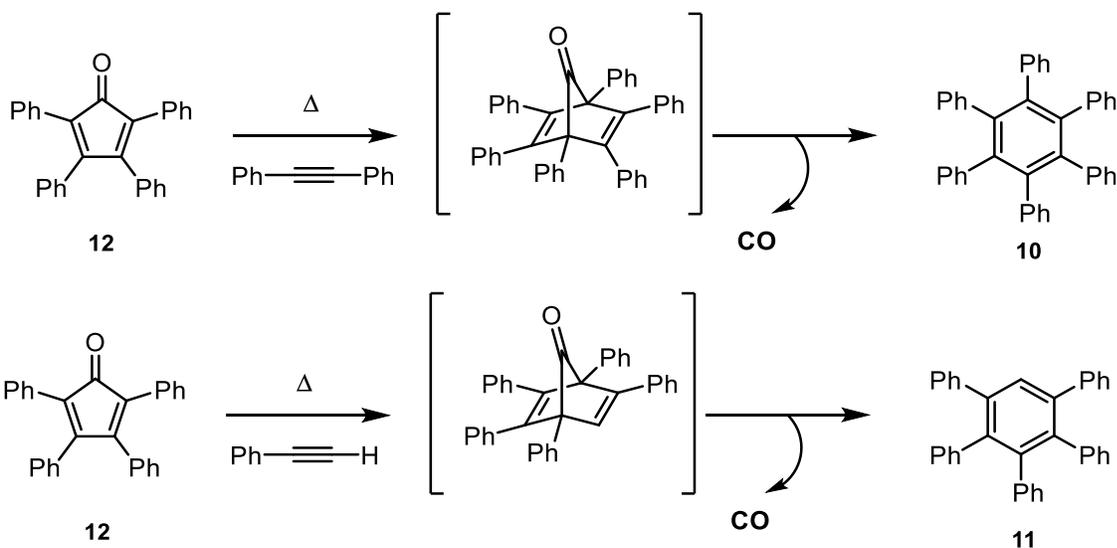
procedure, spectroscopic data and a short discussion of the proposed mechanistic pathway are all outlined in the Supporting Information document.<sup>9,10</sup>



Scheme 4 – Thermal decomposition of phencyclone cycloadduct **5**. An adapted view of the X-ray crystal structure of **9** is also shown (The phenyl rings are shown in wireframe form and hydrogen atoms have been removed to allow a clearer view of the carbon skeleton).

### Example 3: Diels-Alder / thermal cheletropic reaction sequences to make hexaphenylbenzene (**10**) or pentaphenylbenzene (**11**)

The preparation of hexaphenylbenzene (**10**) is a well-known teaching laboratory activity, since it offers a simple demonstration of a pericyclic sequence involving a Diels-Alder reaction followed by cheletropic CO extrusion reaction (Scheme 5).<sup>3</sup> A slightly modified version of the detection protocol described above provides an opportunity to demonstrate to students that CO gas is evolved from this reaction sequence.



Scheme 5 – Diels-Alder and cheletropic CO extrusion sequence to prepare hexaphenylbenzene **10** and pentaphenylbenzene **11**.

An example textbook procedure<sup>3</sup> for the preparation of hexaphenylbenzene involves heating a mixture of tetracyclone (**12**, 2,3,4,5-Tetraphenyl-2,4-cyclopentadien-1-one) in an open test tube with diphenylacetylene (the latter serves as the dieneophile and as the solvent<sup>11</sup>). Various high boiling point solvents can be used in this reaction,<sup>12</sup> in our teaching laboratory course we have found that using silicone oil is the most convenient option. In a typical procedure, the reagents were mixed with a small volume of silicone oil in a round bottom flask and heated until the dark red/purple colour of the reaction mixture faded. This method was found to be easily compatible with the use of a household carbon monoxide detector since the round bottom flask could be connected to the assembly described above. As the reaction was heated, bubbles of gas were observed that could be subsequently identified as containing CO since the carbon monoxide alarm usually sounded in the latter stages of the reaction (frequently successful detection was achieved without the need for the reaction flask to be flushed with nitrogen). However, as described in the earlier examples, a balloon of nitrogen does ensure the CO gas in the flask headspace can be flushed into the collection bag and activate the audible alarm. On cooling, the product was collected by filtration and NMR spectra were obtained. This method was also found to work well for the reaction of tetracyclone and phenylacetylene to form carbon monoxide and pentaphenylbenzene (**11**). This activity is used in a year 2 optional course, each lab class in this module would typically have 6-10 students working individually in a 3-hour lab session. The reactions to form

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215 compounds **10** and **11** are very reliable and very rarely fail, reaction yields are typically 70-90% although  
can be lowered by transfer losses during filtration. In this case a small number of detectors are needed  
for individual work, so it is possible for students to attach a CO detector to their apparatus with help  
from an instructor. The carbon monoxide detector works very well under the conditions (and level of  
supervision described), so far there have been no instances of a failed attempt to detect the CO gas  
220 released.

## SUMMARY

In summary, we have presented a protocol that employs an inexpensive and readily available household  
225 safety device to serve as a convenient means to detect release of carbon monoxide from a series of  
thermal cheletropic decarbonylation reactions. The experimental set-up also allows the reaction  
products in all cases to be isolated and analysed by IR and NMR spectroscopy if desired. Example 1  
(thermal decarbonylation of cycloadduct **3**) can serve as an extension to an experiment that was  
originally reported by E. A. Harrison in 1991.<sup>5</sup> The original paper alluded to the cheletropic extrusion of  
230 carbon monoxide, this can now be confirmed and the expected triphenylene product (**6**) can be  
characterized. Example 3 is a variation of a popular pericyclic sequence to prepare hexaphenylbenzene  
(**10**) from tetracyclone (**12**).<sup>3</sup> In this case the reaction assembly has been shown to be easily modified to  
allow carbon monoxide release to be detected, in addition to isolating the expected product. In all of the  
examples described, the CO detection protocol has been found to be simple, quick and very reliable. The  
235 ready availability of sensitive detectors from commercial sources has been key to the successful  
development and use of the protocols outlined. In each case, the reactions described allow students to  
observe release of carbon monoxide as the reactions proceed since they can see gas bubbles forming  
and a CO detector response. On completion of the reactions, students can also compare the  
spectroscopic data from the starting materials and products to show that a carbonyl group is not present  
240 in the products due to loss as CO gas.

## HAZARDS

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A laboratory coat and safety glasses must be worn at all times. Do not allow any of the substances in use to come into contact with skin. Toluene, petroleum ether and methanol are flammable and harmful by inhalation, ingestion or skin absorption. Norbornene, norbornadiene, phenylclone and tetracyclone should be considered as potential skin and eye irritants. All solvent waste should be collected in appropriate containers for proper disposal. A small quantity of carbon monoxide gas is released during the decomposition process so it is advised that the glassware and detection equipment is assembled in a fumehood. Although the quantity of gas released is small, it is important to make all participants aware that carbon monoxide is a highly toxic and flammable gas.

## ASSOCIATED CONTENT

### Supporting Information

A set of technical notes, including relevant IR and NMR spectra have been provided (.DOCX and .PDF files). X-ray Crystallography data for compounds **5** and **9** has also been provided (.CIF files). In addition, short videos (.MP4 files) that show thermal decomposition of **5** are included. The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.XXXXXXX.

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