

# Flash vacuum pyrolysis over magnesium. Part 1. Pyrolysis of benzylic, other aryl/alkyl and aliphatic halides

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Flash vacuum pyrolysis over a bed of freshly sublimed magnesium on glass wool results in efficient coupling of benzyl halides to give the corresponding bibenzyls. Where an *ortho* halogen substituent is present further dehalogenation gives some dihydroanthracene and anthracene. Efficient coupling is also observed for halomethylnaphthalenes and halodiphenylmethanes while chlorotriphenylmethane gives 4,4'-bis(diphenylmethyl)biphenyl. By using  $\alpha,\alpha'$ -dihalo-*o*-xylenes, benzocyclobutenes are obtained in good yield, while the isomeric  $\alpha,\alpha'$ -dihalo-*p*-xylenes give a range of high thermal stability polymers by polymerisation of the initially formed *p*-xylylenes. Other haloalkylbenzenes undergo largely dehydrohalogenation where this is possible, in some cases resulting in cyclisation. Deoxygenation is also observed with haloalkyl phenyl ketones to give phenylalkynes as well as other products. With simple alkyl halides there is efficient elimination of HCl or HBr to give alkenes. For aliphatic dihalides this also occurs to give dienes but there is also cyclisation to give cycloalkanes and dehalogenation with hydrogen atom transfer to give alkenes in some cases. For 5-bromopent-1-ene the products are those expected from a radical pathway but for 6-bromohex-1-ene they are clearly not. For 2,2-dichloropropane and 1,1-dichloropropane elimination of HCl occurs but for 1,1-dichlorobutane, -pentane and -hexane partial hydrolysis followed by elimination of HCl gives *E,E*-, *E,Z*- and *Z,Z*- isomers of the dialk-1-enyl ethers and fully assigned <sup>13</sup>C NMR data are presented for these. With 6-chlorohex-1-yne and 7-chlorohept-1-yne there is cyclisation to give methylenecycloalkanes and -cycloalkynes. The behaviour of 1,2-dibromocyclohexane and 1,2-dichlorocyclooctane under these conditions is also examined. Various pieces of evidence are presented that suggest that these processes do not involve generation of free gas-phase radicals but rather surface-adsorbed organometallic species.

Pyrolytic processes in organic chemistry normally involve either fragmentation or rearrangement. The thermal generation of species such as radicals or carbenes may be followed by dimerisation but their high reactivity frequently leads to other competing processes. In order to develop a general method for C–C bond formation in the gas phase we decided to examine the pyrolysis of organic halides over solid magnesium. Despite its clear advantages as a method of “clean synthesis”, there has been little previous work on gas phase pyrolysis over solid metals in contrast to pyrolysis over solid bases which has been used effectively by Denis and coworkers.<sup>1</sup> Dehydrofluorination of alicyclic precursors over iron or nickel has been used to obtain fluorinated benzenes<sup>2</sup> and heterocycles<sup>3</sup> and pyrolysis of hexachlorocyclopentadiene over iron results in C–C bond formation to give perchlorofulvalene.<sup>4</sup> The few studies using other metals have all involved the generation of highly reactive species for spectroscopic detection. Thus, benzocyclobutadiene was first generated by flash vacuum pyrolysis (FVP) of diiodobenzocyclobutene over zinc at 230 °C<sup>5</sup> and can alternatively be formed by FVP of  $\alpha,\alpha,\alpha',\alpha'$ -tetrabromo-*o*-xylene over magnesium at 440–470 °C,<sup>6</sup> while FVP of PXCl<sub>3</sub> (X = O, S) over silver at 880 °C leads to generation of the reactive P(III) species, Cl–P=X,<sup>7</sup> and FVP of trichloroacetyl chloride over zinc at 420 °C gives dichloro ketene.<sup>8</sup> We report here that FVP of organic halides over freshly resublimed magnesium at 600 °C provides a versatile and preparatively useful method for C–C bond formation.<sup>9</sup>

## Results and discussion

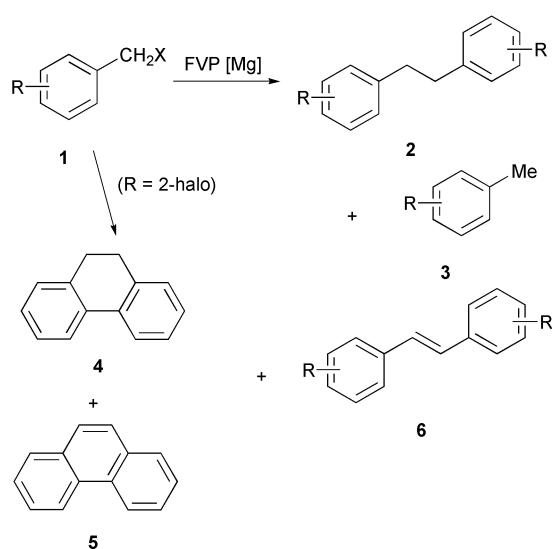
Initial experiments using benzyl chloride established that for maximum activity the magnesium had to be used in the range 500–700 °C and was best prepared by freshly subliming the metal over the surface of glass wool. Careful observation of the inside of the furnace during this process revealed an initial vigorous reaction on the wool with formation of blue–grey magnesium silicide, but this was subsequently covered by magnesium and is not thought to play a significant part in the reactions. It did however have important implications during disposal of the used furnace packing in dilute acid when there was spontaneous ignition of the gases evolved due to low molecular weight silanes formed by hydrolysis of the magnesium silicide. FVP of benzyl chloride through the system at 600 °C gave a liquid in the cold-trap which proved to be toluene (16%) and a solid at the furnace exit which was mostly bibenzyl (58%) together with stilbene (4%) and diphenylmethane (6%). Benzyl bromide gave the same products with bibenzyl being obtained in 69% yield. By using an excess of benzyl chloride it was established that approximately 20% of the magnesium used was available for reaction assuming conversion to MgCl<sub>2</sub>. It should be noted that FVP of the benzyl halides under these conditions without magnesium gave no reaction. The products obtained here are to be contrasted with those from flow pyrolysis of benzyl chloride under the much more severe conditions of 650 °C at atmospheric pressure under nitrogen which gave toluene (5%), bibenzyl (14%), stilbene (30%) and anthracene (40%).<sup>10</sup>

**Table 1** Pyrolysis of benzylic halides over magnesium at 600 °C

R	X	Pressure/Torr	Pyrolysis products yield (%)					Other products	
			2	3	4	5	6		
<b>1a</b>	H	Cl	$1.0 \times 10^{-1}$	58	16	—	—	4	Diphenylmethane (6%)
<b>1b</b>	H	Br	$2.0 \times 10^{-1}$	69	20	—	—	2	Diphenylmethane (1%)
<b>1c</b>	2-Me	Br	$1.5 \times 10^{-1}$	70	20	—	—	1	Benzocyclobutene (3%)
<b>1d</b>	4-Me	Cl	$6.0 \times 10^{-1}$	60	23	—	—	2	Di(4-methylphenyl)methane (3%)
<b>1e</b>	2-F	Cl	$2.0 \times 10^{-2}$	73	7	4	—	—	Toluene (5%)
			1.0	50	4	5	9	10	Toluene (5%)
<b>1f</b>	2-F	Br	$4.0 \times 10^{-2}$	80	11	3	—	—	Toluene (4%)
			1.1	51	10	11	8	—	Stilbene (8%), toluene (8%)
<b>1g</b>	3-F	Cl	$7.6 \times 10^{-2}$	49	15	—	—	—	3-Fluorobibenzyl (5%), bibenzyl (5%)
			1.1	59	19	—	—	2	Bibenzyl (5%)
<b>1h</b>	3-F	Br	$1.3 \times 10^{-2}$	67	12	—	—	5	3-Fluorobibenzyl (2%), bibenzyl (3%)
			$8.0 \times 10^{-1}$	59	19	—	—	2	Bibenzyl (5%)
<b>1i</b>	4-F	Cl	$7.0 \times 10^{-2}$	63	5	—	—	—	Toluene (6%), bibenzyl (2%), 4-fluorobibenzyl (5%)
			1.0	58	22	—	—	5	Bibenzyl (2%), 4-fluorobibenzyl (4%)
<b>1j</b>	4-F	Br	$3.5 \times 10^{-2}$	53	23	—	—	—	Bibenzyl (2%), 4-fluorobibenzyl (3%)
			1.0	73	12	—	—	—	Toluene (5%), bibenzyl (1%), 4-fluorobibenzyl (6%)
<b>1k</b>	2-Cl	Cl	$7.0 \times 10^{-3}$	69	23	—	—	—	Toluene (2%)
			$6.5 \times 10^{-1}$	25	15	6	1	—	Toluene (2%), bibenzyl (1%)
<b>1l</b>	4-Cl	Cl	$1.8 \times 10^{-1}$	37	5	—	—	1	Toluene (4%), bibenzyl (6%), stilbene (6%), 4-chlorobibenzyl (4%)
			4.8	10	6	—	—	—	Toluene (12%), bibenzyl (22%), stilbene (12%)
<b>1m</b>	2-Br	Br	$2.0 \times 10^{-2}$	51	24	2	6	—	Toluene (2%), bibenzyl (3%)
			$8.0 \times 10^{-1}$	22	12	21	17	—	Toluene (10%), bibenzyl (2%), 2-bromobibenzyl (2%)
<b>1n</b>	4-Br	Br	$8.0 \times 10^{-3}$	43	28	—	—	—	—
			1.2	—	—	—	—	—	Toluene (14%), stilbene (2%), bibenzyl (38%)
<b>1o</b>	2-I	Cl	$2.5 \times 10^{-2}$	40	11	16	6	—	Bibenzyl (10%), 2-iodobibenzyl (4%), 2-iodostilbene (6%)
			$6.0 \times 10^{-1}$	40	1	31	12	—	Bibenzyl (4%), 2-iodostilbene (3%)

The behaviour of benzyl chloride over calcium at 800 °C and zinc at 400 °C was then examined and proved to be rather surprising. In the first case only toluene (43%) and benzene (11%) were obtained while in the second the products were toluene (32%), bibenzyl (7%) and diphenylmethane (5%). The dependence of the products on the metal used indicates that the processes are unlikely to involve formation of radicals in the gas phase and we are perhaps dealing with surface-adsorbed organometallic species similar to those involved in reactions of highly activated metals in solution.<sup>11</sup> Why the reduction product toluene should be favoured over the coupling product bibenzyl when we move from magnesium to calcium or zinc is unclear.

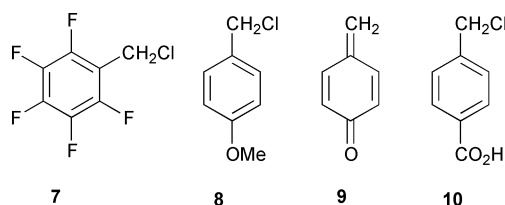
Once the optimum conditions had been established, the method was applied to a wide range of substituted benzyl halides **1** and, as shown in Table 1, this generally gave the substituted bibenzyls **2** in moderate to good yield. Other products, shown in Scheme 1, were the substituted toluenes **3** which were

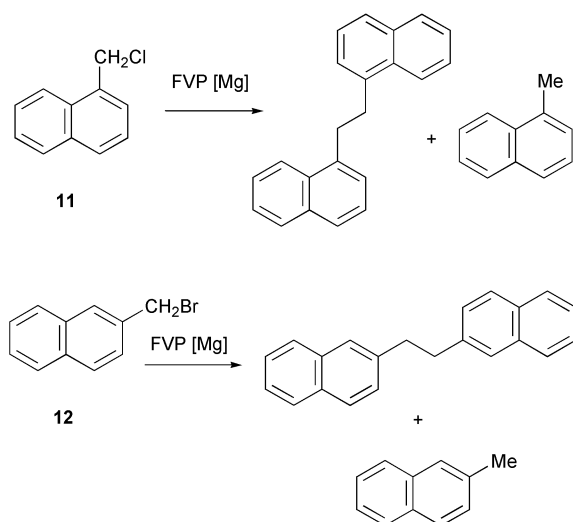
**Scheme 1**

formed in almost every case and stilbenes **6** together with 9,10-dihydroanthracene **4** and anthracene **5** which were formed by further dehalogenation where an *ortho* halogen substituent was present. The bibenzyl products **2** were obtained as solids at the furnace exit separate from many of the more volatile products which were collected in the cold trap. Recrystallisation of the solid gave the bibenzyls in pure form and this represents a convenient alternative to the classical Wurtz coupling and also newer methods employing tungsten reagents<sup>12</sup> and Rieke nickel.<sup>13</sup> The best yields were generally obtained by working at higher vacuum and by using a poorer vacuum (nitrogen leak) the formation of **4** and **5** was increased together with loss of halogen from the bibenzyl and stilbene products **2** and **6**. It is also clear from Table 1 that there is no great difference between the results for fluorobenzyl chlorides and the corresponding bromides.

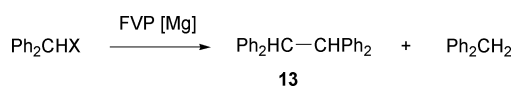
Pyrolysis of the pentafluorobenzyl chloride **7** also gave the decafluorobibenzyl (35%) together with pentafluorotoluene (23%). The behaviour of 4-methoxybenzyl chloride **8** was not so satisfactory with the corresponding bibenzyl only being formed in 14% yield and the major product being an insoluble polymer presumably derived from *p*-quinomethane **9**. The carboxylic acid **10** failed to give the expected coupling product and the products obtained were *p*-toluic acid (20%) together with toluene (5%) and *p*-xylene (2%). The two halomethylnaphthalenes behaved similarly to the benzyl halides **1**, with **11** giving the dinaphthylethane in 28% yield and 1-methylnaphthalene (67%) while **12** gave the isomeric dinaphthylethane (36%) and 2-methylnaphthalene (30%) (Scheme 2).

We now turned our attention to halodi- and halotri-phenylmethanes. Chlorodiphenylmethane gave tetraphenylethane **13**

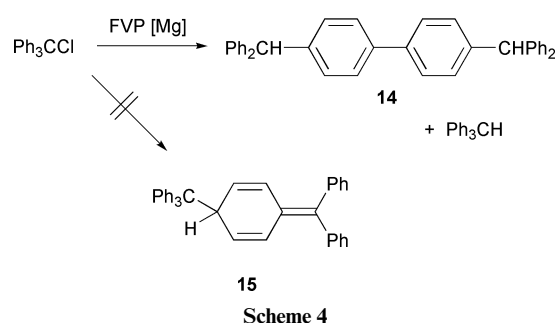




in 71% yield together with diphenylmethane (20%) while bromodiphenylmethane gave the same products in 61% and 19% yields, respectively (Scheme 3). Further evidence that these



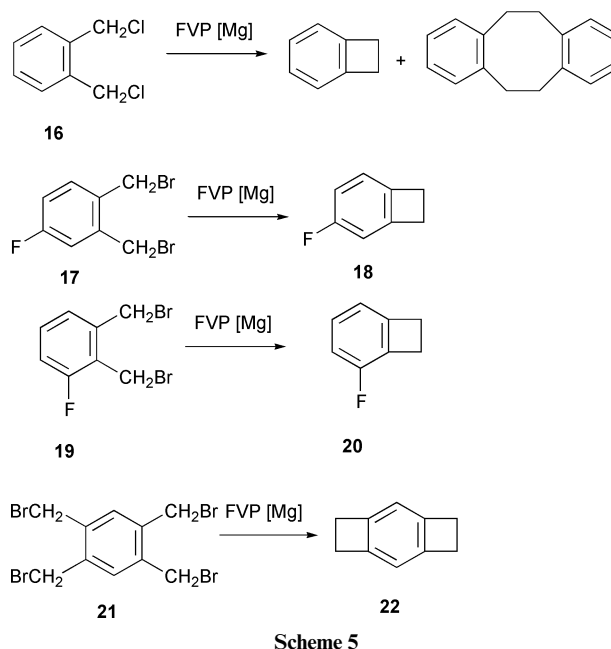
processes do not involve free gas phase radicals came from the result for chlorotriphenylmethane (Scheme 4). The products



in this case were triphenylmethane (39%) and a hydrocarbon (46%) identified as the bis(diphenylmethyl)biphenyl **14**. There was no trace of the dimer **15** formed in solution from triphenylmethyl radicals.<sup>14</sup> It is interesting to note that the product **14** has been obtained in solution by dimerisation of triphenylmethyl cations,<sup>15</sup> and under conditions where hydrogen atom mobility is possible and thermodynamically stable products are favoured, we are perhaps reaching the minimum on the C<sub>2</sub>Ph<sub>6</sub> energy surface.

The very low yield of benzocyclobutene formed from  $\alpha$ -bromo-*o*-xylene **1c** contrasts with the behaviour of such substrates upon FVP under more severe conditions (>700 °C) without magnesium present where the benzocyclobutene is formed as the major product in a process involving 1,4-loss of HX to give an *o*-xylylene intermediate.<sup>16</sup> Pyrolysis of aromatic substrates bearing *ortho* Me and CH<sub>2</sub>X groups has been used to obtain a variety of substituted benzocyclobutenes,<sup>17</sup> benzodicyclobutene,<sup>18</sup> and most famously [6]radialene,<sup>19</sup> and this is a standard method for preparation of benzocyclobutenes,<sup>20</sup> and thus the related cyclophanes.<sup>21</sup> It is important to note however that pyrolysis in the absence of magnesium results only in loss of HCl and so for example  $\alpha,\alpha'$ -dichloro-*o*-xylene **16**

gives chlorobenzocyclobutene.<sup>22</sup> In contrast, FVP of **16** over magnesium resulted in efficient dehalogenation to give benzocyclobutene in 73% yield together with *o*-xylene (15%) and only a trace of the dibenzocyclooctene (Scheme 5). To illustrate the



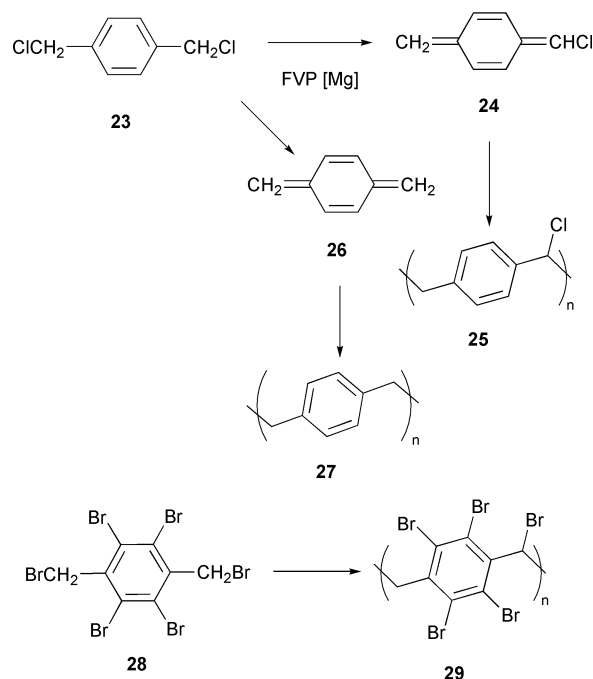
usefulness of this method for benzocyclobutene synthesis we prepared the fluorinated dibromides **17** and **19**. In a literature report,<sup>23</sup> these were converted into the benzocyclobutenes **18** and **20** in a three-step procedure involving reaction with sodium sulfide to give the dihydrobenzothiophenes, oxidation to the corresponding sulfones and then extrusion of SO<sub>2</sub> using FVP. Subjecting the dibromides to FVP over magnesium gave the same products **18** (80%) and **20** (77%) directly in one step together with 8% of the fluorinated *o*-xylenes in each case from reduction. In a similar way the tetrabromide **21** gave benzodicyclobutene ‡ **22** in 47% yield.

We saw an opportunity to apply this method to polymer formation. FVP of  $\alpha,\alpha'$ -dichloro-*p*-xylene **23** over magnesium was initially found to give a polymer which gave elemental analysis data roughly corresponding to those expected for the structure **25** formed from polymerisation of **24** (Scheme 6). By increasing the amount of magnesium used, a second polymer could be obtained which was essentially chlorine free and corresponds to polymer **27** formed from *p*-xylylene **26**. Although both polymers were insoluble, solid state NMR analysis of **27** gave data in accord with expectation and allowed estimation of the molecular weight as around 2200 from end-group analysis. Both polymers showed good thermal stability with **27** in particular being stable up to 520 °C in nitrogen. The ability to deposit a thin uniform film of inert polymer on a solid substrate from the gas phase may have some technological applications. Generation of **26** from gas-phase pyrolysis of [2.2]paracyclophane and its use to form thin films of **27** is used industrially,<sup>24</sup> and solution dehydrohalogenation of chlorinated *p*-xylenes has also been used to obtain polymers including **25**.<sup>25</sup>

There is considerable interest in preparing polymers with fire-retardant properties and in this context it is important to incorporate as much bromine as possible.<sup>26</sup> We therefore prepared the hexabromo-*p*-xylene **28** and found that FVP over magnesium gave poor results with part of the starting material recovered unchanged from the inlet accompanied by a polymer of indefinite composition. In contrast, FVP of **28** at 650 °C in

† The IUPAC name for benzocyclobutene is bicyclo[4.2.0]octa-1,3,5-triene.

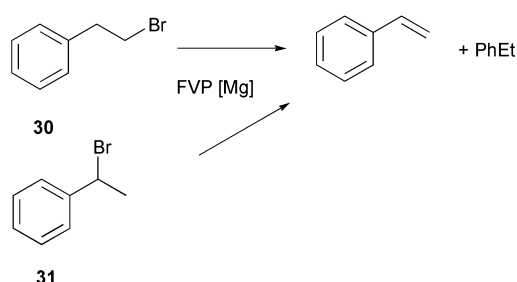
‡ The IUPAC name for benzodicyclobutene is tricyclo[6.2.0.0.3.6]deca-1,3(6),7-triene.



Scheme 6

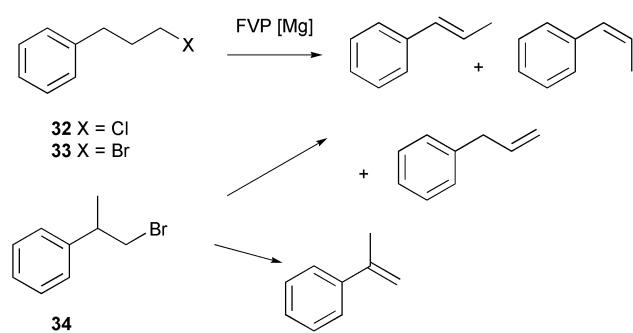
the absence of metal led to extrusion of elemental bromine and formation of a polymer at the furnace exit which gave elemental analysis data in good agreement with expectation for the pentabromo-*p*-xylylene polymer **29**.

Pyrolysis of other haloalkylbenzenes over magnesium was now examined. Both (2-bromoethyl)benzene **30** and (1-bromoethyl)benzene **31** were found to undergo clean elimination of HBr to give styrene in high yield together with ethylbenzene as a byproduct (Scheme 7). Similar elimination from (1,2-di-



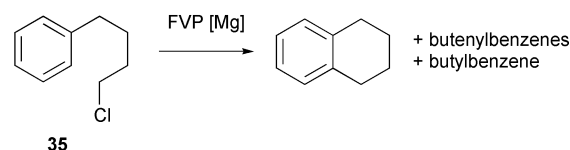
Scheme 7

chloroethyl)benzene to give  $\beta$ -chlorostyrene by pyrolysis over alumina at 360–400 °C was reported some time ago.<sup>27</sup> The halopropylbenzenes **32** and **33** also underwent elimination of HX but this was accompanied by isomerisation of the initially formed allylbenzene to give the *E*- and *Z*-isomers of  $\beta$ -methylstyrene (Scheme 8). The formation of these products from static pyrolysis of **33** at 390–450 °C was previously



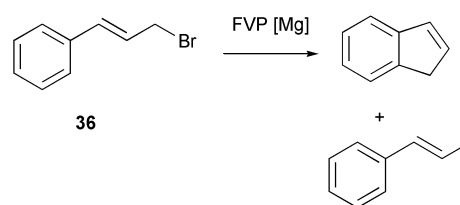
Scheme 8

observed in the course of a kinetic study.<sup>28</sup> FVP of 1-bromo-2-phenylpropane **34** rather surprisingly gave mainly the same three products together with  $\alpha$ -methylstyrene (14%). The ready isomerisation of the carbon skeleton which occurs under these conditions was also found to occur, although to a lesser extent, upon solution reaction of **34** with Mg–CoBr<sub>2</sub>.<sup>29</sup> Further information on the equilibration of these products under the conditions involved was obtained by FVP of  $\alpha$ -methylstyrene,  $\beta$ -methylstyrene and allylbenzene over magnesium at 600 °C. The  $\alpha$ -methylstyrene was recovered unchanged,  $\beta$ -methylstyrene showed 14% conversion into allylbenzene and allylbenzene showed 86% conversion into  $\beta$ -methylstyrene. This indicates that migration of the double bond into conjugation is highly favoured but the skeletal rearrangement for **34** must occur at the stage of the reactive intermediate rather than the final hydrocarbon product. With the chlorobutylbenzene **35** (Scheme 9) the expected mixture of isomeric butenylbenzenes



Scheme 9

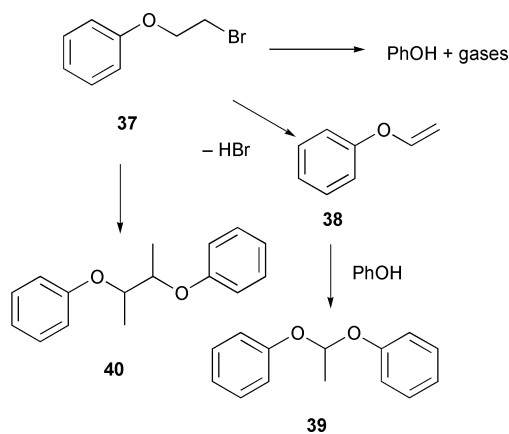
and butylbenzene (54%) was accompanied by tetrahydronaphthalene (36%). There was also a trace amount of styrene and the yield of this product was markedly increased by carrying out the pyrolysis at higher pressure, the more severe conditions apparently favouring fragmentation of the intermediate with loss of ethene. Cyclisation was also observed for cinnamyl bromide **36** (Scheme 10) which gave indene (48%) together with  $\beta$ -methylstyrene (12%).



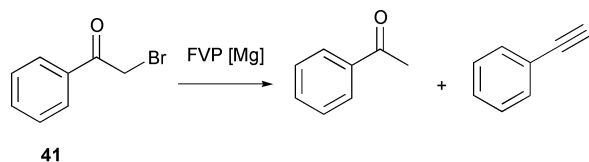
Scheme 10

The bromoethyl phenyl ether **37** gave rather unexpected products: phenol (36%), 1,1-diphenoxyethane **39** (13%), acetaldehyde (5%) and the diphenoxybutane **40** (9%). Pyrolysis of **39**, readily prepared by reaction of phenol with phenyl vinyl ether **38**, under the same conditions led to elimination to give phenol (57%) and **38** (30%) together with benzaldehyde (27%). It was shown that **38** is unreactive under the pyrolysis conditions and indeed even allyl phenyl ether requires a temperature of 950 °C for complete dissociation to phenoxyl and allyl radicals.<sup>30</sup> We interpret these findings in terms of the process shown in Scheme 11 where **37** breaks down partly by elimination of phenol and partly by loss of HBr to give **38** which is then efficiently trapped by phenol (this is literature method for preparation of **39**), perhaps in the cold trap, to give **39**. The formation of **40** is attributed to isomerisation by a 1,2-hydrogen shift in the reactive intermediate formed from **37** by loss of the bromine atom followed by dimerisation. The isomeric 1-bromoethyl phenyl ether which might be expected to lead to **40** is reported to be unstable and decomposes rapidly in moist air to give a polymer.<sup>31</sup>

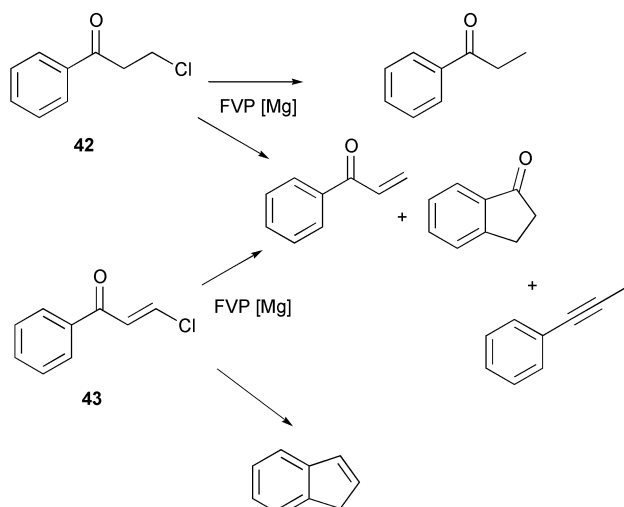
The next group of substrates to be examined were haloalkyl phenyl ketones (Scheme 12). With  $\alpha$ -bromoacetophenone **41** the products were acetophenone (42%), phenylacetylene (31%) and styrene (6%). The formation of acetophenone provides further evidence for the non-involvement of radicals since pyrolysis of  $\alpha$ -iodoacetophenone at 500 °C in the absence of a metal is



Scheme 11



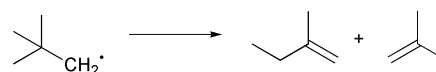
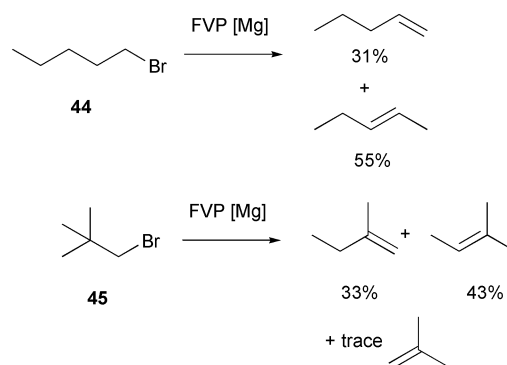
41



Scheme 12

known to produce phenacyl radicals but these rapidly rearrange with loss of CO to give benzyl radicals.<sup>32</sup> The formation of phenylacetylene shows for the first time that the magnesium has deoxygenating as well as dehalogenating ability although the nature of the metal-adsorbed intermediate involved in forming this product is unclear. As might be expected, elimination of HCl was the main process observed for  $\beta$ -chloropropiophenone **42** giving acrylophenone in 64% yield but this was accompanied by propiophenone (10%) from reduction, indanone (11%) from the alternative loss of HCl with cyclisation, and finally phenylpropyne (5%) from deoxygenation. The major products from the  $\alpha,\beta$ -unsaturated haloketone **43** were mostly the same as for **42**: indanone (20%), acrylophenone (4%) and phenylpropyne (5%), but these were accompanied now by indene (15%) showing another aspect to the reductive capability of magnesium under these conditions.

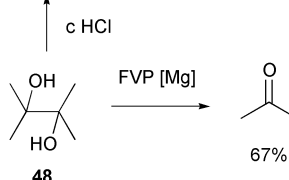
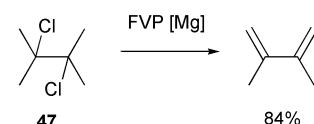
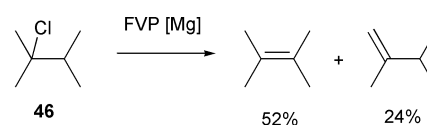
Turning now to aliphatic halides, the simple primary halide 1-bromopentane **44** was first examined and this cleanly lost HBr to give a mixture of pent-1-ene and the more thermodynamically stable isomer pent-2-ene. It was of interest to examine a halide in which direct elimination of HX is impossible and neopentyl bromide **45** was found to give 2-methylbut-1-ene and 2-methylbut-2-ene as the major products together with a small amount of 2-methylpropene. Comparison with the products from both neopentyl radical<sup>33</sup> and the



Scheme 13

carbene neopentylidene<sup>34</sup> under similar conditions (Scheme 13) indicates that neither of these can be intermediates in the skeletal rearrangement involved here and we believe that this may be a surface-adsorbed organometallic species.

For the tertiary halide **46**, elimination of HCl again occurred to give mainly the more stable 2,3-dimethylbut-2-ene with less of the isomeric 2,3-dimethylbut-1-ene favoured statistically. The clean conversion of the dichloride **47** readily obtained from pinacol **48** into 2,3-dimethylbutadiene in good yield is of synthetic interest since the value of this product is approximately ten times that of **48** (Scheme 14). Pinacol itself readily under-



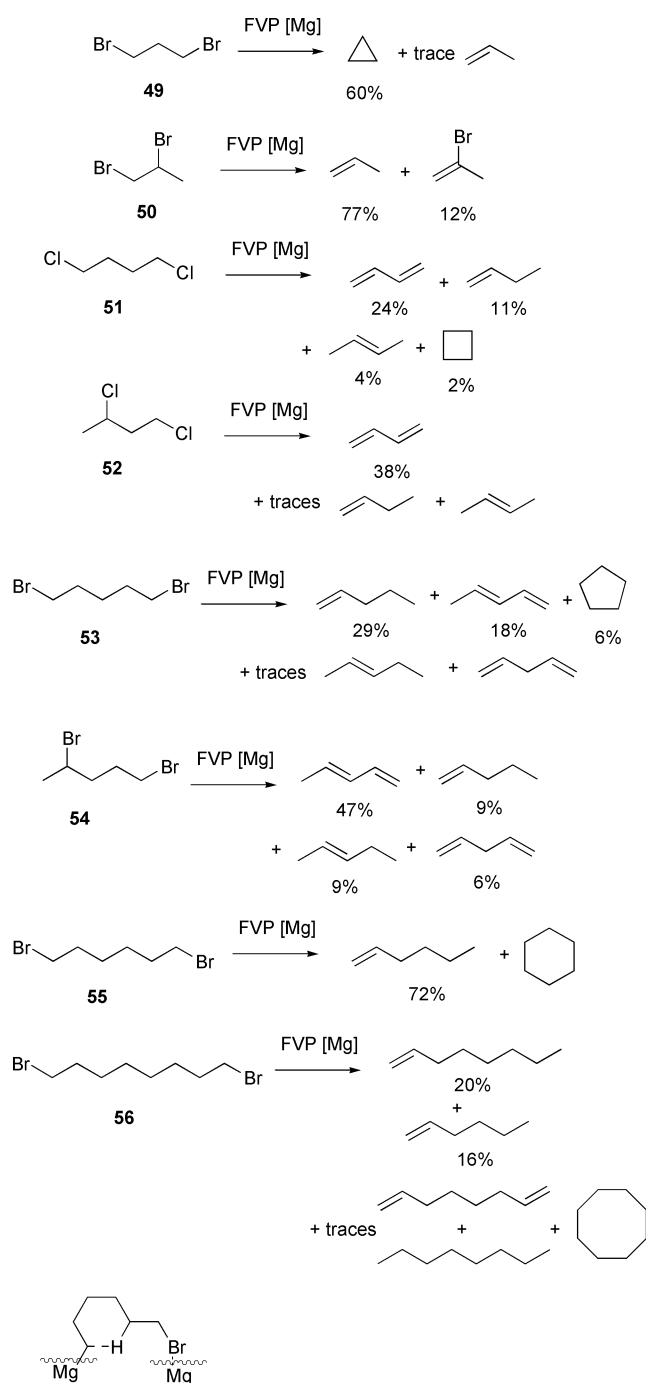
Scheme 14

goes dehydration to give dimethylbutadiene upon pyrolysis over alumina<sup>35</sup> or copper.<sup>36</sup> It was therefore unexpected to find that under our conditions efficient oxidative cleavage to give acetone occurred.

The thermal decomposition of a variety of 1,2- and 1,3-dichloroalkanes over the range 100–300 °C is reported to result in loss of one molecule of HCl to give isomeric mixtures of chloroalkenes.<sup>37</sup> In a recent detailed study,<sup>38</sup> dehydrochlorination of 1,2-dichloropropane both by pyrolysis and laser-induced dielectric breakdown was also found to give isomeric chloropropenes by either radical or concerted elimination mechanisms depending on the temperature. In contrast to this, pyrolysis over magnesium was found to result in complete dehalogenation to give mainly hydrocarbons. With



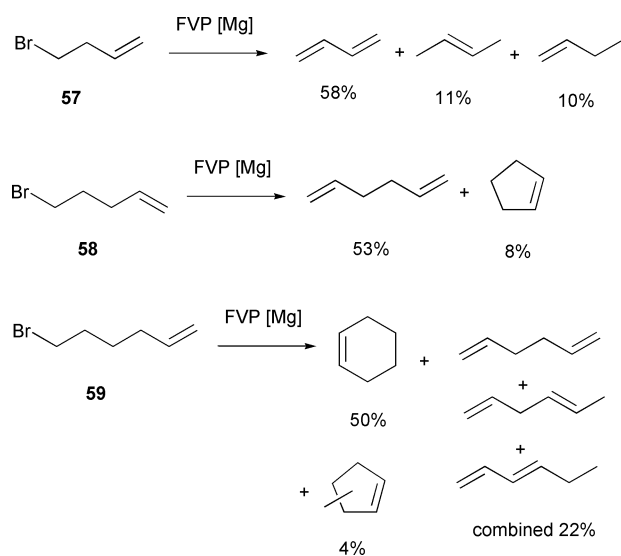
1,3-dibromopropane **49** the main product was found to be cyclopropane together with a small amount of propene. The isomeric 1,2-dibromopropane **50** gave mainly propene together with a low yield of 2-bromopropene. Examination of higher aliphatic dihalides revealed a rather interesting pattern of behaviour. Cyclisation of  $\alpha,\omega$ -dihalides to give cycloalkanes as observed for **49** is only a minor process for **51**, **53**, **55** and **56**. Besides double HX elimination to give isomeric dienes, loss of  $X_2$  with rearrangement to give alk-1-enes (perhaps the process which led to propene from **49**) becomes increasingly important until for 1,6-dibromohexane **55** it affords hex-1-ene in 72% yield. We believe that this may involve a mechanism (Scheme 15)



in which initial loss of bromine from one end of the chain gives a magnesium bound bromoalkyl group which transfers a proton *via* a cyclic transition state at the same time as the second bromine is lost. Two carbon degradation presumably with loss of ethene results in formation of some hex-1-ene from 1,8-

dibromooctane **56**. A combination of double elimination of HX to give dienes and loss of  $X_2$  to give alkenes is also observed for 1,3-dichlorobutane **52** and 1,4-dibromopentane **54** with no cyclic products in these cases.

A series of  $\omega$ -bromoalk-1-enes **57–59** was now examined, both to clarify their possible intermediacy in the reaction of the dihalides and to look for possible cyclisation of the intermediates. FVP of 4-bromobut-1-ene **57** led mainly to elimination of HBr to afford butadiene together with isomeric butenes. The result for the homologue 5-bromopent-1-ene **58** was rather surprisingly indicative of pent-4-enyl radical involvement since this species is known<sup>39</sup> to both cyclise to cyclopentyl and degrade by loss of ethene to give the stable allyl radical which could then dimerise to give the observed major product hexa-1,5-diene. However this may simply be a coincidence and the actual magnesium bound intermediate may just happen to react in the same way. Clearer evidence that this is the case comes from the behaviour of 6-bromohex-1-ene **59** which gave cyclohexene as the main product together with isomeric hexadienes and only 4% of a product potentially derived from cyclopentylmethyl radical. The rapid cyclisation of hex-5-enyl radical to give overwhelmingly cyclopentylmethyl derived products is well known<sup>40</sup> and suggests that such an intermediate is not involved here (Scheme 16).



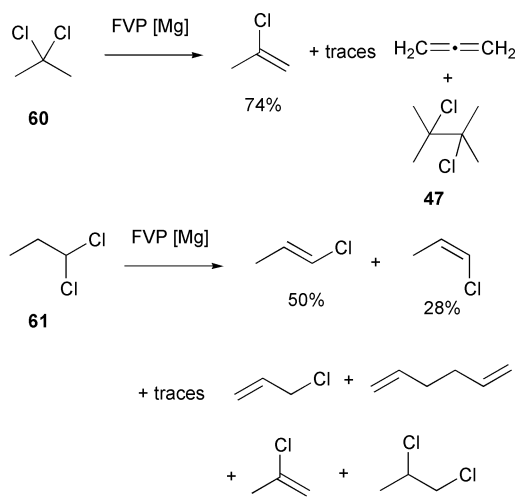
Pyrolysis of trihalomethanes generally results in dehydrohalogenation to give dihalocarbenes and this method has been used synthetically.<sup>41</sup> Gas phase pyrolysis of 1,1-dichloroalkanes in the range 390–460 °C results in elimination of HCl to give 1-chloroalkenes<sup>42</sup> and a similar process is observed in molten ionic salt mixtures.<sup>43</sup> FVP of 2,2-dichloropropane **60** and 1,1-dichloropropane **61** over magnesium also led to elimination of HCl to give the corresponding chloropropenes as the major products (Scheme 17). The recently published <sup>1</sup>H NMR spectrum for *Z*-1-chloropropene<sup>44</sup> allowed the *E* and *Z* isomers to be distinguished and the major isomer identified as *E*. Minor products in the first case were a small amount of allene from further HCl elimination and product **47** from dehalogenative coupling while, in the second, traces of isomeric chloropropenes, dichloropropane and hexa-1,5-diene were formed.

FVP of 1,1-dichloroalkanes **62–64** gave an unexpected result. The products were liquids which showed a highly consistent pattern of <sup>13</sup>C NMR signals consistent with *E,E*-, *E,Z*- and *Z,Z*- isomers being present. In the cases of **63** and **64** small amounts of the terminal alkynes were also formed. The main products were initially assumed to be those expected from elimination of HCl followed by dehalogenative coupling *i.e.* the conjugated octa-, deca- and dodecadienes. However

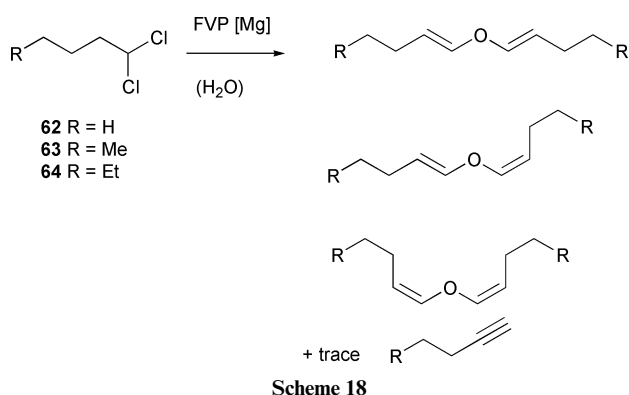
**Table 2** Characterisation of substituted bibenzyls 2

R	Mp/°C	Lit. mp/°C	Ref.	$\delta_{\text{H}}$ CH <sub>2</sub>	Aromatic	$\delta_{\text{C}}$		<i>m/z</i>	
						CH <sub>2</sub>	aromatic		
<b>2c</b>	2-Me <sup>a</sup>	66–67	65	57	2.88	7.25	34.1	126.0, 126.1, 128.8, 130.2, 135.9 (C-2), and 140.1 (C-1)	210
<b>2d</b>	4-Me <sup>b</sup>	81–83	82	58	2.91	7.20	37.6	128.3 (4 C), 129.0 (4 C), 135.3 (C-4) and 138.8 (C-1)	210
<b>2e</b>	2-F <sup>c</sup>	39–40	40–41	59	3.00	7.0–7.4	29.7	115.2 (d, <i>J</i> 22, C-3), 123.9 (d, <i>J</i> 3, C-5), 127.8 (d, <i>J</i> 8, C-4), 128.3 (d, <i>J</i> 24, C-1), 130.7 (d, <i>J</i> 5, C-6) and 161.2 (d, <i>J</i> 245, C-2)	218
<b>2g</b>	3-F <sup>d</sup>	32–34	34–35	59	2.97	6.9–7.5	37.2	112.9 (d, <i>J</i> 21, C-4), 115.3 (d, <i>J</i> 21, C-2), 124.1 (d, <i>J</i> 2, C-6), 129.8 (d, <i>J</i> 8, C-5), 143.8 (d, <i>J</i> 7, C-1) and 162.9 (d, <i>J</i> 245, C-3)	218
<b>2i</b>	4-F <sup>e</sup>	92–93	90	59	2.92	7.0–7.25	37.1	115.1, (d, <i>J</i> 21, C-3, C-5), 129.8 (d, <i>J</i> 8, C-2, C-6), 137.0 (C-1) and 161.4 (d, <i>J</i> 244, C-4)	218
<b>2k</b>	2-Cl	61–62	62	60	3.10	7.2–7.6	33.8	126.7, 127.5, 129.5, 130.6, 134.0 (4ry) and 139.0 (4ry)	250/252/254
<b>2l</b>	4-Cl	100–101	101	60	2.86	<sup>f</sup>	37.0	128.4 (4 C), 129.8 (4 C), 131.7 (4ry) and 139.6 (4ry)	250/252/254
<b>2m</b>	2-Br	84–86	83–84	61	3.10	7.05–7.75	36.4	124.5 (C-2), 127.4, 127.8, 130.6, 132.8 and 140.5 (C-1)	338/340/342
<b>2n</b>	4-Br	117–118	114	62	2.90	<sup>g</sup>	37.0	119.8 (C-4), 130.2 (4 C), 131.4 (4 C) and 140.1 (C-1)	338/340/342
<b>2o</b>	2-I	102–103	102	63	3.04	<sup>h</sup>	41.8	101.2 (C-2), 128.5, 128.9, 130.3, 140.0 and 144.2 (C-1)	434
<i>i</i>	—	109–110	108	55	3.07	—	21.9	112.9 (2 C, t, <i>J</i> 32, C-1), 138.2 (4 C, d of m, <i>J</i> 252), 140.9 (2 C, d of m, <i>J</i> 253, C-4) and 145.8 (4 C, d of m, <i>J</i> 244)	362

<sup>a</sup> Me  $\delta_{\text{H}}$  2.35;  $\delta_{\text{C}}$  19.3. <sup>b</sup> Me  $\delta_{\text{H}}$  2.34;  $\delta_{\text{C}}$  21.0. <sup>c</sup>  $\delta_{\text{F}}$  –92.1 (d of t, *J* 9, 5). <sup>d</sup>  $\delta_{\text{F}}$  –86.6 (t of d, *J* 10, 6). <sup>e</sup>  $\delta_{\text{F}}$  –90.6 (t of t, *J* 9, 6). <sup>f</sup> 7.04 and 7.22 (8 H, A<sub>2</sub>B<sub>2</sub> pattern, *J* 9). <sup>g</sup> 7.10 and 7.50 (8 H, A<sub>2</sub>B<sub>2</sub> pattern, *J* 9). <sup>h</sup> 6.9–7.1 (2 H, m), 7.25–7.45 (4 H, m) and 7.9–8.1 (2 H, m). <sup>i</sup> 2,2',3,3',4,4',5,5',6,6'-Decafluorobibenzyl,  $\delta_{\text{F}}$  –117.7 (4 F, d of d, *J* 21, 8), –129.2 (2 F, t, *J* 21) and –135.5 (4 F, t of d, *J* 21, 8).



comparison with the available <sup>1</sup>H and <sup>13</sup>C NMR data for the various isomers of octa-3,5-diene,<sup>45</sup> deca-4,6-diene<sup>46</sup> and dodeca-5,7-diene<sup>47</sup> showed that the products obtained here had a much greater polarisation of the double bonds than would be expected for a hydrocarbon. Examination of the mixtures by GCMS showed that the products had *m/z* 16 greater than expected and were in fact the dialkenyl ethers (Scheme 18). Once



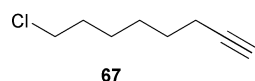
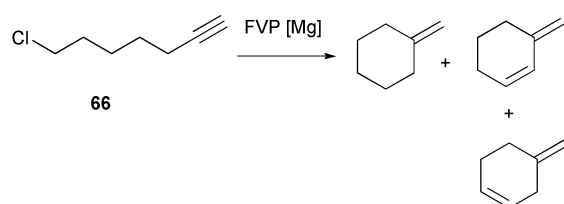
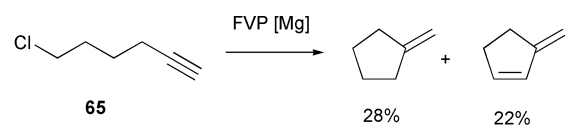
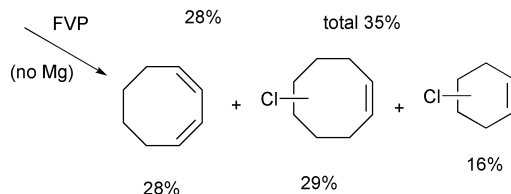
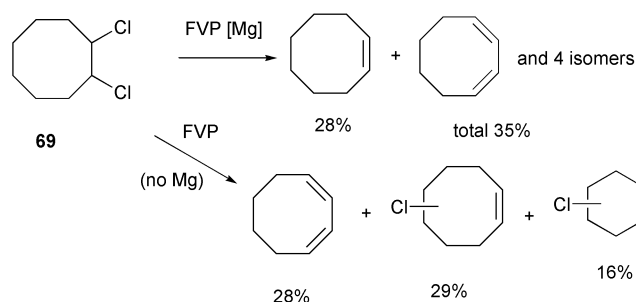
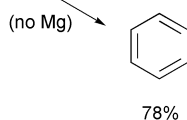
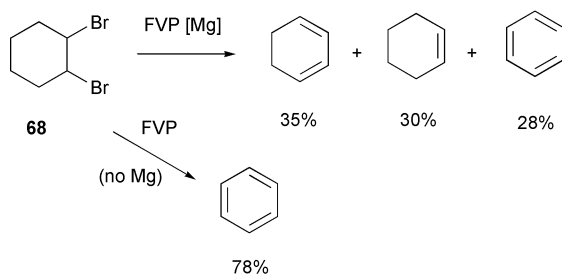
this was appreciated the <sup>1</sup>H and <sup>13</sup>C NMR data could be compared with those for the *E,Z*- and *Z,Z*-isomers of dipropenyl ether<sup>48</sup> and were found to be in excellent agreement. Because of the consistently unequal isomer ratio obtained in all three cases the data could be completely assigned (Table 3) although it should be noted that our assignment of the lower of the C-1 signals to the *E*-alkenyl group in the *E,Z*-isomer based on the consistently lower value for C-1 in the *E,E*-isomer than the *Z,Z*-isomer is clearly opposite to that for dipropenyl ether<sup>18</sup> and it is difficult to say which is correct. It appears likely that the rather moisture sensitive 1,1-dihaloalkanes, although freshly prepared from the corresponding aldehydes, have partly hydrolysed to give the  $\alpha,\alpha'$ -dichloroethers and FVP over magnesium has then resulted in elimination of HCl to give the alkenyl ethers. Treatment of the  $\alpha,\alpha'$ -dichloroethers with *N,N*-diethylaniline was used by Brandsma and Arens<sup>49</sup> to prepare dialk-1-enyl ethers including dibut-1-enyl and dipent-1-enyl ether but owing to the early date of the work no spectra were obtained. Other workers have claimed that  $\alpha$ -haloethers are highly unstable,<sup>31</sup> and although the synthesis here was clearly arrived at by accident, it may be preferable to attempting to isolate the  $\alpha,\alpha'$ -dichloroethers and then dehydrochlorinate them using a base.

The chloroalkynes **65** and **66** were now examined and in both cases cyclic products were formed: methylenecyclopentane and 3-methylenecyclopentene from **65** and methylenecyclohexane and 3- and 4-methylenecyclohexane from **66** (Scheme 19). It appears that cyclisation onto a triple bond is more readily achieved with this method than onto a double bond as for **48** and **49**. It seems unlikely that these reactions involve initial elimination of HCl to give enynes since pyrolysis of hex-1-en-5-yne which would be derived from **65** is known<sup>50</sup> to give equal quantities of 3- and 4-methylenecyclopentene under similar conditions and the latter was not formed here, and other products from the enyne such as methylcyclopentadienes and benzene were also absent. Perhaps not surprisingly the chloroalkyne **67** did not undergo cyclisation so easily and gave a very complex mixture of products which could not be identified.

In the hope of generating cyclic dienes or cycloalkenes, dibromocyclohexane **68** and dichlorocyclooctane **69** were also examined (Scheme 20). FVP of **68** over magnesium gave an almost equal mixture of cyclohexa-1,3-diene, cyclohexene and benzene. In contrast simple FVP of this substrate without

**Table 3** Yield and  $^{13}\text{C}$  NMR data for dialk-1-enyl ethers

Compound	Yield (%)	$\delta_{\text{C}}$ for <i>E</i> -alkenyl group						$\delta_{\text{C}}$ for <i>Z</i> -alkenyl group					
		C-1	C-2	C-3	C-4	C-5	C-6	C-1	C-2	C-3	C-4	C-5	C-6
<i>E,Z</i> -Diprop-1-enyl ether	—	144.9	104.1	12.2				142.5	102.8	9.3			
<i>Z,Z</i> -Diprop-1-enyl ether	—							143.7	102.8	9.3			
<i>E,E</i> -Dibut-1-enyl ether	38	142.6	110.5	17.6	14.3								
<i>E,Z</i> -Dibut-1-enyl ether	26	141.2	110.1	17.5	14.35			144.0	111.8	20.8	14.85		
<i>Z,Z</i> -Dibut-1-enyl ether	6							142.9	111.3	20.8	14.9		
<i>E,E</i> -Dipent-1-enyl ether	39	142.9	108.1	25.95	22.6	13.4							
<i>E,Z</i> -Dipent-1-enyl ether	25	141.5	107.7	25.9	23.3	13.3		144.3	109.4	29.4	23.2	13.2	
<i>Z,Z</i> -Dipent-1-enyl ether	6							143.3	108.9	29.4	22.0	13.35	
<i>E,E</i> -Dihex-1-enyl ether	31	143.0	108.7	31.8	23.7	22.3	13.8						
<i>E,Z</i> -Dihex-1-enyl ether	23	141.5	108.2	31.9	27.1	22.1	13.8	144.4	109.9	32.6	27.1	22.1	13.8
<i>Z,Z</i> -Dihex-1-enyl ether	6							143.3	109.5	32.5	31.3	22.5	14.0

**Scheme 19****Scheme 20**

magnesium led to complete loss of HBr and aromatisation giving only benzene. This is in contrast to the action of heat on **68** in the condensed phase which gave a 25% yield of the 1,3-diene.<sup>51</sup> The results for **69** were less satisfactory and the situation was improved to some extent by lowering the temperature to 500 °C when cyclooctene together with isomeric cyclooctadienes were obtained. By way of comparison FVP at 600 °C without magnesium led to only partial loss of HCl so that cycloocta-1,3-diene was accompanied by chlorinated cyclooctenes and chlorocyclohexene, while at 500 °C without magnesium mainly chlorocyclooctenes were obtained. The

formation of six carbon products is not surprising in view of the ready thermal ring opening of cyclooctene which has been reported.<sup>52</sup>

## Experimental

Melting points were recorded on a Kofler hot-stage microscope and are uncorrected. NMR spectra were obtained for  $^1\text{H}$  at 80 MHz using a Bruker WP80 instrument or at 300 MHz using a Bruker AM300 instrument, for  $^{13}\text{C}$  at 75 MHz using a Bruker AM300 instrument and for  $^{19}\text{F}$  at 75 MHz using a Bruker WP80 instrument. All spectra were run in solutions in  $\text{CDCl}_3$  unless otherwise stated with internal  $\text{Me}_4\text{Si}$  as reference for  $^1\text{H}$  and  $^{13}\text{C}$  and  $\text{CFCl}_3$  for  $^{19}\text{F}$ . Chemical shifts are reported in ppm to high frequency of the reference and coupling constants  $J$  are in Hz; 4ry means quaternary. Solid state CP-MAS  $^{13}\text{C}$  NMR spectra were obtained at 125 MHz on a Bruker MSL 500 spectrometer. Mass spectra were obtained on an A. E. I. MS-902 spectrometer using electron impact at 70 eV. GCMS was carried out using a Hewlett Packard 5890A coupled to a Finnigan-Incos 50 mass spectrometer. Thermogravimetric analysis was conducted using a Perkin Elmer Series 7 thermal analysis system over the temperature range 30–900 °C.

## General procedure for pyrolysis over magnesium

The apparatus used was as described previously.<sup>53</sup> The pyrolyses were conducted at 600 °C unless otherwise stated and at pressures in the range  $10^{-2}$ – $10^{-1}$  Torr. The appropriate quantity (generally 1–2 g) of Grignard grade magnesium turnings was placed in the centre of the pyrolysis tube sandwiched between two loosely packed plugs of glass wool. The system was connected up as normal except that a stopper was used in place of the inlet tube, and the pyrolysis tube was briefly heated to 650–700 °C until the magnesium was observed to sublime evenly over the surface of the glass wool. The furnace was then cooled to the pyrolysis temperature, the pump was isolated and the system cautiously refilled with dry nitrogen to atmospheric pressure. The stopper was then removed, the inlet tube containing the substrate attached (CAUTION: admission of air at this stage may lead to an explosion) and the pyrolysis continued as normal. In certain cases problems were encountered with volatile substrates passing through the furnace too rapidly even without heating the inlet tube. To overcome this, the normal horizontal inlet tube was replaced by a right-angled connector leading to a vertical test tube which could be cooled in ice or solid  $\text{CO}_2$  as necessary to control the rate of volatilisation.

After the pyrolysis was complete for the benzylic halides, the products were removed from the cold trap and analysed using the normal methods. In order to ensure that volatile products from the aliphatic halides were not lost,  $\text{CDCl}_3$  was added to the cold trap whilst it was still cooled in liquid nitrogen and only then was it allowed to warm up. In this way we have



previously found that even products as volatile as methane (bp  $-162\text{ }^{\circ}\text{C}$ ) and ethene (bp  $-104\text{ }^{\circ}\text{C}$ ) can be efficiently trapped and detected by NMR. The used pyrolysis tube was disposed of by cautiously placing it in a bath of 2 M HCl behind a safety shield (CAUTION: this may result in a vigorous reaction accompanied by spontaneous ignition of the small bubbles of pyrophoric gases evolved). All products were identified either by isolation in pure form or, where this was not possible, by comparison of  $^1\text{H}$  and/or  $^{13}\text{C}$  NMR and GCMS data with those for authentic samples. Yields of volatile or mixed products were determined by adding an accurately weighed amount of an internal standard, usually  $\text{CH}_2\text{Cl}_2$  and comparing  $^1\text{H}$  NMR integrals.

#### Pyrolysis of benzyl halides over magnesium, calcium and zinc

**Benzyl chloride 1a over magnesium.** FVP of the title compound (1.0 g,  $600\text{ }^{\circ}\text{C}$ ,  $1.0 \times 10^{-1}$  Torr, inlet  $25\text{ }^{\circ}\text{C}$ , 1.0 g magnesium) gave a liquid in the cold trap and a solid at the furnace exit. Analysis by  $^1\text{H}$  NMR showed that the liquid was toluene (16%) while the solid was mainly bibenzyl. GCMS showed that the solid also contained small amounts of stilbene (4%) and diphenylmethane (6%). Recrystallisation of the solid from ethanol gave pure bibenzyl (58%), mp  $52.5\text{--}53\text{ }^{\circ}\text{C}$  (lit.,<sup>54</sup>  $52\text{ }^{\circ}\text{C}$ ).

**Benzyl bromide 1b over magnesium.** FVP of the title compound (1.0 g) gave a liquid and a solid. Analysis by  $^1\text{H}$  NMR indicated that the liquid fraction was toluene (20%), while the solid fraction consisted of bibenzyl (69%), stilbene (2%) and diphenylmethane (1%). All compounds were further confirmed with authentic samples using GC (NPGS,  $170\text{ }^{\circ}\text{C}$ ). Pure bibenzyl, mp  $53\text{--}53.5\text{ }^{\circ}\text{C}$ , was obtained by recrystallisation of the solid product from methanol.

**Determination of available magnesium using excess benzyl chloride 1a.** FVP of benzyl chloride (3.1 g, 1.0 g magnesium) gave a mixture of solid and liquid as product. The  $^1\text{H}$  NMR integration indicated a 37% (1.16 g) recovery of starting material. Therefore the amount of reacted benzyl chloride was 15.3 mmol. Assuming 1 mole of magnesium reacts with 2 moles of benzyl chloride, for 1 g of Mg (41.1 mmol) therefore, the proportion of the magnesium available for reaction is about 20%.

**Benzyl chloride 1a over calcium.** In this case a temperature of  $850\text{--}900\text{ }^{\circ}\text{C}$  was used to sublime the metal over silica wool. FVP of the title compound (0.70 g,  $800\text{ }^{\circ}\text{C}$ , 4.0 g calcium) gave a liquid product which consisted of only toluene (43%), and benzene (11%).

**Benzyl chloride 1a over zinc.** In this case a temperature of  $425\text{--}450\text{ }^{\circ}\text{C}$  was used to sublime the metal over the glass wool. FVP of the title compound (0.60 g,  $400\text{ }^{\circ}\text{C}$ , 5.0 g zinc) gave a liquid product which consisted of toluene (32%), bibenzyl (7%) and diphenylmethane (5%).

#### Pyrolysis of substituted benzyl halides 1 over magnesium

The benzyl halides used are commercially available and were used without further purification except for 4-methoxybenzyl chloride and 2,3,4,5,6-pentafluorobenzyl chloride which were prepared from the corresponding benzyl alcohols by treatment with thionyl chloride.

**2,3,4,5,6-Pentafluorobenzyl chloride 7.** From 2,3,4,5,6-pentafluorobenzyl alcohol (80%) as a colourless liquid, bp  $50\text{ }^{\circ}\text{C}/1.0$  Torr (lit.,<sup>55</sup>  $156\text{--}157\text{ }^{\circ}\text{C}/750$  Torr);  $\delta_{\text{H}}$  4.60 (br s);  $m/z$  216/218 (3 : 1).

**4-Methoxybenzyl chloride 8.** From 4-methoxybenzyl alcohol

(76%) as a colourless liquid, bp  $90\text{ }^{\circ}\text{C}/0.5$  Torr (lit.,<sup>56</sup>  $116\text{--}120\text{ }^{\circ}\text{C}/15$  Torr);  $\delta_{\text{H}}$  3.70 (3 H, s), 4.50 (2 H, s) and 6.80 and 7.23 (4 H,  $\text{A}_2\text{B}_2$  pattern,  $J$  9).

Pyrolysis of substituted benzyl halides **1c–o** was carried out under a variety of conditions and the results are shown in Table 1. In each case the major product, the bibenzyl **2**, was obtained in pure form by recrystallisation of the solid fraction of the product. The characterisation of these is summarised in Table 2.

**4-Methoxybenzyl chloride 8.** FVP of the title compound (0.42 g) gave a product which consisted of a small amount of liquid and a larger solid fraction. The liquid contained mainly 4-methylanisole, 4-ethylanisole, *p*-cresol, toluene and anisole. The solid fraction was mainly an insoluble polymer, but the dichloromethane soluble part consisted mainly of 4,4'-dimethoxybibenzyl (14%) [ $\delta_{\text{H}}$  2.80 (4 H, s), 3.73 (6 H, s) and 6.75 and 6.95 (8 H,  $\text{A}_2\text{B}_2$  pattern,  $J$  9);  $m/z$  242], with small amounts of *p*-cresol (1%), 4,4'-dimethoxydiphenylmethane (1%) and 4,4'-dimethoxystilbene (1%).

**4-Chloromethylbenzoic acid 10.** FVP of the title compound (0.79 g) gave a liquid and a colourless solid. The liquid was mainly toluene (5%) with a trace of *p*-xylene (2%), while the solid was *p*-toluic acid (20%).

**1-(Chloromethyl)naphthalene 11.** FVP of the title compound (1.47 g) gave a liquid and a colourless solid. The liquid was 1-methylnaphthalene (67%) while the solid was 1,2-di(1-naphthyl)ethane (28%) [ $\delta_{\text{H}}$  3.60 (4 H, s) and 7.3–8.2 (14 H, m)].

**2-(Bromomethyl)naphthalene 12.** FVP of the title compound (0.42 g) gave a liquid and a colourless solid. The liquid was 2-methylnaphthalene (30%) while the solid was 1,2-di(2-naphthyl)ethane (36%) [ $\delta_{\text{H}}$  3.20 (4 H, s) and 7.3–8.0 (14 H, m)].

#### Pyrolysis of halodiphenylmethanes and chlorotriphenylmethane over magnesium

**Chlorodiphenylmethane.** FVP of the title compound (0.40 g) gave two solid fractions, one in the cold trap and the other at the furnace exit. The former was a mixture of diphenylmethane (20%) and 1,1,2,2-tetraphenylethane, while the latter was mainly 1,1,2,2-tetraphenylethane (total yield 71%). Recrystallisation of the second fraction from ethanol gave pure 1,1,2,2-tetraphenylethane **13**, mp  $214\text{ }^{\circ}\text{C}$  (lit.,<sup>64</sup>  $211\text{ }^{\circ}\text{C}$ );  $\delta_{\text{H}}$  4.77 (2 H, s) and 7.0–7.25 (20 H, m);  $\delta_{\text{C}}$  55.3, 124.8 (4 C, C-4), 127.1 (8 C), 127.5 (8 C) and 142.4 (4 C, C-1).

**Bromodiphenylmethane.** FVP of the title compound (0.14 g) gave the same product mixture as chlorodiphenylmethane, namely diphenylmethane (19%) and 1,1,2,2-tetraphenylethane **13** (61%).

**Chlorotriphenylmethane.** FVP of the title compound (2.0 g) gave a colourless solid which proved to be a mixture of triphenylmethane (39%) and 4,4'-bis(diphenylmethyl)biphenyl **14** (46%) [ $\delta_{\text{H}}$  5.04 (2 H, s), 7.05–7.4 (24 H, m) and 7.80 (4 H, d,  $J$  5);  $\delta_{\text{C}}$  54.3 ( $\text{Ph}_2\text{CH}$ ), 119.8 (4 C), 125.3 (4 C), 126.7 (4 C), 127.2 (8 C), 128.6 (8 C), 140.9 (2 C, 4ry), 141.5 (2 C, 4ry) and 147.8 (4 C, 4ry)].

#### Pyrolysis of substituted bis(halomethyl)benzenes over magnesium

The required halides were commercially available and were used without further purification except for  $\alpha,\alpha'$ -dibromo-4-fluoro-*o*-xylene,  $\alpha,\alpha'$ -dibromo-3-fluoro-*o*-xylene and  $\alpha,\alpha',2,3,5,6$ -hexabromo-*p*-xylene which were prepared as follows.

**$\alpha,\alpha'$ -Dibromo-4-fluoro-*o*-xylene 17.** Diazotisation of 4-amino-*o*-xylene with  $\text{NaNO}_2\text{--HCl}$  followed by reaction with  $\text{NaBF}_4$

and thermal decomposition of the diazonium tetrafluoroborate gave 4-fluoro-*o*-xylene (56%) as a colourless liquid, bp 60 °C/20 Torr (lit.,<sup>65</sup> 143–144 °C/730 Torr);  $\delta_{\text{H}}$  2.11 (6 H, br s) and 6.6–7.1 (3 H, m);  $\delta_{\text{C}}$  18.8, 19.7, 112.4 (d, *J* 21), 116.4 (d, *J* 21), 130.85 (d, *J* 8, C-6), 132.1 (d, *J* 3, C-1), 138.7 (d, *J* 7, C-2) and 161.6 (d, *J* 242, C-4); *m/z* 124.

Photochemical bromination of this product with bromine in  $\text{CCl}_4$  gave **17** (77%) as a colourless lachrymatory liquid which solidified with time, mp 61 °C (lit.,<sup>23</sup> 60 °C);  $\delta_{\text{H}}$  4.56 (2 H, s), 4.58 (2 H, s), 6.97 (1 H, m), 7.09 (1 H, m) and 7.32 (1 H, m);  $\delta_{\text{C}}$  29.0, 29.2, 116.2 (d, *J* 21), 117.8 (d, *J* 23), 132.3 (d, *J* 3, C-1), 132.8 (d, *J* 9, C-6), 138.8 (d, *J* 8, C-2) and 162.4 (d, *J* 250, C-4); *m/z* 280/282/284 (1 : 2 : 1).

**$\alpha,\alpha'$ -Dibromo-3-fluoro-*o*-xylene 19.** Diazotisation of 3-amino-*o*-xylene with  $\text{NaNO}_2\text{-HCl}$  followed by reaction with  $\text{NaBF}_4$  and thermal decomposition of the diazonium tetrafluoroborate gave 3-fluoro-*o*-xylene (47%) as a colourless liquid, bp 60 °C/20 Torr (lit.,<sup>23</sup> 58.5–60 °C/26 Torr);  $\delta_{\text{H}}$  2.10 (3 H, d, *J* 2), 2.18 (3 H, br s) and 6.8–7.1 (3 H, m);  $\delta_{\text{C}}$  10.6 (d, *J* 6, 2-Me), 19.5 (d, *J* 3, 1-Me), 112.7 (d, *J* 23, C-4), 123.6 (d, *J* 16, C-2), 125.3 (d, *J* 2, C-6), 126.5 (d, *J* 9, C-5), 139.2 (d, *J* 4, C-1) and 161.7 (d, *J* 243, C-3); *m/z* 124.

Photochemical bromination of this product with bromine in  $\text{CCl}_4$  gave **19** (84%) as a colourless lachrymatory liquid which solidified with time, mp 41–42 °C (lit.,<sup>66</sup> 41–42.5 °C);  $\delta_{\text{H}}$  4.73 (2 H, s), 4.81 (2 H, d, *J* 2) and 7.0–7.5 (3 H, m);  $\delta_{\text{C}}$  21.0 (d, *J* 7, 2- $\text{CH}_2$ ), 28.9 (d, *J* 3, 1- $\text{CH}_2$ ), 116.2 (d, *J* 22, C-4), 125.0 (d, *J* 15, C-2), 127.1 (d, *J* 3, C-6), 131.1 (d, *J* 10, C-5), 139.3 (C-1) and 161.7 (d, *J* 250, C-3); *m/z* 280/282/284 (1 : 2 : 1).

**$\alpha,\alpha',2,3,5,6$ -Hexabromo-*p*-xylene 28.** Photochemical bromination of 2,3,5,6-tetrabromo-*p*-xylene using bromine in  $\text{CCl}_4$  gave **28** (98%) as colourless crystals insoluble in conventional solvents, mp 271 °C (lit.,<sup>26</sup> 268–269 °C) (Found: C, 16.8; H, 0.6.  $\text{C}_8\text{H}_4\text{Br}_6$  requires C, 16.6; H, 0.7%);  $\delta_{\text{C}}$  (solid state) 42.0 (2  $\text{CH}_2$ ), 125.0 (4 C) and 145.0 (2 C); *m/z* 574/576/578/580/582/584/586 ( $\text{M}^+$ , 0.5/3/8/10/8/3/0.5%), 498/500 (82/83), 419 (100), 338 (15), 259 (18), 179 (5) and 98 (8).

**$\alpha,\alpha'$ -Dichloro-*o*-xylene 16.** FVP of the title compound (0.6 g) gave a liquid as the major product, with a small amount of semi-solid.  $^1\text{H}$  NMR and GCMS analysis of the liquid showed that it consisted of benzocyclobutene (73%), *o*-xylene (15%) and a trace of toluene. The small amount of semi-solid consisted of a complex mixture of dimeric products including 2,2'-dimethylbibenzyl, 2,2'-dimethylstilbene and 5,6,11,12-tetrahydrodibenzo[*a,e*]cyclooctene (total yield <5%).

**$\alpha,\alpha'$ -Dibromo-4-fluoro-*o*-xylene 17.** FVP of the title compound (1.27 g) gave a colourless liquid which consisted of 4-fluorobenzocyclobutene (80%) and 4-fluoro-*o*-xylene (8%). Kugelrohr distillation gave pure 4-fluorobenzocyclobutene **18**, bp 60 °C/20 Torr (lit.,<sup>67</sup> 153–154 °C/760 Torr);  $\delta_{\text{H}}$  2.95 (4 H, s), 6.68 (1 H, m) and 6.75–6.9 (2 H, m);  $\delta_{\text{C}}$  28.9 (1- $\text{CH}_2$ ), 29.0 (d, *J* 2, 2- $\text{CH}_2$ ), 110.5 (d, *J* 22), 114.2 (d, *J* 23), 124.1 (d, *J* 9, C-6), 140.8 (d, *J* 3, C-1), 147.0 (d, *J* 7, C-2) and 163.0 (d, *J* 243, C-4).

**$\alpha,\alpha'$ -Dibromo-3-fluoro-*o*-xylene 19.** FVP of the title compound (1.04 g) gave a liquid product, which consisted of 3-fluorobenzocyclobutene (77%) and 3-fluoro-*o*-xylene (8%). Kugelrohr distillation gave pure 3-fluorobenzocyclobutene **20**, bp 60 °C/20 Torr (lit.,<sup>23</sup> 74 °C/100 Torr);  $\delta_{\text{H}}$  3.00 (4 H, br s), 6.75 (2 H, m) and 7.05 (1 H, m);  $\delta_{\text{C}}$  27.1, 30.0, 113.7 (d, *J* 21, C-4), 119.1 (d, *J* 4, C-6), 129.2 (d, *J* 6, C-5), 129.7 (d, *J* 16, C-2), 148.8 (d, *J* 10, C-1) and 156.3 (d, *J* 255, C-3).

**1,2,4,5-Tetrakis(bromomethyl)benzene 21.** FVP of the title compound (0.57 g) gave a white solid in the cold trap which

consisted mainly of tricyclo[6.2.0.0.<sup>3,6</sup>]deca-1,3(6),7-triene (benzodicyclobutene) **22** (47%) [ $\delta_{\text{H}}$  3.22 (8 H, s) and 6.87 (2 H, s);  $\delta_{\text{C}}$  29.5 (4  $\text{CH}_2$ ), 117.4 (2 C) and 143.5 (4 C, 4ry); *m/z* 130], with a trace amount of 1,2,4,5-tetramethylbenzene as the only byproduct.

**$\alpha,\alpha'$ -Dichloro-*p*-xylene 23.** FVP of the title compound (1.05 g, 1.2 g magnesium) gave a yellow polymer which was insoluble in conventional solvents. Microanalysis of the material gave a result indicative of poly( $\alpha$ -chloro-*p*-xylylene) **25** (Found: C, 66.9; H, 5.9.  $(\text{C}_8\text{H}_7\text{Cl})_n$  requires C, 69.3; H, 5.1%). Assuming this formula, the yield of the polymer was 61%.

Thermal analysis of the material showed that it was stable in a nitrogen atmosphere up to 360 °C and in air up to 300 °C, after which there was a gradual weight loss up to 550–600 °C at which point it decomposed. The degradation point in nitrogen was sharp while in air it was gradual.

Repeat pyrolysis of the title compound using a higher magnesium to substrate ratio (0.72 g, 2.0 g magnesium) gave a white brittle polymer, which was also insoluble in conventional solvents. Microanalysis of this material gave a result indicative of poly(*p*-xylylene) **27** (Found: C, 90.0; H, 7.8.  $(\text{C}_8\text{H}_8)_n$  requires C, 92.3; H, 7.7%). Assuming this formula, the yield of the polymer was 72%. Solid state  $^{13}\text{C}$  NMR of the material gave results consistent with those expected for poly(*p*-xylylene);  $\delta_{\text{C}}$  39.9 ( $\text{CH}_2$ ), 129.2 (CH), and 139.7 (4ry). Using a small  $\text{CH}_3$  ( $\delta_{\text{C}}$  21.1) end-group signal, the polymer was estimated to consist of 21 units, giving an approximate molecular weight of 2184.

Thermogravimetric analysis showed that the polymer was stable up to 520 °C in nitrogen and 480 °C in air. There was no weight loss in nitrogen up to 520 °C while in air a steady loss of about 40% weight was observed over the range 300–500 °C.

**$\alpha,\alpha',2,3,5,6$ -Hexabromo-*p*-xylene 28.** FVP of the title compound (0.67 g) gave nothing in the cold-trap. However there was a polymeric material and solid in the inlet tube. Microanalysis and the melting point of the solid, indicated that it was just recovered starting material (0.32 g, 48%). Microanalysis of the polymer indicated that it did not correspond to the expected compositions (Found: C, 17.3; H, 1.7%.  $(\text{C}_8\text{H}_3\text{Br}_5)_n$  requires C, 19.3; H, 0.6% and  $(\text{C}_8\text{H}_4\text{Br}_4)_n$  requires C, 22.9; H, 1.0%).

Repeat pyrolysis at 650 °C without magnesium gave a white solid at the furnace exit with red elemental bromine in the cold trap. Microanalysis of the solid gave a result in good agreement with expectation for poly( $\alpha,2,3,5,6$ -pentabromo-*p*-xylylene) **29** (Found: C, 19.4; H, 1.0.  $(\text{C}_8\text{H}_3\text{Br}_5)_n$  requires C, 19.3%; H, 0.6%). Assuming this composition the yield was 69%.

#### Pyrolysis of other haloalkylbenzenes over magnesium

The required substrates were commercially available and were used without further purification except for 1-bromo-2-phenylpropane, 1,1-diphenoxyethane and  $\beta$ -chloroacrylophenone which were prepared as follows.

**1-Bromo-2-phenylpropane 34.** To 2-phenylpropan-1-ol (6.3 g, 46.3 mmol) cooled in an ice-bath, phosphorus tribromide (4.2 g, 15.5 mmol) was added dropwise and the mixture stirred for 18 h. It was then heated on a waterbath for 1 h, cooled, poured into ice-water and extracted with ether. The organic layer was dried, evaporated and the residue Kugelrohr distilled to give **34** (6.4 g, 70%) as a colourless liquid, bp 100 °C/20 Torr (lit.,<sup>68</sup> 106–108 °C/18 Torr);  $\delta_{\text{H}}$  1.35 (3 H, d, *J* 7), 3.0–3.6 (3 H, m) and 7.30 (5 H, m).

**1,1-Diphenoxyethane 39.** 2-Bromoethyl phenyl ether **37** was first dehydrobrominated by heating under reflux with  $\text{KOH}$ <sup>69</sup> to give phenyl vinyl ether **38**, bp 154–155 °C (lit.,<sup>70</sup> 155–156 °C);  $\delta_{\text{H}}$  4.45 (1 H, dd, *J* 6, 2), 4.82 (1 H, dd, *J* 14, 2), 6.70 (1 H, dd, *J* 14, 6) and 7.0–7.5 (5 H, m). This was then reacted with phenol

in the presence of *p*-chloranil (tetrachloro-1,4-benzoquinone) to afford **39**, bp 150 °C/0.1 Torr (lit.,<sup>71</sup> 152–153 °C/0.1 Torr);  $\delta_{\text{H}}$  1.60 (3 H, d, *J* 5), 5.88 (1 H, q, *J* 5) and 6.8–7.2 (10 H, m); *m/z* 214.

**$\beta$ -Chloroacrylophenone**<sup>72</sup>. Reaction of acetophenone with sodium and ethyl formate gave benzoylactaldehyde which was then reacted with thionyl chloride to afford the title compound as a pale yellow liquid;  $\delta_{\text{H}}$  7.1–7.5 (5 H, m) and 7.9–7.7 (2 H, m).

**(2-Bromoethyl)benzene 30**. FVP of the title compound (0.43 g) gave a colourless liquid as the major product which consisted mainly of styrene (70%), ethylbenzene (14%) and toluene (5%).

Pyrolysis of the title compound at 600 °C through a tube packed only with glass wool gave the unchanged starting material.

**(1-Bromoethyl)benzene 31**. FVP of the title compound (0.39 g) gave a colourless liquid which contained only styrene (80%) and ethylbenzene (19%).

**1-Chloro-3-phenylpropane 32**. FVP of the title compound (0.42 g) gave a colourless liquid which consisted of *E*- $\beta$ -methylstyrene (45%), *Z*- $\beta$ -methylstyrene (20%), allylbenzene (26%), bibenzyl (2%), ethylbenzene (1%), and a trace of toluene.

**1-Bromo-3-phenylpropane 33**. FVP of the title compound (0.41 g) gave a similar product mixture to **32**, namely *E*- $\beta$ -methylstyrene (41%), *Z*- $\beta$ -methylstyrene (15%), allylbenzene (21%), toluene (6%), styrene (5%), bibenzyl (4%), and a trace of ethylbenzene.

**1-Bromo-2-phenylpropane 34**. FVP of the title compound (0.42 g) gave a colourless liquid. This consisted of *E*- $\beta$ -methylstyrene (40%), *Z*- $\beta$ -methylstyrene (19%), allylbenzene (18%),  $\alpha$ -methylstyrene (14%) and traces of styrene and toluene.

**Control pyrolysis of *E*- $\beta$ -methylstyrene,  $\alpha$ -methylstyrene and allylbenzene**. Each of the title compounds was pyrolysed separately under the normal conditions with magnesium at 600 °C.  $\alpha$ -Methylstyrene gave unchanged starting material, *E*- $\beta$ -methylstyrene gave allylbenzene (14%) and the starting material (86%), and allylbenzene gave *E*- $\beta$ -methylstyrene (86%) and the starting material (14%).

**1-Chloro-4-phenylbutane 35**. FVP of the title compound (0.36 g) gave a colourless liquid which consisted of 1,2,3,4-tetrahydronaphthalene (36%), four isomers of butenylbenzene and butylbenzene, with a combined yield of 54%. Trace amounts of styrene, toluene and bibenzyl were also observed by GCMS. A repeat pyrolysis at a longer contact time (1.0 Torr) gave the same mixture of compounds as above, except that the yield of styrene was greatly increased to about 20%.

**Cinnamyl bromide 36**. FVP of the title compound (0.49 g) gave a colourless liquid which was shown by <sup>1</sup>H NMR to contain indene (48%) and  $\beta$ -methylstyrene (12%).

**2-Bromoethyl phenyl ether 37**. FVP of the title compound (0.43 g) gave a dark liquid with strong phenolic odour which consisted of phenol (36%), 1,1-diphenoxyethane **39** (13%), acetaldehyde (5%), and a compound suspected to be 2,3-diphenoxybutane **40** (9%) [ $\delta_{\text{H}}$  2.10 (6 H, d, *J* 5), 6.30 (2 H, q, *J* 5) and 6.8–7.2 (10 H, m)]. Biphenyl (<2%) was also found to be present by GCMS. Repeat pyrolysis at a longer contact time (15 Torr) gave mainly phenol (57%) with small amounts of the other products.

**1,1-Diphenoxyethane 39**. FVP of the title compound (0.29 g) gave a liquid shown by <sup>1</sup>H NMR to consist of phenol (57% assuming 2 PhOH per substrate), phenyl vinyl ether **38** (30%), benzaldehyde (27%), toluene (11%) and small amount of starting material.

**Phenyl vinyl ether 38**. FVP of the title compound over magnesium at 600 °C gave unchanged starting material.

**$\alpha$ -Bromoacetophenone 41**. FVP of the title compound (0.37 g) gave a light yellow liquid shown by NMR and GCMS to consist of acetophenone (42%), phenylacetylene (31%), and styrene (6%).

**$\beta$ -Chloropropiophenone 42**. FVP of the title compound (0.30 g) gave a yellow oil which was shown by NMR and GCMS to consist of acrylophenone (64%), propiophenone (10%), indan-1-one (11%) and 1-phenylpropyne (5%), with traces of styrene, phenylacetylene and acetophenone.

**$\beta$ -Chloroacrylophenone 43**. FVP of the title compound (1.0 g) gave a colourless liquid and an oily solid. Analysis of the liquid by <sup>1</sup>H NMR and GCMS showed the presence of toluene (1%), styrene (3%), benzocyclobutene (3%), indene (15%), 1-phenylpropyne (5%) and acrylophenone (4%), while the oily solid contained the unchanged starting material and indan-1-one (20%).

#### Aliphatic halides

The starting aliphatic halides were commercially available and were used as received except for the following.

2-Chloro-2,3-dimethylbutane **46** was prepared by the method of Whitmore *et al.*<sup>73</sup> involving reaction of 3,3-dimethylbutan-2-ol with fuming hydrochloric acid to give the product (50%) as a lachrymatory liquid, bp (oven temp.) 40 °C/20 Torr (lit.,<sup>73</sup> 116–117.5 °C/760 Torr);  $\delta_{\text{H}}$  1.00 (6 H, d, *J* 6), 1.50 (6 H, s) and 1.82 (1 H, septet).

2,3-Dichloro-2,3-dimethylbutane **47** was prepared by reaction of 2,3-dimethylbutane-2,3-diol **5** with fuming hydrochloric acid to give the product (64%) as a solid, bp 80 °C/20 Torr (lit.,<sup>74</sup> 136–146 °C/760 Torr);  $\delta_{\text{H}}$  1.70 (s).

1,1-Dichlorobutane **62** was prepared by reaction of butyraldehyde with phosphorus pentachloride in dichloromethane to give the product (31%) as a colourless liquid, bp 50 °C/20 Torr (lit.,<sup>75</sup> 114–115 °C/760 Torr);  $\delta_{\text{H}}$  0.97 (3 H, t, *J* 6), 1.5–1.7 (2 H, m), 1.9–2.1 (2 H, m) and 5.95 (1 H, t, *J* 6);  $\delta_{\text{C}}$  13.4 (C-4), 18.2 (C-3), 40.9 (C-2) and 93.5 (C-1).

1,1-Dichloropentane **63** was prepared by reaction of pentanal with thionyl chloride and a catalytic amount of DMF in dichloromethane to give the product (58%) as a light yellow liquid, bp 60 °C/20 Torr (lit.,<sup>76</sup> 139.4–140.2 °C/760 Torr);  $\delta_{\text{H}}$  0.85 (3 H, t, *J* 6), 1.27 (2 H, m), 1.38 (2 H, m), 1.93 (2 H, m) and 5.75 (1 H, t, *J* 6);  $\delta_{\text{C}}$  13.5 (C-5), 21.8 (C-4), 26.6 (C-3), 38.4 (C-2) and 93.2 (C-1).

1,1-Dichlorohexane **64** was prepared by reaction of hexanal with thionyl chloride and a catalytic amount of DMF in dichloromethane to give the product (80%) as a light yellow liquid, bp 65 °C/20 Torr (lit.,<sup>77</sup> 62–62.5 °C/20 Torr);  $\delta_{\text{H}}$  0.85 (3 H, t, *J* 6), 1.25 (4 H, m), 1.37 (2 H, m), 1.90 (2 H, m) and 5.75 (1 H, t, *J* 6);  $\delta_{\text{C}}$  12.9 (C-6), 21.5 (C-3), 23.5 (C-5), 30.2 (C-4), 38.0 (C-2) and 92.6 (C-1).

1,2-Dibromocyclohexane **68** was prepared by reaction of cyclohexene with bromine in carbon tetrachloride to give the product (59%) as a colourless liquid, bp 120 °C/20 Torr (lit.,<sup>78</sup> 116 °C/29 Torr);  $\delta_{\text{H}}$  1.50–2.10 (6 H, m), 2.30–2.60 (2 H, m) and 4.50 (2 H, m).

1,2-Dichlorocyclooctane **69** was prepared by the method of Ghelfi *et al.*<sup>79</sup> involving reaction of cyclooctene with manganese dioxide and chlorotrimethylsilane in THF to give the product



(84%) as a colourless liquid, bp 150 °C/20 Torr (lit.,<sup>79</sup> 105–119 °C/10 Torr);  $\delta_{\text{H}}$  1.3–1.7 (8 H, m), 1.85–2.15 (4 H, m) and 4.07 (2 H, m).

Samples of 6-chlorohex-1-yne **65**,<sup>80</sup> 7-chlorohept-1-yne **66**,<sup>81</sup> and 8-chlorooct-1-yne **67**<sup>82</sup> were kindly provided by Professor F. D. Gunstone, University of St Andrews.

### Pyrolysis of alkyl halides

**1-Bromopentane 44.** FVP of the title compound (1.32 g) gave a colourless liquid as product which consisted of pent-1-ene (31%) and pent-2-ene (55%).

**1-Bromo-2,2-dimethylpropane (neopentyl bromide) 45.** FVP of the title compound (1.32 g) gave a colourless liquid as product which consisted of 2-methylbut-1-ene (33%) and 2-methylbut-2-ene (43%). A trace amount of 2-methylpropene (ca. 5%) was also evident.

**2-Chloro-2,3-dimethylbutane 46.** FVP of the title compound (0.52 g, ice-cooled vertical inlet tube) gave a liquid product which consisted of two major compounds namely 2,3-dimethylbut-2-ene (52%) and 2,3-dimethylbut-1-ene (24%). Another batch run under the same conditions but at 500 °C gave 2,3-dimethylbut-2-ene (46%) and 2,3-dimethylbut-1-ene (37%).

**2,3-Dichloro-2,3-dimethylbutane 47.** FVP of the title compound (0.16 g) gave a colourless liquid which proved to be 2,3-dimethylbuta-1,3-diene (84%).

**2,3-Dimethylbutane-2,3-diol (pinacol) 48.** FVP of the title compound (0.44 g) gave a liquid which consisted mainly of acetone (67%) with small amounts of 2,3-dimethylbuta-1,3-diene (8%), 2,3-dimethylbut-2-ene (3%), 2,3-dimethylbut-1-ene (10%) and 3,3-dimethylbutan-2-one (pinacolone, 7%).

Repeat pyrolysis under the same conditions at a higher temperature of 700 °C, gave mainly acetone (84%) with traces of the other products mentioned above.

Repeat pyrolysis without magnesium gave a solid, which was mainly the starting material. Repeat pyrolysis at a higher temperature of 700 °C and without magnesium gave a mixture of acetone (20%), 2,3-dimethylbutadiene (20%), and 3,3-dimethylbutan-2-one (20%), with small amounts of 2,3-dimethylbut-1-ene, 2,3-dimethylbut-2-ene and starting material.

### Pyrolysis of dihaloalkanes

**1,3-Dibromopropane 49.** FVP of the title compound (0.69 g, ice-cooled vertical inlet tube) gave a gaseous product which was trapped with  $\text{CDCl}_3$ . NMR analysis of the product showed it to be cyclopropane (60%) [ $\delta_{\text{H}}$  0.25 (s);  $\delta_{\text{C}}$  -3.1]. A trace amount of propene was also observed.

**1,2-Dibromopropane 50.** FVP of the title compound (0.62 g) gave a gaseous product which was trapped with  $\text{CDCl}_3$ .  $^1\text{H}$  NMR analysis showed that the product consisted mainly of propene (77%) with a small amount of 2-bromopropene (12%).

**1,4-Dichlorobutane 51.** FVP of the title compound (0.31 g, inlet ice-cooled vertical inlet tube) gave a liquid with gaseous components which was trapped with  $\text{CDCl}_3$ . This consisted of buta-1,3-diene (24%), but-1-ene (11%), but-2-ene (4%) and cyclobutane (2%).

**1,3-Dichlorobutane 52.** FVP of the title compound (0.64 g, ice-cooled vertical inlet tube) gave a liquid with gaseous components, which was trapped with  $\text{CDCl}_3$ . The main product was clearly buta-1,3-diene (38%) with small amounts of but-2-ene and but-1-ene.

**1,5-Dibromopentane 53.** FVP of the title compound (0.46 g) gave a liquid as product which consisted of pent-1-ene (29%), penta-1,3-diene (18%) and cyclopentane (6%), with traces of pent-2-ene and penta-1,4-diene.

Repeat pyrolysis at a temperature of 700 °C gave the same mixture of compounds namely pent-1-ene (23%), penta-1,3-diene (18%) and cyclopentane (7%) with traces of pent-2-ene and penta-1,4-diene while at 500 °C the mixture consisted of pent-1-ene (31%), penta-1,3-diene (22%) and cyclopentane (9%), with traces of pent-2-ene and penta-1,4-diene.

**1,4-Dibromopentane 54.** FVP of the title compound (0.38 g) gave a liquid which consisted mainly of penta-1,3-diene (47%), a mixture of pent-1-ene and pent-2-ene (18% total) and penta-1,4-diene (6%).

**1,6-Dibromohexane 55.** FVP of the title compound (1.22 g) gave a colourless liquid which was hex-1-ene (72%) with small amounts of cyclohexane and butenes.

**1,8-Dibromooctane 56.** FVP of the title compound (1.14 g) gave a liquid product which consisted of oct-1-ene (20%), hex-1-ene (16%), octa-1,7-diene (3%), octane (2%), cyclooctane (trace) and an unidentified compound (12%) with  $m/z$  112 which may have been ethylcyclohexane.

### Pyrolysis of haloalkenes

**4-Bromobut-1-ene 57.** FVP of the title compound (0.51 g, inlet ice-cooled vertical inlet tube) gave a liquid with gaseous components which was buta-1,3-diene (58%) together with but-2-ene (11%) and but-1-ene (10%).

**5-Bromopent-1-ene 58.** FVP of the title compound (0.79 g) gave a liquid product which was hexa-1,5-diene (53%) with small amounts of cyclopentene (8%) and a further compound (6%) with  $m/z$  110 which may have been (prop-2-enyl)-cyclopentane.

**6-Bromohex-1-ene 59.** FVP of the title compound (0.17 g) gave a liquid product which consisted mainly of cyclohexene (50%), three isomeric hexadienes, the 1,3-isomer, the 1,4-isomer and the 1,5-isomer with a combined yield of 22% and methylcyclopentene (4%).

### Pyrolysis of geminal dihaloalkanes

**2,2-Dichloropropane 60.** FVP of the title compound (0.35 g, ice-cooled vertical inlet tube) gave a colourless liquid which consisted mainly of 2-chloropropene (74%) with trace amounts of allene and 2,3-dichloro-2,3-dimethylbutane. A repeat run under the same conditions but with a pressure of 1.0 Torr gave the same products namely 2-chloropropene (74%), allene (2%) and 2,3-dichloro-2,3-dimethylbutane (6%).

**1,1-Dichloropropane 61.** FVP of the title compound (0.64 g, inlet ice-cooled vertical inlet tube) gave a liquid which consisted mainly of *E*-1-chloropropene (50%) and *Z*-1-chloropropene (28%). Also present were small amounts of 3-chloropropene, hexa-1,5-diene, 2-chloropropene and 1,2-dichloropropane.

**1,1-Dichlorobutane 62.** FVP of the title compound (0.35 g) gave a liquid product which consisted of the three isomers of dibut-1-enyl ether. For yields and  $^{13}\text{C}$  NMR data see Table 3. Due to peak overlap, only the  $^1\text{H}$  NMR signals of the major *E,E*-isomer could be assigned with certainty:  $\delta_{\text{H}}$  1.00 (6 H, t, *J* 7), 2.15 (4 H, quintet of d, *J* 7, 2), 4.60 (2 H, q, *J* 7) and 6.20 (2 H, d of t, *J* 7, 2); GCMS of the product showed 3 peaks with identical mass spectral fragmentation patterns;  $m/z$  126 ( $\text{M}^+$ , 18%), 111 (8), 97 (5), 57 (40) and 55 (100).

**1,1-Dichloropentane 63.** FVP of the title compound (0.85 g) gave a liquid which consisted of the three isomers of dipent-1-enyl ether. For yields and  $^{13}\text{C}$  NMR spectra see Table 3. Due to peak overlap, only the  $^1\text{H}$  NMR signals of the major *E,E*-isomer could be assigned with certainty:  $\delta_{\text{H}}$  0.84 (6 H, t, *J* 7), 1.2–1.45 (4 H, m), 2.03 (4 H, quintet of d, *J* 7, 2), 4.37 (2 H, q, *J* 7) and 6.12 (2 H, d of t, *J* 7, 2); GCMS of the product showed 3 peaks with identical mass spectral fragmentation patterns; *m/z* 154 ( $\text{M}^+$ , 13%), 125 (24), 83 (18), 69 (27), 57 (48) and 41 (100). Also present was a very small amount of pent-1-yne.

**1,1-Dichlorohexane 64.** FVP of the title compound (0.57 g) gave a liquid which consisted of the three isomers of dihex-1-enyl ether. For yields and  $^{13}\text{C}$  NMR spectra see Table 3. Due to peak overlap, only the  $^1\text{H}$  NMR signals of the major *E,E*-isomer could be assigned with certainty:  $\delta_{\text{H}}$  0.79 (6 H, t, *J* 7), 1.2–1.3 (8 H, m), 2.04 (4 H, quintet of d, *J* 7, 2), 4.36 (2 H, q, *J* 7) and 6.02 (2 H, d of t, *J* 7, 2); GCMS of the product showed 3 peaks with identical mass spectral fragmentation patterns; *m/z* 182 ( $\text{M}^+$ , 18%), 139 (20), 97 (20), 82 (60), 67 (29), 55 (100) and 41 (48). Also present was a very small amount of hex-1-yne.

#### Pyrolysis of haloalkynes

**6-Chlorohex-1-yne 65.** FVP of the title compound (0.47 g, ice-cooled vertical inlet tube) gave a liquid which consisted mainly of 3-methylenecyclopentene (22%) and methylenecyclopentane (28%). There were also small amounts of cyclohexene, cyclopentane, cyclohexa-1,3-diene and benzene.

**7-Chlorohept-1-yne 66.** FVP of the title compound (0.60 g, ice-cooled vertical inlet tube) gave a liquid which was mainly methylenecyclohexane together with 3-methylenecyclohexene and 4-methylenecyclohexene. Due to the complex nature of the spectra it was impossible to determine the yields of the products. Repeat pyrolysis under the same conditions but at 500 °C gave mainly the starting materials.

**8-Chlorooct-1-yne 67.** FVP of the title compound (0.53 g) gave a liquid product. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the product were complex and peak assignment was impossible. GCMS showed a mixture of various compounds ranging from  $\text{C}_4$  to  $\text{C}_8$  hydrocarbons. Repeat pyrolysis at 500 °C under the same conditions gave mainly unreacted starting material, with a complex mixture of unidentified compounds.

#### Pyrolysis of cyclic dihalides

**1,2-Dibromocyclohexane 68.** FVP of the title compound (0.82 g) gave a colourless liquid which proved to be a mixture of benzene (28%), cyclohexa-1,3-diene (35%) and cyclohexene (30%).

Repeat pyrolysis of dibromocyclohexane through a tube packed with only glass wool gave a dark liquid which continuously evolved hydrogen bromide and proved to be benzene (78%).

**1,2-Dichlorocyclooctane 69.** FVP of the title compound (0.62 g) gave a liquid which consisted of compounds with *m/z* 108 ( $\text{C}_8\text{H}_{12}$ , seven isomers), *m/z* 110 ( $\text{C}_8\text{H}_{14}$ ); *m/z* 106 ( $\text{C}_8\text{H}_{10}$ ), *m/z* 96 ( $\text{C}_7\text{H}_{12}$ ) and traces of benzene, toluene and cyclohexadiene.

Repeating the pyrolysis at a lower temperature of 500 °C gave a liquid which consisted of cyclooctene (28%) and compounds with *m/z* 108 (five isomers with a combined yield of 35%) with traces of other compounds. In both experiments no halogenated products were observed.

Repeating the pyrolysis at 600 °C without magnesium gave a bright yellow liquid which darkened on exposure to air, with vigorous evolution of HCl gas. The products obtained were cycloocta-1,3-diene (28%), chlorocyclohexene (16%), 1-

chlorocyclooct-1-ene and 3-chlorocyclooct-1-ene (29% total), with traces of benzene, toluene and compounds with *m/z* 108. When the pyrolysis was carried out at 500 °C without magnesium, the products were cycloocta-1,3-diene (26%) and four compounds with the same *m/z* as chlorocyclooctene (combined yield of 55%); with only a trace of chlorocyclohexene.

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#### References

- J.-C. Guillemin and J.-M. Denis, *Tetrahedron*, 1988, **44**, 4431; J.-C. Guillemin, J.-M. Denis, M.-C. Lasne and J.-L. Ripoll, *Tetrahedron*, 1988, **44**, 4447.
- P. L. Coe, C. R. Patrick and J. C. Tatlow, *Tetrahedron*, 1960, **16**, 240.
- R. E. Banks, A. E. Ginsberg and R. N. Haszeldine, *J. Chem. Soc.*, 1961, 1740.
- A. E. Ginsberg, R. Paatz and F. Korte, *Tetrahedron Lett.*, 1962, 779.
- O. L. Chapman, C. C. Chang and N. R. Rosenquist, *J. Am. Chem. Soc.*, 1976, **98**, 261.
- T. Koenig, D. Imre and J. A. Hoobler, *J. Am. Chem. Soc.*, 1979, **101**, 6446.
- M. Binnewies, B. Solouki, H. Bock, R. Becherer and R. Ahlrichs, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 731.
- B. Rozsondai, J. Tremmel, I. Hargittai, V. N. Khabashesku, N. D. Kagramanov and O. M. Nefedov, *J. Am. Chem. Soc.*, 1989, **111**, 2845.
- Preliminary communication, R. A. Aitken, P. K. G. Hodgson, A. O. Oyewale and J. J. Morrison, *Chem. Commun.*, 1997, 1161.
- M. G. Voronkov, E. N. Deryagina, L. G. Shagun and V. Yu. Vitkovskii, *Zh. Org. Khim.*, 1983, **19**, 1079.
- A. Fürstner, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 164.
- Y. Fujiwara, R. Ishikawa and S. Teranishi, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 589.
- S. Inaba, H. Matsumoto and R. D. Rieke, *J. Org. Chem.*, 1984, **49**, 2093.
- J. M. McBride, *Tetrahedron*, 1974, **30**, 2009.
- E. E. Van Tamelen and T. M. Cole, Jr., *J. Am. Chem. Soc.*, 1971, **93**, 6158.
- A. G. Loudon, A. MacColl and S. K. Wong, *J. Am. Chem. Soc.*, 1969, **91**, 7577; J. L. Charlton and M. M. Alauddin, *Tetrahedron*, 1987, **43**, 2873.
- P. Schiess, M. Heitzmann, S. Rutschmann and R. Stäheli, *Tetrahedron Lett.*, 1978, 4569; M. J. Morello and W. S. Trahanovsky, *Tetrahedron Lett.*, 1979, 4435; K. A. Walker, L. J. Markoski and J. S. Moore, *Synthesis*, 1992, 1265.
- R. Gray, L. G. Harruff, J. Krymowski, J. Peterson and V. Boekelheide, *J. Am. Chem. Soc.*, 1978, **100**, 2892.
- L. G. Harruff, M. Brown and V. Boekelheide, *J. Am. Chem. Soc.*, 1978, **100**, 2893; P. Schiess and M. Heitzmann, *Helv. Chim. Acta*, 1978, **61**, 844.
- R. P. Thummel, *Acc. Chem. Res.*, 1980, **13**, 70.
- V. Boekelheide, *Acc. Chem. Res.*, 1980, **13**, 65.
- P. Schiess, S. Rutschmann and V. V. Toan, *Tetrahedron Lett.*, 1982, **23**, 3669.
- W. Adcock, B. D. Gupta and T.-C. Khor, *Aust. J. Chem.*, 1976, **29**, 2571.
- W. F. Gorham, *J. Polym. Sci., Part A1*, 1966, **4**, 3027.
- H. G. Gilch and W. L. Wheelwright, *J. Polym. Sci., Part A1*, 1966, **4**, 1337.
- R. Burkhardt, E.-N. Peterson and N. Vollkommer, *Chem.-Ztg.*, 1978, **102**, 11.
- W. S. Emerson and E. P. Agnew, *J. Am. Chem. Soc.*, 1945, **67**, 518.
- G. Chuchani and I. Martin, *J. Phys. Org. Chem.*, 1990, **3**, 77.
- W. B. Smith and J. D. Anderson, *J. Am. Chem. Soc.*, 1960, **82**, 656.
- F. P. Lossing and J. C. Traeger, *J. Am. Chem. Soc.*, 1975, **97**, 1579.
- M. F. Shostakovskii and A. V. Bogdanova, *Zh. Obshch. Khim.*, 1951, **21**, 388.
- P. H. Kasai, D. McLeod Jr. and H. C. McBay, *J. Am. Chem. Soc.*, 1974, **96**, 6864.



- 33 M. R. Banks, J. I. G. Cadogan, I. Gosney, P. K. G. Hodgson, A. G. C. Jack and D. R. Rodger, *J. Chem. Soc., Chem. Commun.*, 1989, 1033.
- 34 J. S. Shapiro and E. S. Swinbourne, *J. Chem. Soc., Chem. Commun.*, 1967, 465; J. I. G. Cadogan, J. B. Husband and H. McNab, *J. Chem. Soc., Perkin Trans. 1*, 1983, 1489.
- 35 L. Schmerling, B. S. Friedman and V. N. Ipatieff, *J. Am. Chem. Soc.*, 1940, **62**, 2448.
- 36 L. P. Kyriakides, *J. Am. Chem. Soc.*, 1914, **36**, 985.
- 37 L. A. Shevtsova and S. V. Levanova, *Zh. Prikl. Khim. (Leningrad)*, 1982, **55**, 950.
- 38 A. Ouchi and M. Sakuragi, *Eur. J. Org. Chem.*, 1999, 2249.
- 39 K. W. Watkins and D. K. Olsen, *J. Phys. Chem.*, 1972, **76**, 1089.
- 40 C. Walling and M. S. Pearson, *J. Am. Chem. Soc.*, 1964, **86**, 2262.
- 41 V. E. Platonov and G. G. Yakobson, *Synthesis*, 1976, 374; R. E. Busby, M. Iqbal, J. Parrick and C. J. G. Shaw, *J. Chem. Soc., Chem. Commun.*, 1969, 1344.
- 42 K. A. Holbrook and K. A. W. Parry, *J. Chem. Soc. (B)*, 1971, 1762.
- 43 S. Kikkawa, M. Nomura and M. Shimizu, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 2586.
- 44 T. Okayama, T. Takino, K. Sato and M. Ochiai, *J. Am. Chem. Soc.*, 1998, **120**, 2275.
- 45 J. F. Normant, G. Cahiez, C. Chuit and J. Villieras, *J. Organomet. Chem.*, 1974, **77**, 269.
- 46 A. Claesson, *Acta Chem. Scand. Ser. B*, 1975, **29**, 609; J. E. Bäckvall, H. E. Schink and Z. D. Renko, *J. Org. Chem.*, 1990, **55**, 826.
- 47 S. Yamada, H. Ohsawa, T. Suzuki and H. Takayama, *J. Org. Chem.*, 1986, **51**, 4934; C. Conn, D. Lloyd-Jones, G. S. K. Kannangara and A. T. Baker, *J. Organomet. Chem.*, 1999, **585**, 134.
- 48 E. Taskinen and R. Virtanen, *J. Org. Chem.*, 1977, **42**, 1443; E. Taskinen, *J. Org. Chem.*, 1978, **43**, 2776.
- 49 L. Brandsma and J. F. Arens, *Recl. Trav. Chim. Pays-Bas*, 1962, **81**, 33.
- 50 W. D. Huntsman, J. A. De Boer and M. H. Woosley, *J. Am. Chem. Soc.*, 1966, **88**, 5846; M. Remmler, B. Ondruschka, D. Vorwerk, B. Olk, J. Pola and P. Kubat, *J. Prakt. Chem.*, 1990, 699.
- 51 W. A. P. Chaloner and C. K. Ingold, *J. Chem. Soc.*, 1923, **123**, 2078.
- 52 H. M. Frey and H. Hopf, *J. Chem. Soc. (C)*, 1973, 2016.
- 53 R. A. Aitken and J. I. Atherton, *J. Chem. Soc., Perkin Trans. 1*, 1994, 1281.
- 54 *Dictionary of Organic Compounds*, Ed. J. Buckingham, 5th edn., 1982, Vol. 2, p. 2314.
- 55 J. M. Birchall and R. N. Haszeldine, *J. Chem. Soc.*, 1961, 3719.
- 56 M. M. Tiffeneau, *Bull. Soc. Chim. Fr.*, 1911, **9**, 825.
- 57 T. Reichstein, A. Cohen, M. Ruth and H. F. Meldohl, *Helv. Chim. Acta*, 1936, **19**, 412.
- 58 T. Reichstein and R. Oppenauer, *Helv. Chim. Acta*, 1933, **16**, 1373.
- 59 M. Szwarc and J. S. Roberts, *J. Am. Chem. Soc.*, 1948, **70**, 2831.
- 60 K. M. Johnson and G. H. Williams, *J. Chem. Soc.*, 1960, 1168.
- 61 F. G. Mann, I. T. Millar and B. B. Smith, *J. Chem. Soc.*, 1953, 1130.
- 62 R. J. W. Le Fèvre and E. E. Turner, *J. Chem. Soc.*, 1927, 1113.
- 63 J. E. Leffler and A. F. Wilson, *J. Org. Chem.*, 1960, **25**, 424.
- 64 H. Biltz, *Liebigs Ann. Chem.*, 1897, **295**, 219.
- 65 G. Valkanas, *J. Chem. Soc.*, 1963, 5554.
- 66 J. E. Rice, A. Czech, N. Hussain and E. J. La Voie, *J. Org. Chem.*, 1988, **53**, 1775.
- 67 W. Adcock, M. J. S. Dewar, R. Golden and M. A. Zeb, *J. Am. Chem. Soc.*, 1975, **97**, 2198.
- 68 J. B. Cohen, J. Marshall and H. E. Woodman, *J. Chem. Soc.*, 1915, **107**, 887.
- 69 W. M. Lauer and M. A. Spielman, *J. Am. Chem. Soc.*, 1931, **53**, 1533.
- 70 W. M. Lauer and M. A. Spielman, *J. Am. Chem. Soc.*, 1933, **55**, 1572.
- 71 M. L. Hallensleben, *Chem. Ber.*, 1971, **104**, 3778.
- 72 A. N. Nesmeyanov, N. K. Kochetkov and M. I. Rybinskaya, *Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk*, 1954, 741.
- 73 F. C. Whitmore and H. S. Rothrock, *J. Am. Chem. Soc.*, 1933, **55**, 1106.
- 74 I. Kondakow, *J. Prakt. Chem.*, 1900, **62**, 169.
- 75 A. L. Henne, M. W. Renoll and H. M. Leicester, *J. Am. Chem. Soc.*, 1939, **61**, 938.
- 76 K. F. W. Kohlrausch and F. Koppl, *Monatsh. Chem.*, 1935, **65**, 135.
- 77 J. Normant, *Bull. Soc. Chim. Fr.*, 1963, 1868.
- 78 A. W. Crossley, *J. Chem. Soc.*, 1904, **85**, 1415.
- 79 F. Bellesia, F. Ghelfi, U. M. Pagnoni and A. Pinetti, *J. Chem. Res. (S)*, 1989, 108.
- 80 F. D. Gunstone and M. Lie Ken Jie, *Chem. Phys. Lipids*, 1970, **4**, 1.
- 81 J. A. Barve and F. D. Gunstone, *Chem. Phys. Lipids*, 1971, **7**, 311.
- 82 F. D. Gunstone and P. J. Sykes, *J. Chem. Soc.*, 1962, 3055.