The reaction of benzotrihalides and benzal halides with magnesium. Synthetic and mechanistic studies

E.C. Ashby * and Dheya M. Al-Fekri

School of Chemistry, Georgia Institute of Technology, Atlanta, GA 30332 (U.S.A.)

(Received November 6th, 1989)

Abstract

The benzotrihalides ($PhCX_3$) where X = Cl, Br, and F were allowed to react with magnesium in THF at room temperature. When the halide was chloride or bromide, the trihalide gave diphenylacetylene in high yield in addition to several minor products which were identified. No reaction was observed when the halide was fluoride. When the corresponding dichloride was allowed to react with magnesium in THF, stilbene was formed as the major product. The possible mechanisms for these reactions are discussed.

It is known [1], but not highly publicized, that phenyl Grignard reagents containing a CF_3 group in the *ortho*, *meta*, or *para* positions to chlorine or bromine, can suddenly explode on preparation. It is important to emphasize the danger in making such Grignard reagents since the preparation of *p*-triflouromethylphenyl-magnesium chloride (eq. 1) on a commercial scale resulted in a violent explosion

$$F_3C - \langle\bigcirc\rangle - Cl + Mg \xrightarrow{\text{THF}} F_3C - \langle\bigcirc\rangle - MgCl \qquad (1)$$
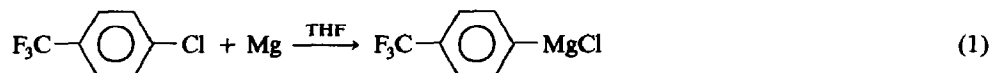
resulting in the destruction of a chemical plant and loss of life [2]. In this report, we have attempted to study the reason for the unpredictability in the preparation of the *p*-trifluoromethylphenyl Grignard reagents by first studying the reactions of benzo-trihalides ($PhCX_3$, where X = F, Cl and Br) with magnesium in THF. Our reasoning is based on the supposition that the CF_3 group itself can react with magnesium, when magnesium is sufficiently activated, as can happen during the reaction of the *p*-chlorophenyl group with magnesium.

There is some prior art in the area of geminal di- and tri-Grignard reagents. In most cases, the preparation of Grignard reagents from alkyl or aryl halides and magnesium is a relatively simple operation; however, the preparation of Grignard reagents from polyhalides, especially those with two or more halogen atoms on the same carbon atom, have presented serious problems [3]. Concerning the aliphatic

polyhalides, Emschwiller [4] showed that methylene iodide and bromide react with magnesium according to eq. 2. The yield was low in both cases (< 15%) and the

$$CH_2X_2 + 2Mg \longrightarrow CH_2(MgX)_2 \qquad (2)$$

addition of water to the organomagnesium product produced methane. In 1932, Chang and Tseng [5] described the preparation of $H_2C(MgI)_2$ in 10% yield. In another article [6] Tseng reported that $CHCl_3$, $CHBr_3$ and CCl_4 do not react with magnesium in ethyl ether even in the presence of I_2, MeI, or EtI. While it was also reported by the same author [6] that iodoform reacts with magnesium to give acetylene, byproducts like CH_2I_2, MeI, MeOH, CH_2O, and HCO_2H could not be identified after hydrolysis of the reaction product. They postulated the formation of a tri-magnesium compound which reacts immediately with more CHI_3 to produce acetylene. On the other hand, Fidler [7] has reported the preparation of the same compounds $(CH_2(MgX)_2)$, but claims that they are reactive only towards H_2O. Concerning specifically the preparation of $CH_2(MgX)_2$, where X = Cl and Br, both Bertini [8] and Bickelhaupt [9] have provided sufficient evidence for the existence of such Grignard reagents in ether solvents when prepared from Mg(Hg) amalgams.

Concerning aromatic compounds containing a polyhaloalkyl group attached directly to the aromatic ring, Chang and Tseng have reported [10] that neither benzal chloride $(PhCHCl_2)$ nor benzotrichloride $(PhCCl_3)$ reacts with magnesium in diethyl ether in the absence of a catalyst. Reaction does take place in the presence of a small amount of EtMgI forming a yellowish amorphous substance which is apparently a mixture of hydrocarbons of high molecular weight. When benzotrichloride was allowed to react with ethylmagnesium bromide in ether, tetrachlorobibenzyl was identified as the sole product [11]. Tris-trimethylsilyl derivatives of benzotrichloride and other aliphatic and aromatic polyhalides were prepared by the reaction of the polyhalo compound with magnesium in THF using trimethylsilylchloride as a co-solvent. The authors concluded, based on the trisilyl products, that tri-Grignard reagents of the corresponding polyhalides were formed [12]. Although some geminal di- and tri-Grignard reagents have been reported, these have been prepared by metal-halogen and metalhydrogen exchange reactions and not by the reaction of an RX Compound with magnesium [13]. It is not surprising that the reaction of benzotrifluoride with magnesium does not appear in the literature due to the unreactive nature of the trifluoromethyl group [14].
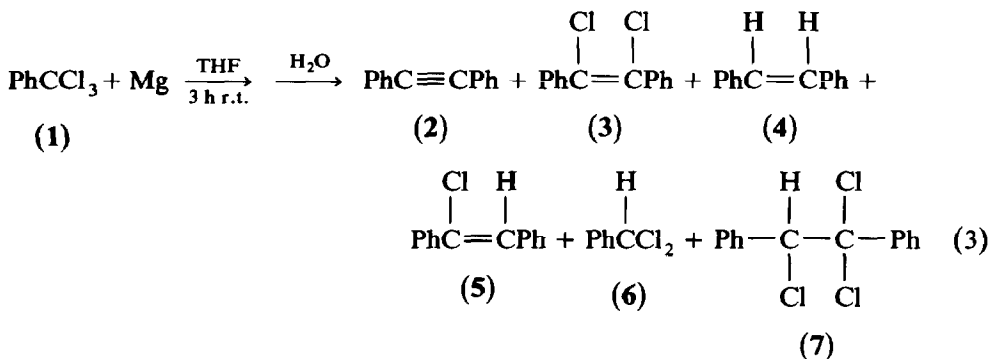
In this report we would like to present evidence for the first time that benzotrihalides $(PhCX_3$, where X = Cl, Br) and benzal chloride $(PhCHCl_2)$ do react with magnesium under conditions normally used for the preparation of Grignard reagents in THF and in diethyl ether to form organic products in high yield. It was not our intention to establish conditions under which the intermediate mono Grignard could be formed because such Grignards would probably be unstable above $-40°C$. On the other hand, we did want to establish the nature of the products formed under the conditions normally used (room temperature) to prepare Grignard reagents in an attempt to determine why the reaction represented by eq. 1 exploded when carried out at room temperature to $70°C$. Having identified the products produced in the reactions reported herein we are pleased to report: (1) that a reasonable explanation for the explosion has been found and (2) that the reactions studied provide a number of interesting synthetic possibilities.

Results and discussion

Each of the benzotrihalides was allowed to react with magnesium in THF and then the same reaction repeated in the presence of ethyl bromide as an entrainment reagent since these reactions were reported to proceed with so much difficulty. The same strategy was applied to the reactions of benzal chloride with magnesium. All reactions were carried out under nitrogen, using only highly purified solvents (distillation over benzophenone ketyl), purified reactants (99 + % pure), and magnesium of 99.95% purity. The yields reported are absolute yields except when specified otherwise.

A. Reaction of benzotrichloride with magnesium in THF

Based on the literature reports presented above and the well known fact that solvents can play a significant role in the formation of Grignard reagents [15], the reaction of benzotrichloride (1) with magnesium was conducted in THF using different ratios of magnesium to the polyhalide under very dry and oxygen free conditions. The major product isolated in this reaction (at all stoichiometries studied) was diphenylacetylene (2); however, five other products (3–7) were isolated and identified (eq. 3). Products 6 and 7 were formed only when an insufficient

$$
\underset{(1)}{PhCCl_3} + Mg \xrightarrow[3\ h\ r.t.]{THF} \xrightarrow{H_2O} \underset{(2)}{PhC\equiv CPh} + \underset{(3)}{\overset{Cl\ \ Cl}{PhC=CPh}} + \underset{(4)}{\overset{H\ \ H}{PhC=CPh}} +
$$

$$
\underset{(5)}{\overset{Cl\ \ H}{PhC=CPh}} + \underset{(6)}{\overset{H}{PhCCl_2}} + \underset{(7)}{\overset{H\ \ Cl}{Ph-\underset{Cl\ \ Cl}{C-C}-Ph}} \quad (3)
$$

amount of magnesium was used to react with all of the benzotrichloride. All products were identified by 300 MHz NMR and MS analysis and also by comparison with authentic samples [16]. Very surprisingly and in contrast to earlier reports involving diethyl ether, the reaction in THF had a very short induction period and indeed sometimes occurred immediately on combination of the reagents. The reaction was accompanied by heat release and color changes from colorless to yellowish, to dark orange, to dark gray, over a 30 min period. When the exothermic nature of the reaction ceased, it was stirred for an additional 3 h at room temperature in order to insure complete reaction. The experimental conditions and the products obtained in this reaction at various stoichiometries of benzotrichloride and magnesium can be found in Table 1. The stoichiometry was studied in order to determine its effect on product formation and hence the true stoichiometry of the reaction.

From Table 1 (exps. 1 and 2), it can be seen that using a ratio of Mg/benzotrichloride of 1.0 results in an insufficient amount of magnesium for complete reaction which resulted in recovery of approximately 2/3 of the starting material with compound 2 still being the major product. When using a Mg/benzotrichloride
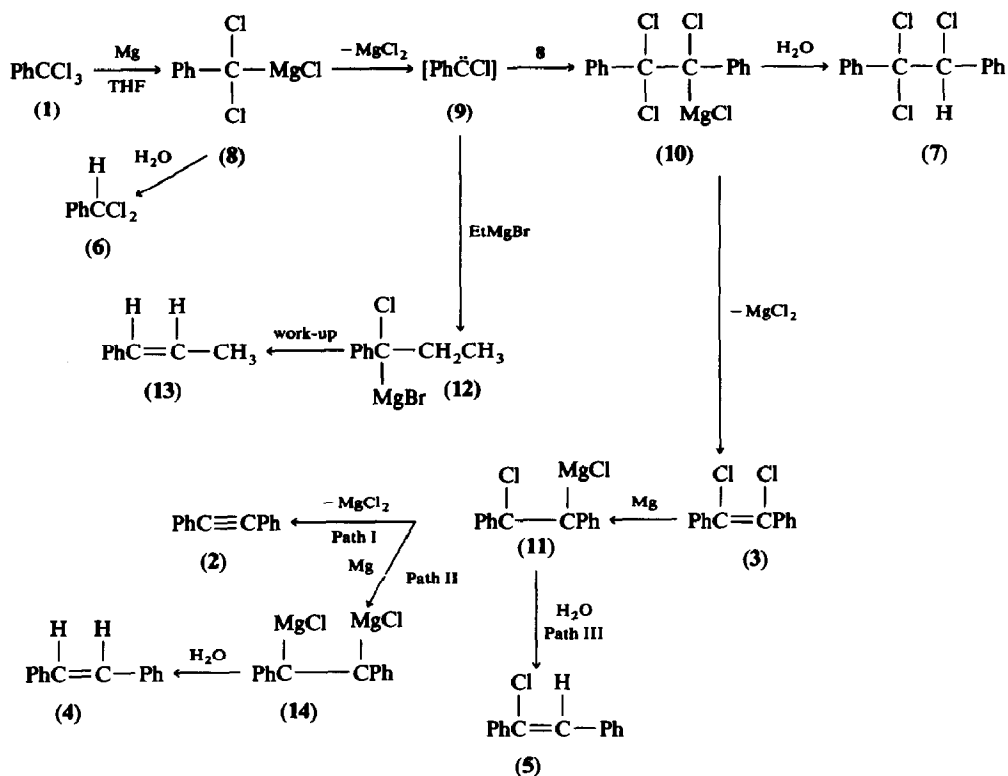
Table 1

Reaction of benzotrichloride (1) with magnesium in THF [a]

Exp.	Ratio Mg/1	Solvent	Product (% yield)						
			PhCCl$_3$ (1)	PhC≡CPh (2)	$\begin{array}{cc} Cl & Cl \\ \| & \| \\ \end{array}$ PhC=CPh (3)	$\begin{array}{cc} H & H \\ \| & \| \\ \end{array}$ PhC=CPh (4)	$\begin{array}{cc} Cl & H \\ \| & \| \\ \end{array}$ PhC=CPh (5)	$\begin{array}{c} H \\ \| \\ \end{array}$ PhCCl$_2$ (6)	$\begin{array}{cc} Cl & Cl \\ \| & \| \\ Ph-C & -C-Ph \\ \| & \| \\ Cl & H \end{array}$ (7)
1	1.0	THF	59.5	65.7	10.7	2.1	16.7	3.9	0.1
2	1.0 [b]	THF	68.3	69.6	9.2	0.3	14.7	2.9	3.4
3	3.15	THF	0.0	69.6	4.9	19.3	0.0	0.0	0.0
4	5.0 [c]	THF	0.0	69.6	4.2	14.6	3.2	0.0	0.0
5	5.0 [a,d]	THF	0.0	92.2	0.0	7.6	0.0	0.0	0.0
6	5.0	Et$_2$O	100	–	–	–	–	–	–
7	5.0 [a]	Et$_2$O	100	–	–	–	–	–	–

[a] All reactions were carried out at room temperature except exp. 5 which was carried out at 60°C and all reactions were stirred for an additional 3 h after heat evolution ceased except exp. 7 which was stirred for 66 h. All yields were determined by GC. No external heat was applied in these reactions. Reaction is exothermic to about 35°C. Reaction temperature depends on rate of addition of PhCCl$_3$; the faster the rate of products 2–7 with recovered starting material calculated separately. [b] All reactions carried out by PhCCl$_3$ addition to magnesium, except exp. 2 where the magnesium was added to PhCCl$_3$. [c] Recovered magnesium shows that the actual reaction ratio was Mg/1 1.63. [d] PhCH$_2$CH$_2$Ph was also formed (2.1% yield).

ratio of 3 or greater in THF (exps. 3–5), the starting material reacted completely and compounds 3, 5–7 reacted further with magnesium so that their presence is diminished in the product mixture. These results indicate that the actual amount of magnesium that reacts is important in determining the products isolated and in the elucidation of the reaction mechanism. Recovery of the unreacted magnesium used in exp. 4 shows that the actual ratio of Mg/benzotrichloride in the reaction is 1.63. To rationalize the formation of diphenylacetylene (2), we believe that magnesium first reacts with one of the three halogen atoms in the starting material to give the α,α-dihalomethylmagnesium intermediate 8 (Scheme 1) which can be considered as the precursor to the carbene 9. Quenching the reaction mixture at an early stage enabled us to identify benzal chloride (6) as a byproduct. Also benzal chloride is a byproduct in exps. 1 and 2 when the reaction was carried out using an insufficient amount of magnesium. The lithium analog of intermediate 8 has been prepared from benzotrichloride and n-butyllithium at $-100°$C [17]. It was shown that the product produces a carbene species upon loss of LiCl resulting in the formation of phenylchlorocarbene. Therefore it is suggested that intermediate 8, upon loss of MgCl$_2$, forms the phenylchlorocarbene intermediate 9. This carbene can then undergo insertion into the C–Mg bond of intermediate 8 to give intermediate 10 which can lose a molecule of MgCl$_2$ to form the key intermediate 3 which accounts for the formation of product 2, 4, and 5. Further reaction of 3 with another mol of magnesium can give intermediate 11 which is the precursor to the major product 2. Intermediate 11 can not only lose MgCl$_2$ to form 2, but it can also react with another mol of magnesium to form 14 and subsequently product 4 upon hydrolysis. There also is precedent in the literature involving elimination of a vicinal halogen and a Grignard moiety to form an olefin [18].

PhCCl₃ —Mg/THF→ Ph—C(Cl)(Cl)—MgCl —(−MgCl₂)→ [PhC̈Cl] —8→ Ph—C(Cl)(Cl)—C(Cl)(MgCl)—Ph —H₂O→ Ph—C(Cl)(Cl)—C(Cl)(H)—Ph

(1) (9) (10) (7)

H—PhCCl₂ (6) ← H₂O / (8)

[PhC̈Cl] ↓ EtMgBr

PhC(Cl)=C(CH₃) ... PhC(Cl)—CH₂CH₃ (MgBr) (12) —work-up→ PhC(H)=C(H)—CH₃ (13)

(10) ↓ −MgCl₂

PhC(Cl)=CPh(MgCl) (11) ← Mg ← PhC(Cl)=CPh(Cl) (3)

PhC≡CPh (2) ← (−MgCl₂, Path I) — (11)

Mg / Path II ↓

PhC(MgCl)—CPh(MgCl) (14) —H₂O→ PhC(H)=C(H)—Ph (4)

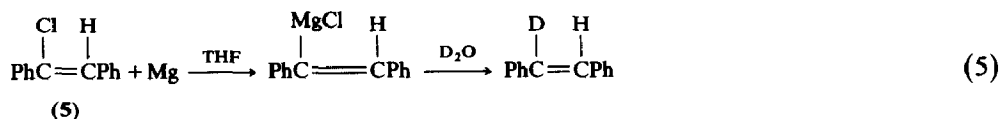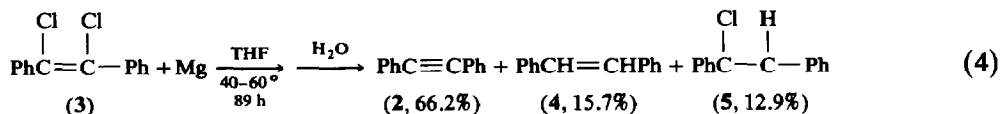(11) ↓ H₂O Path III

PhC(Cl)=C(H)—Ph (5)

Scheme 1. Proposed mechanism for the reaction of benzotrichloride with magnesium in THF at room temperature.

The data presented in Table 1 substantiate the proposed pathway (Scheme 1) with regard to the magnesium/benzotrichloride ratio. According to the above pathway, 3 mol of magnesium are required to produce one mol of diphenylacetylene. In other words, 1.5 mol of Mg is needed to react with one mol of compound 1 to produce 0.5 mol of 2. However, 2 mol of magnesium are needed per one mol of 1 to produce 0.5 mol of compound 4, stilbene. Based on the actual percentage yield ratio of products 2 and 4 (exp. 4), the statistical consumption of magnesium is 1.56 mol per mol of benzotrichloride. The actual ratio of Mg/benzotrichloride based on recovered magnesium (exp. 4), was found to 1.63. The amount of compound 3 formed depends not only on the Mg/benzotrichloride ratio, but also depends on the reaction temperature and method of activation of magnesium. When benzotrichloride was allowed to react with a five-fold excess of magnesium at 60°C, there was a substantial decrease in the formation of products 3–7 and the yield of 2 increased accordingly (exp. 5). The implication of exp. 5 is that at the higher temperature (60°C), 11 loses $MgCl_2$ (Path I) to produce diphenylacetylene (2) faster than it reacts with magnesium via Path II.

Deuterium analysis of the products of exp. 5 after hydrolysis with D_2O indicated the presence of 39.2% monodeuterio stilbene and 15.0% dideuterio stilbene relative to protio stilbene. These results are consistent with the proposed existence of intermediate 14 in Scheme 1; however, the deuterium analysis also suggests that stilbene can be formed by other pathways which will be addressed in Section E.

Further evidence for Scheme 1 was obtained from the reaction of excess magnesium with 1,2-dichlorostilbene (3) [19]. Diphenylacetylene was again obtained as the major product of this reaction (eq. 4) in addition to stilbene (4) and 1-chlorostil-
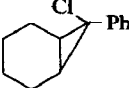
$$\underset{\substack{| \quad | \\ (3)}}{\overset{\text{Cl} \quad \text{Cl}}{\underset{| \quad |}{\text{PhC}=\text{C}-\text{Ph}}}} + \text{Mg} \xrightarrow[40-60°]{\text{THF}} \xrightarrow[\substack{89\,h}]{\text{H}_2\text{O}} \text{PhC}\equiv\text{CPh} + \text{PhCH}=\text{CHPh} + \underset{\substack{| \quad | \\ (5, 12.9\%)}}{\overset{\text{Cl} \quad \text{H}}{\underset{| \quad |}{\text{PhC}-\text{C}-\text{Ph}}}} \qquad (4)$$
$$\qquad\qquad\qquad\qquad (2, 66.2\%) \quad (4, 15.7\%)$$

$$\underset{\substack{| \quad | \\ (5)}}{\overset{\text{Cl} \quad \text{H}}{\underset{| \quad |}{\text{PhC}=\text{CPh}}}} + \text{Mg} \xrightarrow{\text{THF}} \underset{\substack{| \quad | }}{\overset{\text{MgCl} \quad \text{H}}{\underset{| \quad |}{\text{PhC}=\!=\!=\text{CPh}}}} \xrightarrow{\text{D}_2\text{O}} \underset{\substack{| \quad |}}{\overset{\text{D} \quad \text{H}}{\underset{| \quad |}{\text{PhC}=\text{CPh}}}} \qquad (5)$$
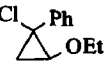
bene (5). When compound 5 was prepared independently [20] and allowed to react with excess magnesium, it gave predominantly stilbene (eq. 5). The reaction mixture was hydrolysed with D_2O and mass spectral analysis showed the main product to be PhCH=CDPh formed in 80.7% yield with 81.7% deuterium incorporation. These results indicate that intermediate 3 is the true precursor of products 2, 4, and 5. An additional reason for carrying out the reaction of 5 with magnesium was to test the possibility of elimination of a molecule of HMgCl to produce compound 2. No diphenylacetylene was observed in this reaction which was carried out in THF using EtBr to activate the magnesium, therefore it does not appear that MgCl and H on adjacent carbon atoms of an alkene eliminate HMgCl to form an alkyne.

Obviously if a carbene species is involved in this reaction it might be trapped by an olefin to give a cyclopropane derivative. The reaction of benzotrichloride with magnesium in THF in the presence of three different olefins was carried out and the results are shown in Table 2. Isolation of the expected cyclopropane adducts establishes the intermediacy of a carbene. The cyclopropane adducts were identified by GC/MS analysis in addition to comparison of the proton NMR spectra with those of the known compounds [20].
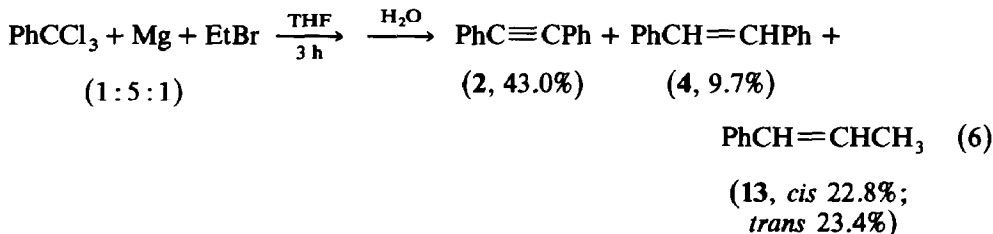
Table 2

Reaction of benzotrichloride with magnesium in the presence of olefin [a]

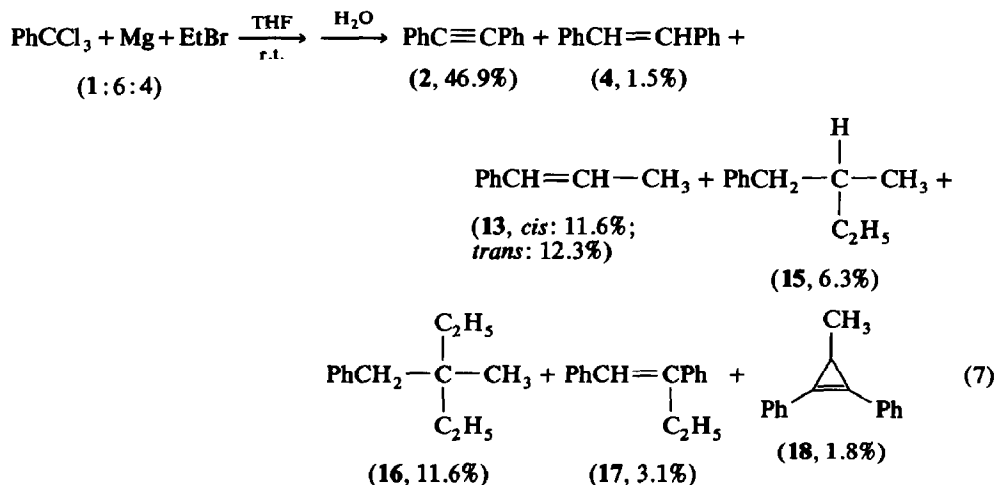| Exp.	Substrate	Olefin	Olefin/1	Products (% yield)
1	PhCCl$_3$(1)	⬡ |	5	Cl⟩–Ph ⬡ (0.4) [b]
2	(1)	=⟨OEt	10	Cl⟩Ph △OEt (3.8) [c]
3	(1)	⟩=⟨	10	Cl⟩Ph △ (12.7) [d]

[a] All reactions were carried out for 3 h in THF solvent at a Mg/1 ratio of 5. [b] Compounds 2 (62.65), 4 (14.6), 3 (10.3%). [c] Compounds 2 (63.53), 4 (7.44), 3 (4.8%). [d] Compounds 2 (64), 4 (7.41%), 5 (trace).

B. Reaction of benzotrichloride with magnesium in the presence of ethyl bromide

The reaction of benzotrichloride with magnesium in the presence of ethyl bromide was studied since equimolar amounts of ethyl bromide are often used in Grignard formation reactions when the starting halide is unreactive (such as in the case under consideration (eq. 1). This reaction took a similar course (Scheme 1) to the reaction in the absence of ethyl bromide except that propenylbenzene (13) is formed as a major product (eq. 6). As shown in Scheme 1, intermediate 9 can

$$PhCCl_3 + Mg + EtBr \xrightarrow[3\,h]{THF} \xrightarrow{H_2O} PhC\equiv CPh + PhCH=CHPh +$$

$$(1:5:1) \qquad\qquad (2, 43.0\%) \qquad (4, 9.7\%)$$

$$PhCH=CHCH_3 \quad (6)$$

$$(13, \text{ cis } 22.8\%;$$
$$\text{trans } 23.4\%)$$

insert into the C–Mg bond of ethylmagnesium bromide to give intermediate 12 which upon hydrolysis and work-up gives the observed product 13, propenylbenzene. It is also possible that 13 is formed from 12 via a carbene intermediate followed by rearrangement. A comparison of this reaction with exp. 4 in Table 1, shows that the new product 13 is formed mainly at the expense of diphenylacetylene (2). This realization prompted us to use an excess of ethyl bromide in a similar reaction in an attempt to optimize the yield of 13. Unfortunately, when a four-fold excess of ethyl bromide was used, other side reactions occurred; however, the main product 2 was still formed in 47% yield (eq. 7). Therefore using an excess of ethyl bromide results only in the reaction becoming more complex as seen by the
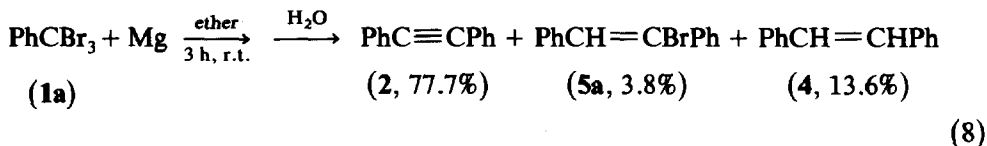
$$PhCCl_3 + Mg + EtBr \xrightarrow[r.t.]{THF} \xrightarrow{H_2O} PhC\equiv CPh + PhCH=CHPh +$$

$$(1:6:4) \qquad\qquad (2, 46.9\%) \qquad (4, 1.5\%)$$

$$PhCH=CH-CH_3 + PhCH_2-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle C_2H_5}{|}}{C}}-CH_3 +$$

$$(13, \text{ cis: } 11.6\%; \qquad\qquad (15, 6.3\%)$$
$$\text{trans: } 12.3\%)$$

$$PhCH_2-\overset{\overset{\displaystyle C_2H_5}{|}}{\underset{\underset{\displaystyle C_2H_5}{|}}{C}}-CH_3 + PhCH=\overset{}{\underset{\underset{\displaystyle C_2H_5}{|}}{C}}Ph \quad + \quad \text{(18, 1.8\%)} \qquad (7)$$

$$(16, 11.6\%) \qquad\qquad (17, 3.1\%)$$

formation of several additional byproducts (15–18) as a result of insertion and addition reactions. Addition of Grignard reagents to a double bond, as in the formation of product 15, or to a triple bond, as in the case of the formation of products 16 and 17, is well known [18].

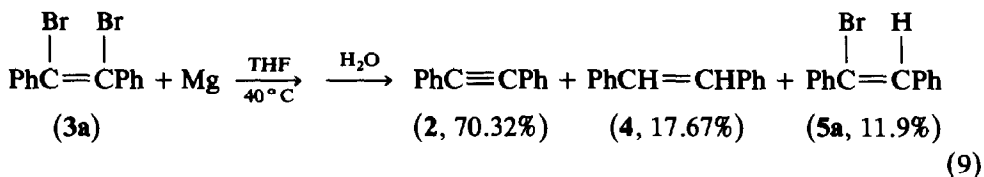### C. Reaction of benzotribromide with magnesium in ether

When benzotribromide (1a) in THF was injected in the GLC for response factor determination, it was observed that this compound is not stable in THF and

decomposes rapidly to benzal bromide ($PhCHBr_2$) plus other unidentified products. Accordingly the reaction of benzotribromide with magnesium was conducted in diethyl ether, a solvent in which it is much more stable.

It appears that the reaction of benzotribromide with magnesium in ether follows a similar reaction sequence as observed for benzotrichloride in THF (Scheme 1) although the reaction of benzotribromide was more exothermic. The major product again is diphenylacetylene (2) (eq. 8); however, α,β-dibromostilbene ($PhCBr=CBrPh$, 3a) was not observed in the product mixture. Compound 3a however was prepared

$$PhCBr_3 + Mg \xrightarrow[3\ h,\ r.t.]{ether} \xrightarrow{H_2O} PhC\equiv CPh + PhCH=CBrPh + PhCH=CHPh$$

(1a)　　　　　　　　　　　　　(2, 77.7%)　　(5a, 3.8%)　　(4, 13.6%)
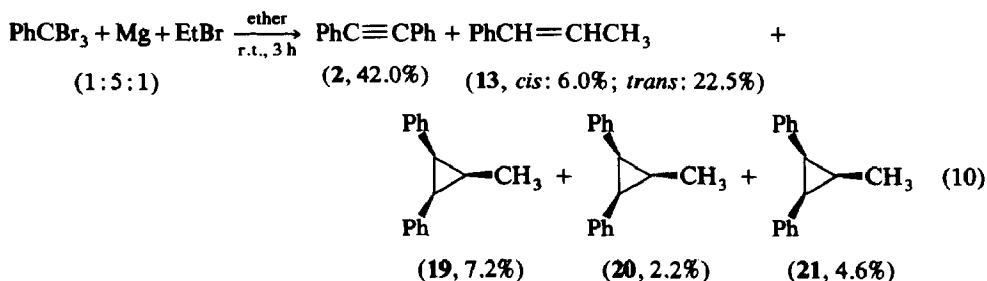
$$(8)$$

in 60% yield by the reaction of benzotribromide with sodium iodide in refluxing acetone for 2 h. (The analogous reaction of benzotrichloride resulted in recovery of the starting material almost quantitatively.) This reaction was originally attempted for the preparation of benzotriiodide from benzotribromide and sodium iodide; however, α,β-dibromostilbene was identified as the sole product. When α,β-dibromostilbene (3a) was allowed to react with magnesium in THF for 17 h using a small amount of ethyl bromide as an activator, 97% of the starting material reacted and the following products were observed (eq. 9). The formation of 2 in such high yield indicates a similar transformation discussed earlier, $3 \rightarrow 11$ followed by the formation of products 2, 4 and 5.

$$\begin{matrix} Br & Br & & & & & & & Br & H \\ | & | & & & & & & & | & | \\ PhC & = CPh \end{matrix} + Mg \xrightarrow[40°C]{THF} \xrightarrow{H_2O} PhC\equiv CPh + PhCH=CHPh + PhC=CPh$$

(3a)　　　　　　　　　　　　(2, 70.32%)　　(4, 17.67%)　　(5a, 11.9%)

$$(9)$$

D. Reaction of benzotribromide with magnesium in the presence of ethyl bromide

In the presence of one equivalent of ethyl bromide, benzotribromide reacts with magnesium to give phenylbromocarbene (9a) which reacts with ethylmagnesium bromide, in a fashion similar to that proposed earlier in the reaction of benzotrichloride to form propenylbenzene [22] (13) (eq. 10). The three cyclopropanes

$$PhCBr_3 + Mg + EtBr \xrightarrow[r.t.,\ 3\ h]{ether} PhC\equiv CPh + PhCH=CHCH_3　　　　+$$

(1:5:1)　　　　　　　(2, 42.0%)　　(13, *cis*: 6.0%; *trans*: 22.5%)

(19, 7.2%)　　(20, 2.2%)　　(21, 4.6%)

(19–21) were assigned structures based on GC/MS and ^{1}H-NMR analyses [18]. These compounds could be formed by in situ trapping of phenylbromocarbene by compound 13, followed by reaction of the resulting 1-bromo-1,2-diphenyl-3-methyl-

cyclopropanes with magnesium to form the corresponding Grignard compounds followed by hydrolysis of the reaction mixture. A comparison of eq. 10 with eq. 7 shows that similar cyclopropanes were also formed; however, these compounds underwent a rapid loss of HCl to give compound 18 (eq. 7). No cyclopropenes were observed in the reactions of benzotribromide with magnesium.

In a control experiment, when the above reaction (eq. 10) was repeated and hydrolysis accomplished with D_2O, no deuterium was observed in any of the cyclopropanes (19–21). This result would indicate formation of the protio carbene [PhC̈H] from the reaction of $PhCBr_3$ with magnesium in ether. Single electron transfer from magnesium to $PhCBr_3$ followed by loss of Br^- would produce $PhCBr_2 \cdot$ which can abstract a hydrogen atom from the solvent to form $PhCBr_2H$. This $PhCBr_2H$ can then form the intermediate phenylcarbene (PhC̈H). This suggestion will be discussed further in Section E.

Table 3 shows the conditions under which attempts were made to react benzotrifluoride with magnesium. It was not too surprising that benzotrifluoride failed to react with magnesium in THF under a variety of conditions involving various methods of magnesium activation (Table 3) since carbon fluorine compounds normally do not react with magnesium in ether solvents. However, we still have not dismissed the possibility that benzotrifluoride can react with magnesium activated during a Grignard preparation as in the case of the reaction represented by eq. 1. This position is further strengthened when one considers that although an alkyl fluoride does not react with magnesium activated in the usual ways, Rieke [24] has shown that specially activated magnesium will react with an alkyl fluoride. Furthermore the explosions experienced in this reaction represented by eq. 1 did not take place in every case, but only occasionally and unpredictably. Because of the extreme violence of the explosions experienced earlier [1], we decided not to pursue reactions of benzotrifluoride with magnesium in THF under more forcing conditions. In any case our best analysis suggests that like the CCl_3 and CBr_3 group attached to a phenyl ring the CF_3 group can also react, albeit with more difficulty and uncertainty, however when the reaction between the CF_3 group and magnesium proceeds, in the presence of ethyl bromide as the entrainment agent, PhC≡CPh and PhCH=CHCH_3 and Ph(H)C=C(H)Ph are formed which can polymerize, using the Grignard as catalyst, and hence produce a run-away reaction.

In conclusion, the benzotrihalides (X = Cl, Br) do react with magnesium smoothly in ether solvents to give the mono-Grignard reagent $PhCX_2MgX$, which collapses to form a phenylhalocarbene which inserts into another molecule of the Grignard reagent to give product 10 which further reacts to produce products 2–5. The

Table 3

Experimental conditions for reaction of benzotrifluoride (39) with magnesium in THF

Exp.	Ratio Mg/39	Relaxation		Mg activation	Product	Recovered 39
		Temp. ($^\circ$C)	Time (h)			
1	4	67	24	EtBr	–	Quantitative
2	2.4	60	55	EtBr ^{a}	–	Quantitative
3	5	70	64	EtBr	–	Quantitative
4	5.2	60	51.5	EtBr,PhBr	PhPh (<1%)	Quantitative

^{a} Sonication used to activate the magnesium metal.

reactions of the benzotrihalides with magnesium in the presence of other Grignard reagents (EtMgBr) results in the formation of **2** and **13** as the major products. Propenylbenzene (**13**) is formed by insertion of the carbene into the C–Mg bond of the EtMgBr followed by dehydrohalogenation in the work-up.
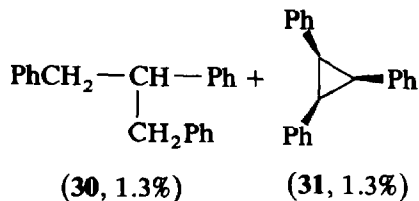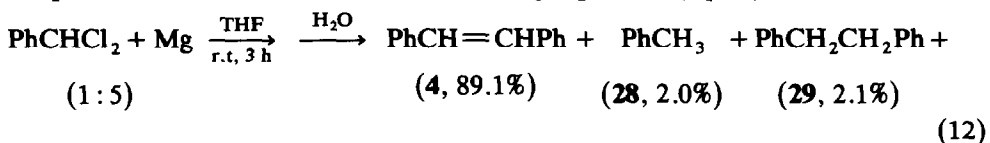
E. Reaction of benzal chloride (PhCHCl$_2$) with magnesium in THF
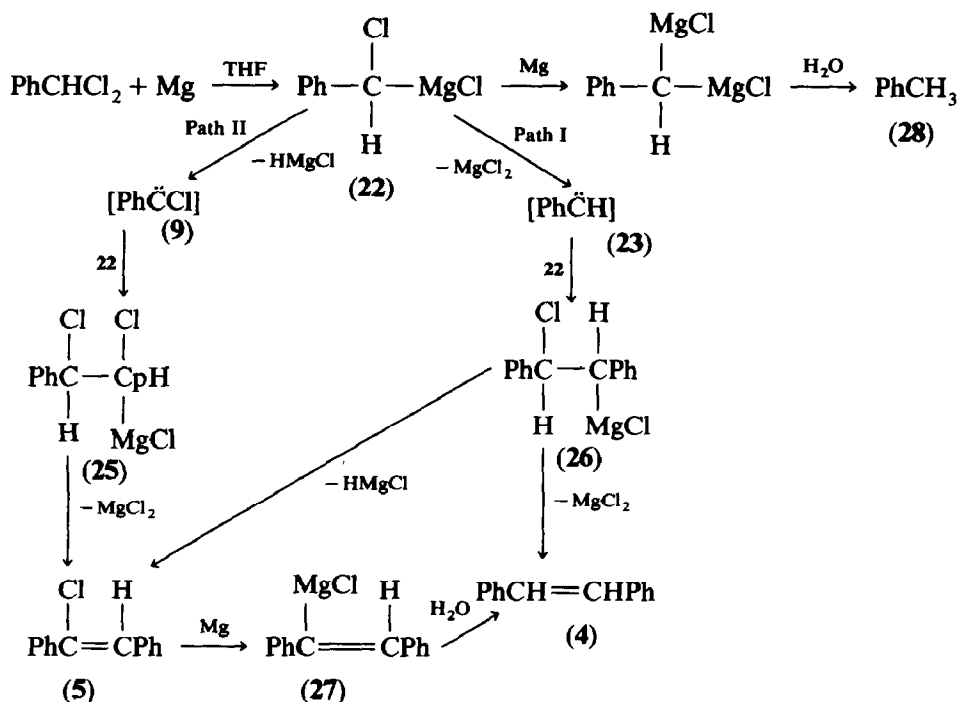
We have suggested that in the reaction of benzotrichloride with magnesium, the first species formed is the mono-Grignard reagent of the polyhalide (a di-halomethylmagnesium compound) which upon expulsion of MgCl$_2$ forms the phenylchlorocarbene (PhCCl). In this reaction neither toluene nor benzyl chloride was observed as a product which fact is indicative of the absence of the di- and tri-Grignard analog of the trihalide at the completion of the reaction. We anticipated that if benzal chloride reacts with magnesium in THF, it would form the mono-Grignard reagent **22**, which upon loss of MgCl$_2$ would form phenylcarbene **23** (eq. 11). However, we also anticipated the possibility of benzal chloride forming the di-Grignard reagent **24** which could be utilized for a variety of synthetic purposes, especially in Wittig like reactions with carbonyl compounds to form olefins (eq. 11). The geminal dimetallic compounds of magnesium, aluminum, and zinc have been previously reported to be prepared by the reactions of methylene bromide and

$$\text{(11)}$$
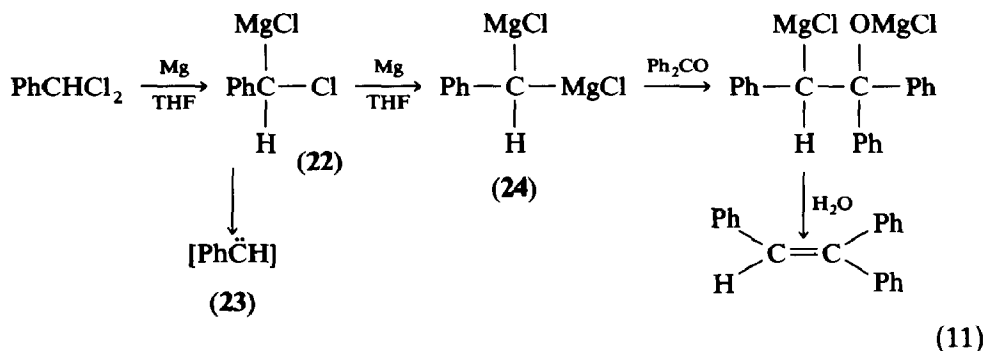
iodide with the corresponding metals [8].

Referring back to the reaction of benzal chloride with magnesium, the first expected intermediate **22** could expel MgCl$_2$ to form the intermediate carbene **23** or it could expel HMgCl to give the phenylchlorocarbene (Scheme 2) as the main product. In addition, the stoichiometry of the reaction (magnesium/benzal chloride ratio) and deuterium incorporation observed on hydrolysis of the product with D$_2$O should help to establish whether the reaction proceeds by Path I or II. Indeed the reaction of benzal chloride with a five-fold excess of magnesium in THF at room temperature for 3 h formed stilbene as the major product (eq. 12).

$$\text{(12)}$$

$$PhCHCl_2 + Mg \xrightarrow{THF} Ph-\underset{\underset{H}{|}}{\overset{\overset{Cl}{|}}{C}}-MgCl \xrightarrow{Mg} Ph-\underset{\underset{H}{|}}{\overset{\overset{MgCl}{|}}{C}}-MgCl \xrightarrow{H_2O} PhCH_3$$

(22)   (28)

Path II $-HMgCl$ Path I $-MgCl_2$

$[Ph\overset{..}{C}Cl]$ $[Ph\overset{..}{C}H]$
(9)   (23)

22   22

$$Ph\underset{\underset{H}{|}}{\overset{\overset{Cl}{|}}{C}}-\underset{\underset{MgCl}{|}}{\overset{\overset{Cl}{|}}{C}}pH$$

(25)

$-MgCl_2$

$$Ph\underset{\underset{H}{|}}{\overset{\overset{Cl}{|}}{C}}-\underset{\underset{MgCl}{|}}{\overset{\overset{H}{|}}{C}}Ph$$

(26)

$-HMgCl$ $-MgCl_2$

$$Ph\underset{|}{\overset{\overset{Cl}{|}}{C}}=\overset{\overset{H}{|}}{C}Ph \xrightarrow{Mg} Ph\overset{\overset{MgCl}{|}}{C}=\overset{\overset{H}{|}}{C}Ph \xrightarrow{H_2O} PhCH=CHPh$$
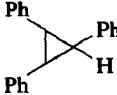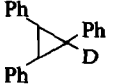
(5)   (27)   (4)

Scheme 2. Proposed mechanism for the reaction of benzal chloride with magnesium in THF.
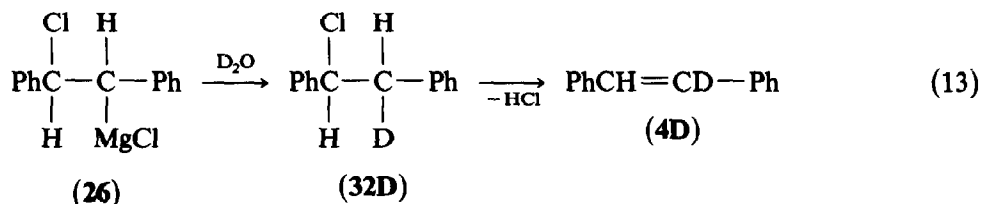
Benzal chloride was found to be less reactive with magnesium in THF than benzotrichloride. In these reactions there is usually at least at 15 min induction period and the reaction needs to be heated gently in order to cause initiation. Once the reaction begins, it is thermally self sustaining. This reaction produced a characteristic color spectrum during the reaction beginning with pale yellow and then proceeding to yellow, then to orange, to dark orange, to pink, to gray, to violet and, at the end of 30 min, the reaction solution turned a deep blue violet color which persisted until the workup at the end of 3 h. The ratio of reacted magnesium to benzalchloride was found experimentally to be 0.97/1.0 which is in agreement with Path I of Scheme 2. If the reaction had taken Path II, then the magnesium/ benzal chloride ratio should have been 1.5/1.0. The reaction was also monitored and samples were taken during the initial stages of the reaction. The predominant product throughout the entirety of the reaction was stilbene. Additionally, benzyl chloride was observed at the beginning of the reaction which indicates that PhC(H)(Cl)MgCl was present before hydrolysis. On the other hand, no diphenyl-acetylene or compound 5 was observed. It is suggested that some of the phenyl-carbene produced in this reaction is trapped by stilbene to give the cyclopropane adduct 31. Moreover this reaction was repeated in the presence of excess 2,3-di-methyl-2-butene and the expected cyclopropane adduct was identified in 6.6% yield in addition to the other expected products (see Experiment). When the reaction mixture represented by eq. 12 was hydrolysed with D_2O, some deuterium incorpora-tion in the products was observed (Table 4). According to the mechanism presented in Scheme 2, no deuterium incorporation should be expected in stilbene if inter-mediate 26 loses $MgCl_2$ to produce stilbene. However some monodeuterio stilbene

Table 4

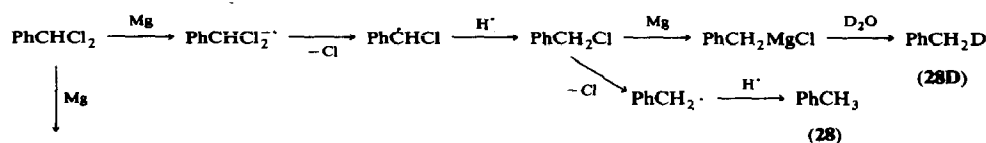Deuterium distribution in the reaction of benzal chloride with magnesium in THF

Product	Yield of protio relative to deuterio compound (%)	Product	Yield of protio relative to deuterio compound (%)
(1) PhCH=CH–Ph	94.7	(3) PhCH$_2$CH–Ph CH$_2$Ph	97.1
PhCH=CD–Ph	5.3		
		PhCH–CH–Ph D CH$_2$Ph	2.5
(2) PhCH$_3$	80.6		
PhCH$_2$D	19.4	(4) PhCH$_2$CH$_2$Ph	100
		PhCHDCH$_2$Ph	0.0
PhCHD$_2$	0.0	(5) [Ph, Ph, Ph, Ph, H triangle]	100
		[Ph, Ph, Ph, Ph, D triangle]	0.0

(5.3%) was observed. This product could arise from the quenching of intermediate **26** to **32** (eq. 13) followed by loss of HCl during the work-up (eq. 12).

$$\underset{(\mathbf{26})}{\overset{\text{Cl H}}{\underset{\text{H MgCl}}{PhC-C-Ph}}} \xrightarrow{D_2O} \underset{(\mathbf{32D})}{\overset{\text{Cl H}}{\underset{\text{H D}}{PhC-C-Ph}}} \xrightarrow[-HCl]{} \underset{(\mathbf{4D})}{PhCH=CD-Ph} \qquad (13)$$

Alternatively some of **4** could have been formed in small amount via Path II by the loss of HMgCl from **26** to **5**, followed by reaction of **5** with magnesium to form **27** which on reaction with D$_2$O would produce **4D**. However, it is clear that most (~ 95%), if not all, of **4** is formed by loss of MgCl$_2$ from **26**.

Since toluene was also formed in the product mixture, the intermediate formation of some di-Grignard reagent of benzal chloride is indicated. However hydrolysis of the reaction mixture with D$_2$O gave no evidence for the presence of PhCHD$_2$ indicative of the di-Grignard intermediate. Deuterium analysis shows only the formation of ~ 19% of PhCH$_2$D which is indicative of the presence of benzylmagnesium chloride. To rationalize the formation of PhCH$_2$D, it is suggested that a radical species is involved. The same rationale would hold for the reaction of benzotrihalide with magnesium to explain the formation of stilbene. Magnesium can donate an electron to benzal chloride to form PhCHCl$_2^-$ which then loses Cl$^-$ to give a radical species PhĊHCl (eq. 14) which can escape the surface of magne-

$$PhCHCl_2 \xrightarrow{Mg} PhCHCl_2^{-\cdot} \xrightarrow[-Cl^-]{} Ph\dot{C}HCl \xrightarrow{H^\cdot} PhCH_2Cl \xrightarrow{Mg} PhCH_2MgCl \xrightarrow{D_2O} PhCH_2D$$
$$\text{(28D)}$$
$$\xrightarrow[-Cl]{} PhCH_2\cdot \xrightarrow{H^\cdot} PhCH_3$$
$$\text{(28)}$$

$$\underset{(\mathbf{23})}{\overset{\text{H}}{\underset{\text{Cl}}{Ph-C-MgCl}}} \xrightarrow{-MgCl_2} [Ph\dot{C}H] + Cl \qquad (14)$$
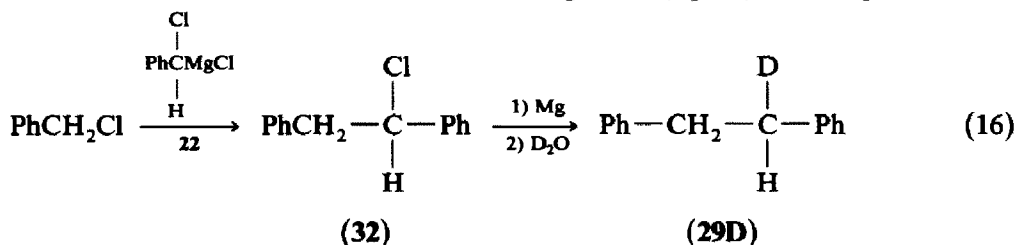
Mg ↓ (from 28)

sium and abstract hydrogen from solvent to form benzyl chloride. This process can be repeated resulting in the formation of toluene, or the α-chlorobenzyl radical can react with magnesium to form the Grignard which on hydrolysis with D_2O forms $PhCH_2D$. Also benzal chloride can react with magnesium to form the Grignard which then loses $MgCl_2$ to give the carbene 23. The formation of radical anions of polyhalo compounds has been suggested by Sargent [25] and others [26] which supports the radical alternative presented here.

Reaction of benzal chloride with magnesium to form bibenzyl can be explained according to eq. 15 and with no deuterium incorporation expected. Also benzyl

$$PhCHCl_2 \xrightarrow{\text{(eq. 14)}} PhCH_2Cl \xrightarrow{\text{Mg}} PhCH_2MgCl \xrightarrow{\text{PhCH}_2Cl} PhCH_2CH_2Ph \qquad (15)$$
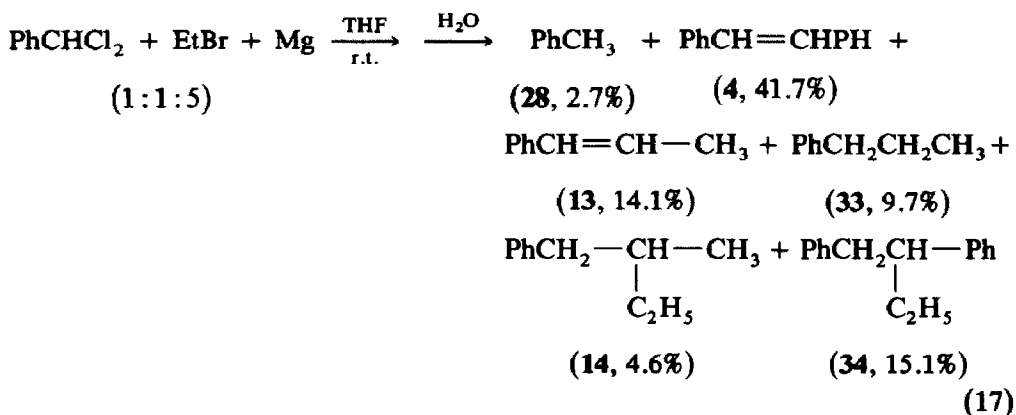
$$(29)$$

chloride could react with intermediate 22 to give 32 (eq. 16) which upon reaction

$$PhCH_2Cl \xrightarrow[22]{\overset{\overset{\displaystyle Cl}{|}}{\underset{\displaystyle H}{\overset{\displaystyle |}{PhCMgCl}}}} PhCH_2 \overset{\overset{\displaystyle Cl}{|}}{\underset{\displaystyle H}{\overset{\displaystyle |}{-C-}}} Ph \xrightarrow[2)\ D_2O]{1)\ Mg} Ph-CH_2 \overset{\overset{\displaystyle D}{|}}{\underset{\displaystyle H}{\overset{\displaystyle |}{-C-}}} Ph \qquad (16)$$

$$(32) \qquad\qquad\qquad (29D)$$

with magnesium and hydrolysis with D_2O would give the monodeuterio bibenzyl 29D. Since there was no deuterium incorporation in the bibenzyl (29) that was formed, this pathway apparently is not important. Therefore the bibenzyl is formed by the reaction represented in eq. 15.

F. Reaction of benzal chloride with magnesium in the presence of ethyl bromide
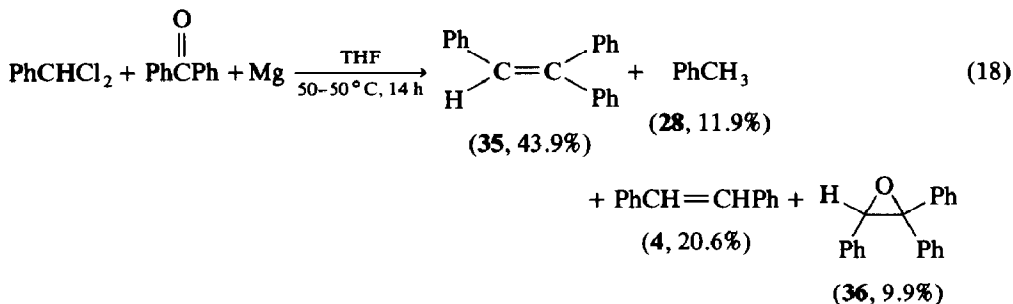
Similar to the reactions of the benzotrihalides with magnesium in the presence of ethyl bromide, benzal chloride was allowed to react with magnesium in the presence of one equivalent of ethyl bromide in THF. Stilbene was produced as the major product in addition to several other compounds (eq. 17). Compound 33 could have

$$PhCHCl_2 + EtBr + Mg \xrightarrow[\text{r.t.}]{\text{THF}} \xrightarrow{\text{H}_2\text{O}} PhCH_3 + PhCH{=}CHPH +$$

$$(1:1:5) \qquad\qquad (28, 2.7\%) \qquad (4, 41.7\%)$$

$$PhCH{=}CH-CH_3 + PhCH_2CH_2CH_3 +$$

$$(13, 14.1\%) \qquad\qquad (33, 9.7\%)$$

$$PhCH_2-\underset{\underset{\displaystyle C_2H_5}{|}}{CH}-CH_3 + PhCH_2\underset{\underset{\displaystyle C_2H_5}{|}}{CH}-Ph$$

$$(14, 4.6\%) \qquad\qquad (34, 15.1\%)$$

$$(17)$$

been formed by the reaction of $PhCH_2MgCl$ (eq. 14) with EtBr and compounds 14 and 34 probably resulted from the addition of EtMgBr across the double bond of 13 and 4 respectively [27,22].

G. Reaction of benzal chloride with magnesium in the presence of benzophenone

Bertini [8] and co-workers in 1970 reported the reaction of benzal bromide with n-amylaldehyde in the presence of Mg/Hg amalgam in ether and isolated the expected olefination product in about 15% yield. They also reacted benzal bromide with Mg/Hg amalgam alone in ether and ether/benzene; however, no product was isolated. On the other hand, we did find that benzal chloride reacts with magnesium in THF and that it also reacts with benzophenone in the presence of magnesium turnings in THF. The expected, triphenylethylene (eq. 18), was formed in 44% yield

$$
PhCHCl_2 + PhCPh + Mg \xrightarrow[50-50°C, 14 h]{THF} \begin{array}{c} Ph \\ H \end{array}C{=}C\begin{array}{c} Ph \\ Ph \end{array} + PhCH_3 \tag{18}
$$

$$
(35, 43.9\%) \qquad (28, 11.9\%)
$$

$$
+ PhCH{=}CHPh + \quad \text{(36, 9.9%)}
$$

$$
(4, 20.6\%)
$$

in addition to the other products expected from the normal reaction of benzal chloride with magnesium. The mechanism of formation of triphenylethylene was previously suggested by Bertini and coworkers [8]. They suggested (eq. 19) that first the mono-Grignard reagent (22) is formed which attacks the carbonyl

$$ (19) $$
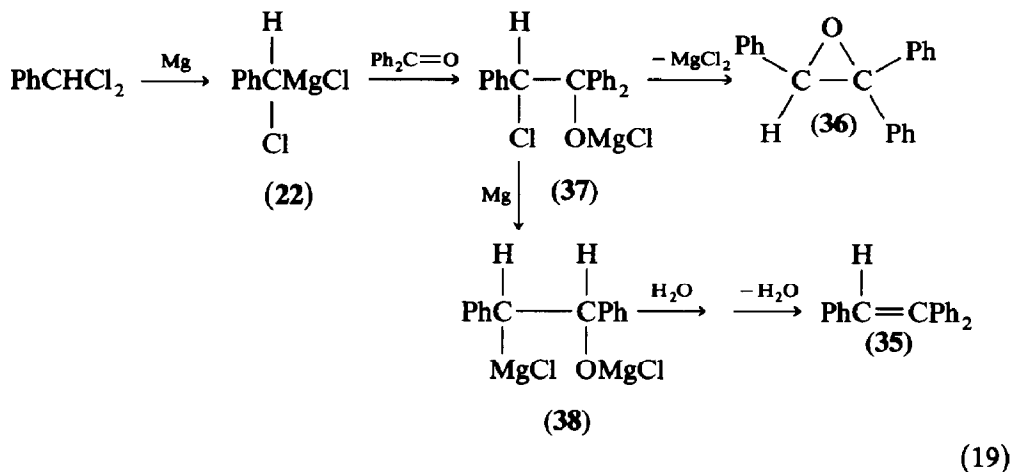
group of benzophenone. Then in a subsequent step, the second halide reacts with magnesium to give the intermediate Grignard (38) which is hydrolyzed under acidic conditions to give the alcohol which readily dehydrates to triphenylethylene. It is probable that compound 36 is formed from compound 37 by attack of the C–OMgCl bond at the backside of the C–Cl bond. We suggested earlier that compound 4 is formed via Scheme 2 and compound 28 is formed via reaction 14. Regardless of the mechanism followed, the final olefin product is Wittig-like. Therefore using the dihalo compound in reactions with magnesium, it is conceivable that one could prepare a variety of important olefinic compounds that might be difficult to prepare by the Wittig reaction. Probably even more important is the fact that several other product types e.g. 2, 3, 5 and 13 can be formed in the reaction of

PhCX$_3$ (where X = Cl and Br) with magnesium. We are presently exploring the optimization of formation of each of these products.

Experimental

Materials

Magnesium turnings (RMC-3, 99.98% purity), was purchased from Reade Manufacturing Company, Inc. and used as received. Acetyl chloride, acetyl bromide, aluminum chloride, aluminum bromide, benzotrichloride, benzal bromide and benzal chloride were purchased from Aldrich and used without further purification. Benzotribromide was prepared by the method reported by Henne and Neuman [28].^{1}H-NMR spectra were recorded on a Bruker WM-300 or Varian T-60 instrument with chemical shifts reported relative to Me$_4$Si in CDCl$_3$. Mass spectral analyses were performed on a Varian MAT-1125 spectrometer. Infrared spectra were recorded on a Perkin Elmer 229 infrared spectrometer.

Quantitative GC analyses were conducted on a Varian Model 3700 coupled to a Varian CDS 111 electronic integrator using a DB1 capillary column. GC yields were determined using internal standards and comparing peak areas which were corrected for response factors. Preparative GC separations were performed on a F & M Model 720 instrument equipped with a thermal conductivity detector. For quantitative GC analyses, a 30 m DB1 capillary column was used to analyze benzotrihalides and their corresponding products. n-Dodecane was used as an internal standard at temperatures of 100 to 290°C using a programmed rate of 20°C per min and 19 psi helium pressure. The same capillary column was also used to analyze benzotrifluoride with n-dodecane as the internal standard at temperatures of 50 to 290°C using a programmed rate of 20°C per min at 19 psi helium pressure.

All products were identified by GC/MS analyses of the reaction mixture. Diphenylacetylene (2) was separated on a 6' × 1/4" Carbowax 20M column at 200–210°C and 30 psi helium pressure with R_t = 7 min. It exhibited an identical ^{1}H-NMR spectrum compared to an authentic sample in CDCl$_3$ (δ 7.51–7.55(4H), δ 7.34–7.29(6H) ppm). In addition, MS and IR analyses were identical to published data [16] and also identical in comparison with authentic samples, α,β-dichlorostilbene, and α-chlorostilbene apparently decomposed during preparative GC separation. Samples obtained from an independent preparation [19,20] were used for spectral identification of these two chlorides and compared to the ones obtained in the reaction mixture.

For propenylbenzene isomers the reaction mixture was subjected to the same GC conditions used for separation of compound 2. The collected low boiling compounds eluted at 3 min were subjected again to preparative GC at 190°C using the same column and both isomers were separated from each other and from toluene. ^{1}H-NMR of propenylbenzene was identical to the published data [23]. All other minor isomers were identified by GC/MS analyses by comparison of their fragmentation patterns with those of authentic samples.

Typical procedure for reaction of α-polyhalotoluenes with magnesium

In a one-neck 100 ml round-bottomed flask equipped with a 3-way stopcock and N$_2$ inlet was introduced magnesium turnings. The flask was flamed under vacuum then cooled to room temperature under a N$_2$ atmosphere. Tetrahydrofuran (THF) 2

ml was introduced into the reaction flask using a dry syringe. In a dry vial was mixed 0.492 g of $PhCCl_3$ (2.52 mmol) and 2 ml THF (Mixture A). Mixture A (0.2 ml) was added to the reaction flask and stirring started at room temperature. On some occasions gentle heating was needed to initiate the reaction. In most cases reaction started immediately and the colorless mixture turned pale yellow to yellow in color. To the rest of Mixture A was added 3.5 ml THF and the resulting solution was added dropwise (using a dry syringe) to the reaction mixture with 5–15 min. The reaction usually continued to be exothermic for about 30 min and the color darkened from yellow to dark orange and eventually dark gray at the end of 3 h in the case of $PhCX_3$ and deep violet blue in the case of $PhCHX_2$ when stirring at room temperature. At the end of the reaction, a slight excess of water or D_2O and sometimes NH_4Cl was added to complete the hydrolysis (NH_4Cl was not used when hydrolysing with D_2O). The top organic THF layer was separated, the residual mixture extracted with ether (3 × 10 ml) and the extracts combined with the THF layer. The resulting solution was then dried over anhydrous $MgSO_4$. The solution was concentrated by evaporation of the solvent followed by addition of an internal standard. The products and yields are indicated in the text.

The order of elution of all products in the GC DB1 capillary column (non-polar) is as follows: Product (retention time, min), $PhCH_3$(2.2); $PhCHCl_2$(7.19); $PhCCl_3$(8.4); $PhC≡CPh$(12); $PhCH=CClPh$(12.13); $PhCH=CHPh$(12.41); $PhCCl=CClPh$(12.83). Diphenylacetylene (2), phenanthrene and anthracene exhibited very similar mass spectrum fragmentation patterns but quite different ^{1}H-NMR spectra.

Reaction of α-polyhalotoluenes with magnesium in the presence of olefin

The same procedure above was followed except that the appropriate olefin was added to the flask with the 2 ml THF added at the beginning of the reaction. The analyses of the cyclopropanes were carried out as follows:

(a) 1-chloro-1-phenyl-2,2,3,3-tetramethylcyclopropane. The title compound was separated from the reaction mixture on a Carbowax 20 M column (6′ × 1/4″), at 210°C, injector and detector temperatures at 250°C, with 40 ml/min. He, with a retention time of 2.6 min. The diphenylacetylene was eluted at 7.4 min and stilbene, at 10.1 min. The cyclopropane was characterized by MS 208 (*M*), and a ^{1}H-NMR spectrum which is identical to that published earlier [21a]. This compound partially decomposed during preparative GC separation.

(b) 1-methyl-2,3-diphenylcyclopropane (19–21). These compounds were separated on the same column as above and under the same conditions except the column temperature was 200°C. The title compounds eluted at 3.5 min for the *trans* isomer and 5.8 min for the *cis*. The mixture (19–21) was characterized by MS 208 (*M*+), and ^{1}H-NMR; δ 1.1 ppm (m), (3H); 1.95; m(d), (3H); 6.93–7.1 ppm (m), (5H) and in comparison with the authentic compounds [29].

(c) 1-phenyl-2,2,3,3-tetramethylcyclopropane. The same conditions as in (b) were used to separate this compound and it was characterized by MS 174 (*M*+), and ^{1}H-NMR which were identical to the spectra of the known compounds [30].

(d) 1,2,3-triphenylcyclopropane (31), 1-chloro-1-phenyl-2-ethoxycyclopropane and 7-chloro-7-phenylbicyclo[4.1.0]heptane. All of the above compounds were characterized by studying their MS fragmentation patterns. The assignments were consistent with the data.

Reaction of benzal chloride with magnesium in the presence of benzophenone

Into a 250 ml round-bottomed flask equipped with a side tube, a condenser and a N_2 inlet, was introduced magnesium turnings (0.3328 g, 0.013 mol). The apparatus was flamed under vacuum and then allowed to cool to room temperature under N_2. To the flask was added 2.5 ml THF, then a mixture of 5 ml THF, $PhCHCl_2$ (0.41 g, 2.55 mmol), and benzophenone, (0.54 g, 3 mmol). The reaction mixture was stirred and heated to 40–50 °C for a total of 14 h. To the dark reaction mixture was added 0.75 ml D_2O and the organic layer separated by extraction with 3×10 ml ether. The extracts were dried over anhydrous $MgSO_4$ and the solvent removed under vacuum. The products were identified by comparison with the commercially available authentic samples, using GC retention times and mass spectral analyses. The products and yields are given in eq. 17.

Synthesis of α,β-dichlorostilbene (3)

The same procedure was followed as described in the literature [30] and the product was obtained in 41.3% isolated yield; (MS, 248 (M^+)).

Synthesis of α,β-dibromostilbene

Into a 250 ml one-neck round-bottomed flask equipped with a condenser and a nitrogen inlet was introduced 100 ml acetone; then 1.0 g (0.003 mol) $PhCBr_3$ was added followed by sodium iodide (1.5 g, 0.01 mol). The flask was heated for 2 h at reflux. The reaction mixture was allowed to cool and to the dark brownish mixture was added 750 ml water. The organic layer was then extracted with ether, dried over anhydrous $MgSO_4$, and the resulting solution was concentrated. The crude mixture gave 0.3 g of 1,2-dibromostilbene representing a 59.2% isolated yield. The MS analysis gave 338 M(14%), 257(13%), 179(30%), 178(100%), 176(7%), 150(6%), 137(5%), 89(16%), 88(15.9%), 77(3%), 76(30%), 65(4%), 51(5%), 44(22%), m.p., 187–190 °C.

Synthesis of α-chlorostilbene (5)

The title compound was prepared according to a known procedure and exhibited identical physical data to that reported earlier [13,16]. The MS gave 214 (M^+) with the characteristic pattern of a monochloro compound [31].

Acknowledgment

References

1 (a) I.C. Appelby, Chem. and Ind., (1971) 120; (b) M.M. Boudakian, K. Othmer, Encyclopedia of Chemical Technology, Wiley Interscience, New York, 3rd Ed., 1978-80, p. 919; (c) L. Bretherick, Handbook of Reactive Chemical Hazards, Butterworths, London, 2nd Ed., 1979, p. 616.

2 Post Tribune; Gary, Indiana; November 6th, 1981.

3 M. Kharasch, O. Reinmuth, Grignard Reactions of Nonmetallic substances, Prentice Hall, Inc., New York, 1954, p. 32.

4 (a) G. Emschwiller, Comptes Rendus, (1926) 183, 665. (b) G. Emschwiller, ibid., (1929) 188, 1555.

5 D.Y. Change, C.-L. Tseng, Trans. Sci. Soc. China, 7 (1932) 239; Chem. Abstr., 26 (1932) 5544.

6 C.-L. Tseng, Natl. Central Univ. Sci. Rept. Ser. A, 1 (1931) No. 1; Chem. Abstr., 26 (1932) 2166.

7 D.A. Fidler, J.R. Jones, S.F. Clark, M. Stange, J. Am. Chem. Soc., 77 (1955) 6634.

8 F. Bertini, P. Grasseli, G. Zubiani, G. Cainelli, Tetrahedron, 26 (1970) 1281, and ref. cited therein.

9 F. Bickelhaupt, J.W. Bruin, J. Organomet. Chem., 288 (1985) 13.

10 D.Y. Change, C.-L. Tseng, Trans. Sci. Soc. China, 7 (1932) 239; Chem. Abstr., 26 (1932) 5544.

11 G. Sanna, Rend. Seminar Facolta Sci., Univ. Cagliari, 5 (1935) 76.

12 R.L. Merker, M.J. Scott, J. Am. Chem. Soc., 85 (1965) 2243.

13 Th. Cuvigney, H. Normant, Bull. Soc. Chem. France, (1964) 2000.

14 J.D. Roberts, D.Y. Curtin, J. Am. Chem. Soc., (1958) 68, and refs. cited therein.

15 G.E. Parris, E.C. Ashby, J. Am. Chem. Soc., 93 (1971) 1206.

16 J.G. Grasselli, (Ed.), Atlas of Spectra Data and Physical Constants for Organic Compounds, CRC Press, 1975.

17 D.F. Hoeg, D.I. Lust, A.L. Crumbliss, J. Am. Chem. Soc., 87 (1965) 4147.

18 J. von Braun, W. Sobecki, Ber., 44 (1911) 3266.

19 M. Ballester, C. Molinet, J. Rosa, Tetrahedron, 109 (1959) 1958.

20 A. v. Dombrovskii, Zh. Obshch. Khim., 27 (1957) 3041; Chem. Abstr. 52, 8087e.

21 (a) R.A. Moss, J. Org. Chem., 27 (1962) 2683; (b) G.L. Closs, J.J. Coyle, ibid., 31 (1966) 2759.

22 H. Lehmkuhl, D. Reinehr, J. Brandt, G. Schroth, J. Organomet. Chem., 57 (1973) 39.

23 F.H. Rummens, J.W. De Haan, 2 (1970) 351.

24 R. Rieke, S. Bales, P. Hudnall, G. Poindexter, Org. Synth., 59 (1980) 85.

25 G.D. Sargent, C.M. Tatum, Jr., S.M. Dastner, J. Am. Chem. Soc., 94 (1972) 7174.

26 P.R. Singh, B. Jayaraman, Chem. Lett., (1976) 1333.

27 H. Lehmkuhl, D. Reinehr, G. Schomburg, D. Heneberg, H. Damen, G. Schroth, Liebigs Ann. Chem., (1975) 103.

28 A.L. Henne, M.S. Neumann, J. Am. Chem. Soc., 60 (1938) 1697.

29 J.A. Condgrebe, A.G. Kirk, J. Org. Chem., 32 (1967) 3499.

30 C.P. Casey, S.W. Polichnowski, A.J. Shusterman, C.R. Jones, J. Am. Chem. Soc., 101 (1979) 7282.

31 F.W. McLafferty, Interpretation of Mass Spectra, 3rd Ed. University Science Books, Mill Valley, California, p. 19.