Dehalogenation of organic halides by flash vacuum pyrolysis over magnesium: a versatile synthetic method

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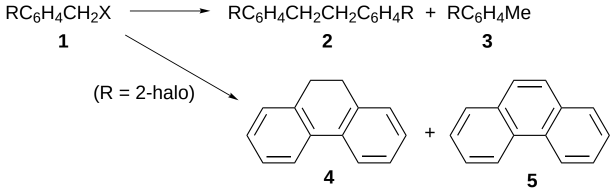
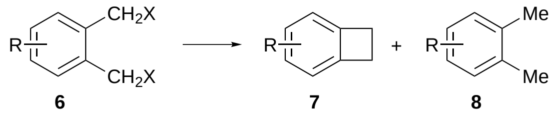
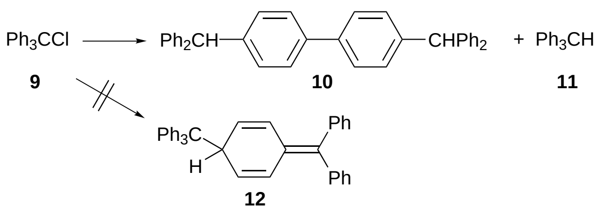
Flash vacuum pyrolysis over magnesium at 600 °C results in efficient dehalogenation of a variety of organic halides and provides a preparatively useful method for C–C bond formation and other reactions.

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. There has been little previous work on gas phase pyrolysis over solid reagents but pyrolysis over solid bases has been used effectively by Denis and co-workers.[1] Dehydrofluorination of alicyclic precursors over iron or nickel has been used to obtain fluorinated aromatics,[2] and pyrolysis of hexachlorocyclopentadiene over iron results in C–C bond formation to give perchlorofulvalene.[3] 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[4] and can alternatively be formed by FVP of α,α,α′α′-tetrabromo-*o*-xylene over magnesium at 440–470 °C,[5] while FVP of $PXCl_3$ (X = O, S) over silver at 880 °C leads to generation of the reactive P^{III} species, Cl–P=X[6] and FVP of trichloroacetyl chloride over zinc at 420 °C gives dichloroketene.[7] 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.

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.† 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 furance exit which was essentially pure bibenzyl (58%). By using excess benzyl chloride it was established that approximately 20% of the magnesium used was available for reaction assuming conversion to $MgCl_2$. The method was equally effective for a range of substituted benzyl chlorides and bromides (Table 1) giving the bibenzyls **2** and toluenes **3** in good to excellent combined yield. The bibenzyls were readily obtained in pure form by a single recrystallisation of the solids from the furnace exit and this represents a gas-phase alternative to the Wurtz coupling. The somewhat unexpected formation of the reduction products was a general observation in these studies and presumably results from sacrificial carbonisation of the substrate. For 2-halobenzyl halides, further dehalogenation to give dihydrophenanthrene **4** and phenanthrene **5** was observed as a minor process. The result for 2-methylbenzyl bromide shows a clear distinction from pyrolysis without magnesium which results in 1,4-loss of HBr and cyclisation of the resulting *o*-xylylene to give benzocyclobutene as the major product.[9] Reaction of 1,2-bis(halomethyl)benzene derivatives results in efficient formation of the benzocyclobutenes and this was used to obtain the 3- and 4-fluoro compounds **7** directly from **6** as compared to the literature method which takes three steps for this transformation.[10] Bromo- and chloro-diphenylmethane behaved similarly giving tetraphenylethane (60–70%) and diphenylmethane (20%), apparently derived respectively from dimerisation and reduction of the corresponding radical. It was therefore of great interest to investigate trityl chloride **9** in view of the long-standing controversy over the structure of the trityl radical dimer.[11] The products were **10** (46%) and triphenylmethane **11** (39%) with none of the non-benzenoid dimer **12** formed from dimerisation of $Ph_3C\cdot$ in solution. The conditions used have obviously favoured *p*–*p* dimerisation of the reactive intermediate involved followed by two 1,5-hydrogen shifts to give the stable aromatic product. It is interesting to note that this is also the product formed from photochemical dimerisation of the trityl cation in solution.[12]







The method it also effective in coupling benzylidene chlorides **13** to give the corresponding stilbenes **14** in moderate yield (Table 1), together with the reduction products **2** and **3**. Convenient direct access to polycyclic aromatic systems is also possible as illustrated by conversion of 2-chlorobenzylidene dichloride into phenanthrene (47%) and 1,3-bis(dibromomethyl)benzene into pyrene (54%) and this method should be amenable to formation of specifically substituted products. An unexpected result was obtained for the 2-methoxy compounds **15a, b** where the main products **16**, formed in 60 and 51% yields, respectively, seem likely to result from the sequence shown in Scheme 1 involving two intramolecular hydrogen atom transfers between the adjacent groups and decarbonyla-

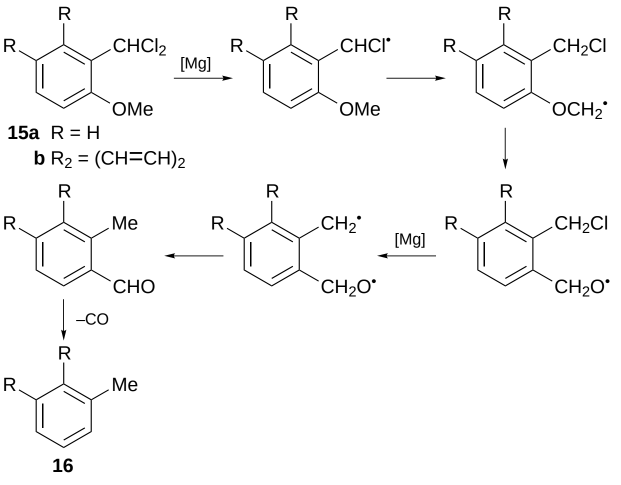
$$\underset{\mathbf{13}}{RC_6H_4CHX_2} \longrightarrow \underset{\mathbf{14}}{RC_6H_4CH{=}CHC_6H_4R} + \mathbf{2} + \mathbf{3}$$

tion. This is in contrast to the pyrolysis of these substrates without magnesium which gives benzofurans by a carbene route.[13]

In order to gain further insight into the nature of the intermediates involved, we examined the reactivity of some aliphatic halides. Neopentyl bromide was of particular interest since the products formed from generation of both neopentyl radical and the carbene, neopentylidene, under very similar conditions have been described.[14] The products obtained over magnesium, 2-methylbut-2-ene (43%) and 2-methylbut-1-ene (33%) together with a trace of 2-methylpropene, indicate that neither the free gas-phase radical (2-methylpropene : 2-methylbut-1-ene, 1.2 : 1) nor the carbene (1,1-dimethylcyclopropane as main product) are involved. Where dehydrohalogenation is possible it usually occurs, as shown by the high yielding synthesis of 2,3-dimethylbuta-1,3-diene (84%) from the inexpensive precursor 2,3-dichloro-2,3-dimethylbutane, but C–C bond formation is also possible as shown by formation of cyclopropane (60%) from 1,3-dibromopropane. For longer α,ω-dihalides an intramolecular hydrogen transfer occurs and this is optimal for 1,6-dibromohexane resulting in the remarkably efficient formation of hex-1-ene (72%) by loss of Br_2. Further evidence against the involvement of free gas-phase radicals was provided by reaction of 6-bromohex-1-ene which gave mainly cyclohexene (50%) and isomeric hexadienes (23%) with no major products derived from cyclopentylmethyl radical.[15] It appears that the reactions may proceed by way of surface-adsorbed organomagnesium species.[‡]

Table 1 FVP of organic halides over magnesium

Starting material	R	X	Products (% yield)
1	H	Cl	**2**(58) **3**(16)
1	H	Br	**2**(69) **3**(20)
1	2-Me	Br	**2**(70) **3**(20)
1	4-Me	Cl	**2**(60) **3**(23)
1	2-F	Cl	**2**(73) **3**(7) **4**(5)
1	2-F	Br	**2**(80) **3**(11) **4**(3)
1	3-F	Br	**2**(67) **3**(12)
1	4-F	Br	**2**(73) **3**(12)
1	4-Cl	Cl	**2**(37) **3**(6)
1	2-Br	Br	**2**(51) **3**(24) **4**(2) **5**(6)
1	4-Br	Br	**2**(43) **3**(28)
1	2-I	Cl	**2**(40) **3**(1) **4**(31) **5**(12)
6	H	Cl	**7**(73) **8**(15)
6	3-F	Br	**7**(77) **8**(8)
6	4-F	Br	**7**(80) **8**(8)
13	H	Cl	**14**(49) **2**(20) **3**(12)
13	2-Me	Cl	**14**(36) **2**(10) **3**(13)
13	3-Me	Cl	**14**(48) **2**(12) **3**(11)
13	4-Me	Cl	**14**(63) **2**(21) **3**(6)
13	2-Cl-6-F	Cl	**14**(58) **3**(2)



Scheme 1

Whatever the nature of the intermediates involved, this method appears to allow a range of synthetically useful transformations and further applications to organic halides and halides of other main group elements will be reported shortly.

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Footnotes

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[†] *Pyrolysis procedure.* Using the normal apparatus for FVP described previously (ref. 8), magnesium turnings (1–2 g) were placed between two plugs of glass wool in the centre of the pyrolysis tube. The system was connected up as normal except that a stopper was used in place of the inlet tube, and the evacuated pyrolysis tube was briefly heated to 650–700 °C until the magnesium melted and sublimed evenly over the surface of the glass wool. Careful observation at this stage revealed an initial vigorous reaction on the wool, interpreted as the formation of magnesium silicide, but this was subsequently covered by magnesium and does not play a significant part in the reactions. The furnace was then cooled to the pyrolysis temperature, usually 600 °C, 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 (5–10 mmol) attached (*CAUTION*: admission of air at this stage may lead to an explosion), and the pyrolysis continued as normal. After the pyrolysis was complete, the products were removed from the cold trap and analysed using the normal methods. The used pyrolysis tube was disposed of by cautiously placing it in a bath of 2 M HCl behind a safety shield (*CAUTION*: this results in a vigorous reaction accompanied by explosive ignition of the pyrophoric gases evolved. This is thought to be due to low molecular weight silanes formed by hydrolysis of the magnesium silicide).

[‡] For comparison, FVP of each substrate was examined without magnesium at 600 °C and this led to formation of the previously reported (refs. 9, 13) dehydrohalogenation products for **1** (R = 2-Me), **6**, **13** (R = 2-Me) and **15** and to recovery of unchanged starting material in all other cases.

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