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MECHANISMS OF PHOTOCHEMICAL REACTIONS IN SOLUTION

LXXX[*]. PHOTOLYTIC DEHYDROMETALATION OF GRIGNARD COMPOUNDS

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Summary

The carbon—magnesium bond is a chromophore exhibiting a molar extinction coefficient of $\epsilon \approx 1000$ l mol^{-1} cm^{-1} at 254 nm.

Grignard compounds in which the carbon ligand is 3-phenyl-1-propyl or 1-phenyl-2-propyl undergo fragmentation on irradiation in ethyl ether with a low pressure mercury lamp into a terminal olefin and HMgX, which disproportionates into MgH_2 and MgX_2. The quantum yield for this process is $\Phi \approx 0.1$. From α-deuterated compounds and a product analysis, it is concluded that the mechanism proceeds by a β-elimination of HMgX with some small probability for a γ- and an ϵ-elimination to form cyclic products (<1%).

Benzylmagnesium halides, which have no β-hydrogen, show an extraordinarily high stability towards ultraviolet light. Ether cleavage and coupling occur with low quantum yield.

Some forty years ago, Gilman and Peterson reported that Grignard compounds do not lose their activity when exposed for several weeks to summer sunlight or for 36 hours to a mercury lamp [2]. Only recently has interest in photochemistry of organometallic compounds of Groups I, II and III arisen [3-9] although there is a good deal of information available concerning the pyrolytic reactions of such compounds, especially the derivatives of Group I and II metals [10-13].

Aliphatic Grignard reagents show absorption maxima in ultraviolet spectra,

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[*] For part LXXIX see ref. 1.

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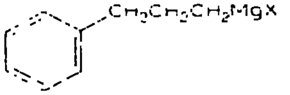
so the carbon—magnesium band can be considered a chromophoric group [14-16]. We were particularly interested in the possibility that photoexcitation might result in heterolytic cleavage providing a unique entry to the field of carbanion chemistry. We find that the possibility is not regularly realized, although it may occur to a limited extent with an ideally constituted substrate such as benzylmagnesium halide. Because of our general interest in bichromophoric systems [17,18] we have concentrated our study on Grignard reagents which contain phenyl groups located in variable relationship to the carbon—metal bonds.

Results and discussion

Compounds I-IV were prepared and their ultraviolet spectra recorded. All except I were irradiated for prolonged periods with 254 nm light.

C_2H_5MgBr

(I)

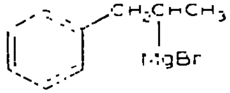


(IIa) X = Cl

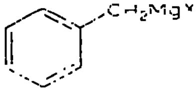
(IIb) X = Br

(IIc) X = $(CH_2)_3C_6H_5$

(IId) $C_6H_5CH_2CH_2CO_2MgBr$



(III)



(IVa) X = Cl

(IVb) X = Br

(IVc) X = $CH_2C_6H_5$

Spectra

Figure 1 shows the ultraviolet spectra of the compounds measured by the technique described previously [15]. Ethylmagnesium bromide, like other alkyl Grignard reagents, shows fairly strong end absorption with no maximum above 220 nm and a long absorption tail extending beyond 300 nm. We presume that the spectrum is that of a monomeric species since it has been reported [19] that organomagnesium bromides, like the iodides and diorganomagnesiums, are not significantly associated at concentrations less than 5 × 10^{-2} *M*.

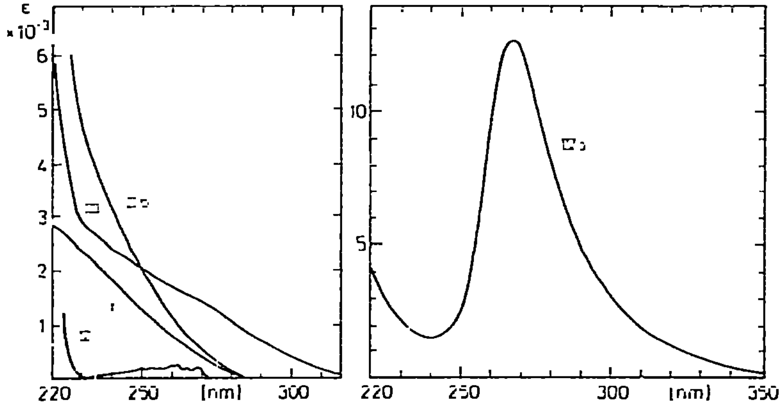


Fig. 1. Absorption spectra of Grignard compounds in diethyl ether at room temperature: I, ethylmagnesium bromide; IIb, 3-phenyl-1-propylmagnesium bromide; III, 2-phenyl-1-methylethylmagnesium bromide; IVa, benzylmagnesium chloride; V, n-propylbenzene.

Our measurements were made in the concentration range 10^{-3} to 6×10^{-2} *M* and absorption obeyed the Beer—Lambert Law throughout the region. Consequently, the absorption tail, which is also shown in the spectrum of ethyllithium in isooctane [7], cannot be readily attributed to association. It may be due to the presence of a variety of molecular species produced by other equilibrium reactions such as the Schlenk disproportionation or solvation—desolvation processes. Had we found high efficiency photolysis of C—Mg bonds, we might have maintained that the pseudo spectral continuum indicated that the excited state was predissociative. Since different photochemistry was observed, we seek explanations based upon the simulation of a broad, shallow potential well for the ground state.

The molar extinction coefficients for various compounds at 254 nm are: I, ϵ = 1020; II, ϵ = 1930 and IIIb, ϵ = 1620 l mol^{-1} cm^{-1}. The extinction coefficient for n-propylbenzene at the same wavelength is 180. The spectra of II and IIIb are similar to that of I, but with increased intensity throughout the region of measurable absorption. In addition, the spectrum of III shows a hint of a shoulder which may indicate the presence of an unresolved band with a maximum in the vicinity of 270 nm. The compounds seem to have electronic transitions similar to that of the saturated Grignard reagent with some "disturbance" added by the phenyl groups. However, the spectrum of IIIb may indicate the availability of a low lying excited state involving strong interaction between the phenyl and C—Mg chromophores. Such a feature could also be entirely buried in the pseudo continuum spectrum of II. Absorption to give localized excited states similar to those of the first excited states of alkylbenzenes would also be hidden. In short, compounds II and III may have low lying excited states in which the excitation is delocalized between the two chromophores, but the absorption spectra do not establish the fact.

The spectrum of IV has an intense maximum (ϵ = 12 600) at 266 nm. The transition must involve strong interaction between the aromatic ring and the C—Mg chromophore. This is not surprising since the molecule contains a classically conjugated system. One could relate the low energy transition to either the higher energy transitions of benzene or to excitation of the C—Mg chromophore*.

Photochemistry

Irradiations were carried out with degassed solutions of 0.02 to 0.2 *M* in ethyl ether using the 254 nm mercury line. After several hours, the inner glass wall was usually coated with a grey-black, sometimes mirror-like deposit, which decreased transmittance considerably. After irradiation, the supernatant solutions were slightly yellow. When the precipitate was brought in contact with water, it dissolved completely with evolution of a gas. After hydrolysis the solutions were analyzed by VPC. The results of analyses for principal products and products from hydrolysis of the parent organometallic compounds are shown in Tables 1-3. Several by-products were produced in small amounts

(continued on p. 6)

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* If the transition is related to the $^1A_{1g}$ excited state of benzene, we would say that the energy is lowered by migration of a C—Mg bonding electron into the vacated π-orbital of the aromatic system: if it were related to the σ,σ^* transition of the C—Mg group, we would say that the energy is lowered by interaction of the σ^* orbital with π^* orbitals of the aromatic system. At the low level of refinement in this discussion the two approaches seem to say the same thing.

TABLE 1

PHOTOLYTIC DECOMPOSITION OF 3-PHENYLPROPYLMAGNESIUM HALIDES, IIa, IIb AND IId AND BIS(3-PHENYLPROPYL)MAGNESIUM, IIc, IN DIETHYL ETHER

Organomagnesium compound	(mmoles)	Irradiation time (h)	n-Propylbenzene[a] (mmoles)	Allylbenzene (mmoles)	MgH_2 (mmoles)
IIa	0.42	5	0.25	0.16	
IIb[b]	0.09	8	0.033	0.041	
IIb[c]	1.09	25	0.70	0.26	0.15
IIb[d]	1.09	66	0.80	0.0	
IIc	0.41	24	0.69	0.20	
IId	0.94	2	0.90	0.03	
IId	0.94	4	0.87	0.06	
IId	0.94	6	0.84	0.08	
IId	0.94	65	0.16	0.59	

[a] Recovered after hydrolysis, not a photoproduct. [b] By-products, cyclopropylbenzene and indane only. [c] Analysis of solid in mmoles: gas developed on hydrolysis 0.23, *acid titre 0.25, Mg^{2+} 0.15, no Br^- and remaining solution: acid titre 0.80, Mg^{2+} 1.04, Br^- 1.20.* [d] 2.86 *mmoles HMPA added, by-products mostly trans-β-*methylstyrene, much less *cis*-compound and indane, no n-amylbenzene, sum of all not more than 0.01 mmole.

TABLE 2

PHOTOLYTIC DECOMPOSITION OF 2-PHENYL-1-METHYLETHYLMAGNESIUM BROMIDE, III, IN DIETHYL ETHER

Organomagnesium compound (mmoles)	Irradiation time (min.)	n-Propylbenzene[a] (mmoles)	Allylbenzene (mmoles)	Φ	*cis*-β-Methylstyrene (mmoles)	Φ	*trans*-β-Methylstyrene (mmoles)	Φ
0.690[b]	125	0.622	0.0171		0.0028		0.0172	
0.690[b]	186	0.589	0.0221		0.0057		0.0221	
0.690[b]	245	0.611	0.0274		0.0070		0.0274	
0.690[b]	361	0.576	0.0355		0.0094		0.0369	
0.690[b]	510	0.551	0.0540		0.0124		0.0533	
0.690[c]	840	0.640	0.0047	0.126	0.0006	0.016	0.0040	0.106
0.690[c]	1320	0.673	0.0058	0.099	0.0010	0.017	0.0049	0.083
0.690[c]	2760	0.654	0.0180	0.127	0.0043	0.030	0.0185	0.131

[a] Recovered after hydrolysis, not a photoproduct. [b] 254 nm circular low pressure lamp, $I \simeq 3 \times 10^{-6}$ E/min. [c] 254 nm low pressure lamp (merry-go-round), $I = 2.87 \times 10^{-8}$ E/min.

TABLE 3

PHOTOLYTIC DECOMPOSITION OF BENZYLMAGNESIUM CHLORIDE, IVa, AND BROMIDE, IVb, AND DIBENZYLMAGNESIUM, IVc, IN DIETHYL ETHER

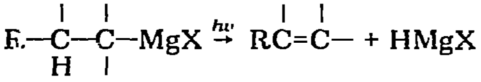
Organomagnesium compound	(mmoles)	Irradiation time (h)	Ethanol	Toluene[a] (mmoles)	n-Propyl-benzene (mmoles)	Dibenzyl (mmoles)
IVa[c]	0.975	60.5	[b]	0.90	0.0058	0.025
IVb[d]	0.90	63		0.755	0.0046	0.056
IVb[d,e]	0.90	63		0.695	trace	0.059
IVc[c]	0.925	60	[b]	0.89	0.0035	0.016

[a] Recovered after hydrolysis, not a photoproduct. [b] Not measured quantitatively. [c] Blank value for dibenzyl: 0.0035 mmoles. [d] Blank value for dibenzyl: 0.034 mmoles. [e] 1.14 mmoles HMPA added.

(< 1%) from II. A number of these were identified by VPC retention times or by VPC—mass spectral analysis. The most important were: cyclopropylbenzene, indane and n-amylbenzene; also detected were: *trans*- and *cis*-β-methylstyrene, 3-methyl-4-butane, a 5-phenylbutene, toluene and ethanol. Several products eluting from VPC columns with retention times slightly longer than ether may have been derived from the solvent. There was no indication of the presence of even traces of 1,6-diphenylhexane or ethyl 3-phenylpropyl ether. Identified trace products from IVb were: ethanol, ethyl formate, ethyl acetate, n-propylbenzene, allylbenzene, benzaldehyde and benzyl alcohol. The latter two compounds are believed to be formed by air oxidation of the Grignard reagent during work-up. No trace of benzyl ethyl ether was found but a very small amount of bibenzyl, but more than was present in an unirradiated sample, was found.

The solids formed on irradiation of IIa, IIb and III were filtered under argon and analyzed. The product from IIa was white and granular and those from IIb and III were grey powders when dried. Relative, rather than absolute, analyses were carried out by (1) measurement of the amount of hydrogen evolved on treatment with water, (2) titration with standard acid, (3) titration of Mg^{2+} with EDTA and (4) titration of halide ion by the Volhard method. The results are shown in Table 4. Infrared spectra were taken in KBr pellets prepared with careful protection from exposure to moisture and the results are shown in Table 5 along with data for the spectrum of magnesium chloride hexahydrate. Ashby and coworkers [20] have studied the spectrum of MgH_2 and our samples showed the principal features which they reported, i.e., broad absorption in the 1000-1300 cm^{-1} region and a band at 550 cm^{-1}. The results indicate that the precipitate from 3-phenyl-1-propylmagnesium chloride is a mixture of magnesium hydride and magnesium chloride and that the precipitate from the bromides, IIb and III is reasonably pure hydride.

The principal products from the Grignard reagents containing β-hydrogen atoms are those expected from β-elimination.


$$\mathrm{R{-}\underset{H}{\overset{|}{C}}{-}\underset{|}{\overset{|}{C}}{-}MgX \xrightarrow{h\nu} R\overset{|}{C}{=}\overset{|}{C}{-} + HMgX} \qquad (1)$$

Ashby and his coworkers [21] have shown that halomagnesium hydrides are not stable, undergoing disproportionation to the hydride and halide. Since

$$2\mathrm{HMgX} \rightarrow \mathrm{MgH_2} + \mathrm{MgX_2} \qquad (2)$$

the chloride is not soluble in ether, it should separate along with the hydride.

TABLE 4

RELATIVE ANALYSIS OF SOLID PHOTOPRODUCTS

Solid from	Equivalent gas	Acid titre	Mg^{2+}	Halide
IIa	0.7	1.06	1.00	1.02
IIb	1.98	1.77	1.00	0
IId	1.66	2.11	1.00	0

TABLE 5

INFRARED FREQUENCIES OF THE SOLID PHOTO-PRODUCTS FROM IIa AND IId IN cm^{-1}

IIa white solid	IId grey solid	$MgCl_2 \cdot 6H_2O$ commercial
	3590 (br)	
3400 (br)	3490 (br)	3340 (br)
2310 (sh)		
2230 m		2240 s
2040 w		2050 (sh)
1840 m		1845 m
1630 s	1625 w	1630 s
1492 w	1494 w	
1450 w	1450 w	
1025 w	1000-1300 (v.br)	1000 (v.br)
600 (br)	550 (br)	605 (br)
430 (br)	420 (br)	470 (br)

The bromide is soluble in ether so one would expect only the hydride to precipitate in the other cases.

We showed that alkanes are not produced as photoproducts by hydrolyzing with D_2O rather than ordinary water. The extent of deuterium incorporation in n-propylbenzene from II and toluene from IV was determined by NMR analysis and found to be the same in blanks and in irradiated samples. We were concerned as to the possibility that magnesium hydride, or other metal hydrides, might effect some hydrogenation of double bonds, or cause double bond migration while homogeneously dissolved or very finely divided. Such reactions would be analogous to those reported to occur with intermediates involved in thermolysis of trialkylchromiums [22]. However, when 1-decene was added to photolysis mixtures no n-decane was produced.

In one run a 0.22 *M* solution of IIb was irradiated in the presence of 0.57 *M* hexamethylphosphoramide (HMPA) and photolysis was entirely inhibited.

Bromides, chlorides and dialkylmagnesiums behaved in qualitatively similar ways in the II and IV series. Differences in yields in long term irradiations may reflect variations in quantum yields but the point is quite uncertain because of variation in optical aberration caused by the solid deposits.

Mechanism

We originally considered six paths for fragmentation:

(1) and (2) Homolytic scission to either $R\cdot$ and $\cdot MgX$ or to $RMg\cdot$ and $X\cdot$;

(3) and (4) Heterolytic scission to either R^- and MgX^+ or to RMg^+ and X^-;

(5) α-Elimination to a carbene and HMgX; and (6) β-Elimination to an olefin and HMgX.

Mechanisms 1-4 could lead to the products observed from II and III if the original fragmentation were followed by disproportionation of the original product pair before they left the solvent cage. However, the mechanisms should also lead to other products as well. It would be extraordinary if radicals, formed by 1 or 2, were to react exclusively by geminate recombination or disproportionation since this seems to be inevitably true of radical pairs in a solvent of viscosity as low as that of ether at room temperature. Although we cannot predict the fate of $\cdot$MgX or RMg$\cdot$ with much certainty, we can be quite certain that $R\cdot$ and $X\cdot$ would abstract hydrogen atoms from the solvent. In the former case this would lead to formation of RH, which has been shown not to be a photoproduct from II and IV. Any HX produced would react rapidly with RMgX, again with production of RH[*].

Dissociation to R^-, the mechanism that we originally hoped to find, may actually be observed with IV, since n-propylbenzene is produced and may arise by nucleophilic displacement by benzyl anion on diethyl ether. An undetermined, small amount of ethanol was also detected in the hydrolyzed solutions[**]. The reaction is little more than a curiosity because the quantum yield is very low and the reaction is no more than a very minor path with compounds such as II, where it may have been the source of the trace of n-amylbenzene detected among the products. We can almost certainly rule out dissociation to carbanions in most cases since they would inevitably have led to R—R (by way of RX). This mechanism is a conceivable source of the trace of bibenzyl produced photochemically from IV.

The α-elimination mechanism is not as easily disposed of as in the case of compounds II and III, since the carbenes would be expected to rearrange to give the olefins which are actually produced. The α,α-dideutero compound, IId was studied as a test of the mechanism, since α-elimination would remove a deuterium from the molecule. After irradiation the principal photoproduct, allylbenzene, was isolated and analyzed by means of its 220 MHz NMR spectrum. The deuterium content was the same as that in the starting material.

The results are entirely consistent with a concerted β-elimination mechanism as the principal open pathway in compounds II and III. However, at the concentrations used in photochemical experiments, we have no guarantee that the reaction occurs in monomeric units rather than in aggregates, since both are probably present. The β-elimination mechanism is unavailable to benzylmagnesium bromide and the compound is relatively stable to photolysis. Interestingly, the reactions which are observed appear to arise from an ionic mechanism rather than from α-elimination.

We anticipated some analogy between the photochemistry of alkylmagnesium compounds and that shown by alkanes in the far ultraviolet. The expectation was partially realized, since β-elimination is a preferred course of alkane photolysis [24]. A second route, the only one available to methane and important with higher alkanes with increasing excitation energy is α-elimination. We have found no real evidence for this mechanism with magnesium compounds although the trace of phenylcyclopropane produced from the II series could be produced from carbenes. This path is apparently not important with IV because no trace of stilbene could be found among the reaction products.

There is a close formal relationship between our photochemical results

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[*] Chen et al. have recently described the behavior of radicals derived from Grignard compounds by reaction with t-butoxy radicals [23].

[**] If n-propylbenzene is produced by this mechanism, one would also expect competitive elimination to produce toluene, ethylene and ethoxide. This may have occurred. The experiments involving hydrolysis with D_2O are not sufficiently precise to eliminate the possibility that toluene is formed photochemically in very low quantum yield comparable to that for formation of n-propylbenzene.

and those obtained in studies of pyrolytic decomposition of organometallic compounds [10-13]. β-Elimination is a preferred route in pyrolysis [12] and dialkylmagnesiums having no β-hydrogen atoms are unusually thermally stable [25]. Another thermal mechanism involves fragmentation to an alkene followed by addition of the parent organometallic compound to the alkene [26, 27]. Such a mechanism could account for the formation of small amounts of toluene and n-amylbenzene from the II compounds. The stabilization of Grignard reagents by addition of HMPA has also been observed in pyrolytic studies by Ducom [28]. He also found that HMPA displaces the Schlenck equilibium so that only monomeric RMgX is present in solutions containing excess of the phosphoramide. This indicates that there must be a coordination vacancy in the valence shell of the magnesium atom to allow β-elimination to occur either photochemically or pyrolytically. Since the β-hydrogen atoms are removed as hydride, this seems like an eminently reasonable requirement for reaction.

The similarity of the behavior of the dialkylmagnesium compound, IIc, so that of the Grignard reagents, IIa and IIb, indicates that interaction between the magnesium and hydrogen atoms is little influenced by the nature of the other principal ligands attached to the magnesium.

Experimental

Preparation and analysis

All preparative work involving organometallic compounds was performed under an argon atmosphere. The magnesium used was supplied by ALFA-Inorganics and guaranteed 99.99% pure. The organic halides used were commercial grade. Mallinckrodt anhydrous diethyl ether was further dried with $LiAlH_4$ and distilled prior to use. The Grignard solutions were prepared in the usual manner. They were analyzed after hydrolysis by titration: acidimetric for active C—Mg bond, with EDTA for magnesium, by Volhard titration for halogen, and by VPC for hydrocarbons.

Irradiations

Irradiations were performed in sealed quartz tubes with a graded seal to pyrex with either 12 mm diameter tubes filled with 5 ml or 29 mm diameter tubes filled with 25-50 ml solution, the latter for preparative purposes. Two lamps were used: a circular 254 nm low pressure mercury lamp with an approximate energy output of 3×10^{-6} E/min as measured by ferrioxalate actinometry, and a 254 nm low pressure lamp in a merry-go-round to measure quantum yields. The energy output of this lamp was constant to within 2.87×10^{-8} E/min over a period of three days. On a preparative scale a medium pressure mercury lamp in an immersion well was used.

Preparation of samples

The tubes, preheated overnight in an oven at 140°C, were evacuated and filled several times with argon, then filled with 5 ml solution and stoppered. The organometallic solutions were transferred with a gas-tight Hamilton syringe. Thereafter the tubes were frozen in liquid nitrogen while attached to the vacuum line and evacuated in a freeze-thaw-cycle three times before being sealed off at a pressure of 5 × 10^{-4} to 10^{-3} mm Hg. It should be noted that the bench vacuum line used to prepare the Grignards contained a mercury manometer*.

Spectra

The technique of taking absorption spectra of air- and moisture-sensitive compounds had been described elsewhere [15]. Diethyl ether (spectroquality) showed a solvent cutoff at 205 nm (absorption 50%) with an optical pathway of 0.020 cm. The absorption spectra were taken with a Cary 14. The molar extinction coefficients were reproducible to ± 15%. The infrared spectra were taken with a Perkin—Elmer 225 instrument in KBr pellets; and the NMR spectra with a Varian HA 60 MHz and a Varian 220 MHz in $CDCl_3$ solution using tetramethylsilane as an internal standard. Mass spectra were taken with an EAI Quadrupole 300 at 70 eV after a VPC separation on column E plus D (see below).

Work-up and analysis

After opening, the tubes were flushed with argon to prevent reaction of the organometallic compounds with air. They were hydrolyzed with water or D_2O (99.8%). For some tubes the volume of gas produced was measured with a simple water manometer. The VPC standard was added (in most cases ethylbenzene, but occasionally biphenyl or octadecane), and the VPC spectra were run with a Hewlett—Packard HP 700 with an electronic integrator. The following columns were used: A, 5ft. 1/8" 5% SE 30 on Chromosorb W; B, 8ft 1/8" 5% SE 30 on Chromosorb P; C, 5ft 1/8" 5% OV 225 on Chromosorb G; D, 9ft 1/8" 10% Carbowax 1540 on Chromosorb W; E, 5ft 1/8" 5% Carbowax 1540 on Chromosorb G; F, 8ft 1/8" 20% DEGS on Chromosorb P; and for preparative work, G, 5ft 1/4" 3% SE 30 on Chromosorb W, and H, 10ft 1/4" 20% Carbowax 20M on Chromosorb W.

Ethylmagnesium bromide, I. The Grignard was prepared from 10.5 g (0.0964 moles) ethyl bromide (distilled, b.p. 38.4°C) and 3.0 g (0.123 moles) magnesium in 100 ml spetroquality diethyl ether. Anal.: H^+, 0.936 M (yield 97.0%); Mg^{2+}, 0.950 M; Br^- 0.973 M. Five concentrations were measured from 0.0194 M to 0.0645 M. The Lambert—Beer law was fulfilled. On hydrolysis the absorption disappeared. λ(nm) (ϵ): 285(60), 275(200), 265(650), 255 (1020), 245(1600), 235(2100), 225(2700), 215(4300).

3-Phenyl-1-propylmagnesium chloride, IIa. The compound was prepared from 7.7 g (0.05 moles) 3-phenyl-1-propyl chloride and 1.3 g (0.0535 moles) magnesium in 200 ml diethyl ether. Anal.: H^+, 0.245 M (yield 98%), Mg^{2+}, 0.245 M, Cl^- not measured. The photolysis was performed with a medium pressure lamp for 5 h with a 0.082 M solution. After hydrolysis, 0.050 M n-propylbenzene and 0.032 M allylbenzene (32.8% yield) were found by VPC. A white precipitate was filtered and analyzed (data see Table 4). A sample was analyzed by GC—mass spectrometry column E plus D, temperature program for 65-150°C. The following substances were identified by their fragmentation patterns: substance (parent peak m/e): toluene (92), n-propylbenzene

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* Glaze and Brewer [5] obtained identical results in the photolysis of ethyllithium using a vacuum line with and without a mercury manometer.

(120), allylbenzene (118), 3-methyl-4-phenylbutane (148), indane (118), cyclopropylbenzene (118), n-amylbenzene (148), and a 5-phenylbutene (146).

3-Phenyl-1-propylmagnesium bromide, IIb. A 12 g (0.06 moles) sample of 3-phenyl-1-propyl bromide was reacted with 1.7 g (0.07 moles) magnesium in 60 ml diethyl ether. Eightly ml of this approximately 1 *M* solution was poured into 100 ml dry n-hexane. A denser, oily phase separated on the bottom. A 5.5 ml sample from this phase was diluted in 100 ml diethyl ether. By this procedure almost all the allylbenzene and most of the 1,6-diphenylhexane, by-products from the preparation, were eliminated. Anal: H^+, 0.272 *M*; Mg^{2+}, 0.295 *M*; Br^-, 0.313 *M*; VPC on column D, 0.290 *M* n-propylbenzene, organic impurities, 0.009%, allylbenzene and 0.05% 1,6-diphenylhexane (0.272 *M* = 100%). The conclusion was drawn from the data, that 0.02 *M* (7.35%) excess $MgBr_2$ and 6.6% n-propylbenzene were present in the solution. With this solution the absorption spectrum was recorded. Measurements were done with seven concentrations from 9.53×10^{-4} to 1.87×10^{-2} *M*. After hydrolysis the spectrum of n-propylbenzene with a considerably lower extinction appeared: λ(nm)(ϵ): 290(27), 280(81), 270(540), 260(1090), 250(2000), 240(3250), 230(4800), 220(7200), 215(10500).

Bis(3-phenylpropyl)magnesium, IIc. To 50 ml purified solution of IIb, 5 ml dioxane was added. At once a white precipitate fell out. The solution was filtered through a glass frit. Anal.: H^+, 0.205 *M*; Mg^{2+} 0.102 *M*; no halogen.

1,1-Dideutero-3-phenyl-1-propylmagnesium bromide, IId. IId was prepared by refluxing 60 g (0.4 moles) dihydrocinnamic acid overnight in 100 ml (1.71 moles) abs. ethanol containing one ml conc. sulfuric acid. The reaction mixture was poured into water. The lower layer was shown to be pure ester by VPC on column A at 170°C. Distillation at 76°C/0.4 mm Hg gave 61.8 g (0.347 moles, 86.8% yield) of ester. A 36.5 g sample of the ester in 100 ml ether was dropped into a slurry of 5.1 g (0.14 moles) $LiAlD_4$ in 100 ml ether. The reaction mixture was worked up by careful addition of water, acidification, extraction with ether, drying and distillation at 73.5°C/0.6 mm Hg. The yield was 27.0 g (0.175 moles, 85.4%). The compound appeared pure on VPC column E at 165°C. Deuteration was nearly 100%, no methylol proton absorption could be seen in a 60 MHz NMR spectrum in deuterochloroform. 1,1-Dideutero-3-phenyl-1-propyl bromide was prepared by adding 3.1 ml (8.84 g, 0.0327 moles) freshly distilled PBr_3 to 12 g (0.078 moles) of the alcohol while maintaining the temperature at 0°C. After the addition, the solution was allowed to warm up to approximately 20°C over a two-hour period and was then further heated for 20 min at 80°C. In the work-up the reaction mixture was poured into crushed ice in a separatory funnel and the bromide was extracted with n-hexane. The extract was washed with 5% NaOH solution, dried and distilled at 65-65.5°C/0.9 mm Hg. Yield, 9.5 g (0.047 moles, 60.3%). The bromide appeared pure on VPC column C. No C_α-proton absorption was found in a 220 MHz NMR spectrum. 1,1-Dideutero-3-phenyl-1-propylmagnesium bromide, IId, was prepared by reaction of 8.05 g (0.04 moles) of the bromide with 1.1 g (0.045 moles) magnesium in 200 ml ether. This solution was used without further purification. Anal.: H^+, 0.1875 *M* (93.8% yield); Mg^{2+} 0.195 *M*; Br^-, 0.20 *M*. VPC analysis of the hydrolysate on column D and A showed: n-propylbenzene 0.1927 *M* (96.35%), allylbenzene 0.0095 *M* (0.48%) and 1,6-diphenylhexane 0.00618 *M* (3.1%). The difference between acidimetric titre and VPC was taken as a measure of the degree of premature hydrolysis: 0.0052 (2.6%) and the difference between the Mg- and Br-titre and the H^+-titre was taken as a measure of excess magnesium bromide: 0.0025 *M* (1.25%).

The quantitative VPC analysis data after irradiation and hydrolysis are compiled in Table 1. The VPC was done with column D, 105°C, using ethylbenzene as an internal standard to determine n-propylbenzene and allylbenzene, and with column A, 150°C, n-octadecane, as the standard to determine 1,6-diphenylhexane. The decrease of IId as measured by n-propylbenzene as well as the increase of allylbenzene was linear with irradiation time.

On a preparative scale two tubes (50 ml, 19.4 mmoles) were irradiated. Tube (a) was hydrolysed with D_2O and tube (b) with H_2O. As a blank (c) 30 ml were hydrolysed with D_2O without irradiation. The solution of tube (a) was filtered before hydrolysis, and the grey solid analyzed by titration (see Table 4). After hydrolysis most of the ether was distilled and n-propylbenzene and allylbenzene were separated on the preparative VPC column H at 135°C. n-Propylbenzene was > 99.9% and allylbenzene > 99.5% pure after a second pass through the column. Both substances were subjected to a bulb to bulb distillation and their NMR spectra were determined in $CDCl_3$ at both 60 and 220 MHz with the following results: tube (a) 1,1,1-trideutero-3-phenylpropane showed after the irradiation the same spectrum as the blank tube (c), 1,1-dideutero-3-phenyl-1-propene, phenyl δ = 7.20 (5H, s), $C_6{-}CH_2$ 3.37 (2H, d, *J* = 6.5 Hz), $C_6{-}C{-}CH$ 5.9—6.2 (1H, broad), no $C_6{-}C{-}C{=}CH_2$ protons at 5 ppm; tube (b) 1,1-dideutero-3-phenylpropane, phenyl δ = 7.18 (5H, s), $C_6{-}CH_2$ 2.58 (2H, t, *J* = 7 Hz), $C_6{-}C{-}CH_2$ 1.63 (2H, q, *J* = 8 Hz), CHD_2 0.91 (1H, broad); 1,1-dideutero-3-phenyl-1-propene showed the same spectrum as the sample in tube (a).

2-Phenyl-1-methylethylmagnesium bromide, III. The Grignard was prepared from 6.0 g (0.03 moles) 2-bromo-1-phenylpropane (Aldrich), which contained < 2% β-methylstyrene (*cis/trans* approx. 0.5/1.0) and 0.9 g (0.037 moles) magnesium in 100 ml ether. Anal.: H^+, 0.193 *M* (yield 64.3%), Mg^{2+} 0.245 *M*, Br^- 0.305 *M*. The impurities after the preparation were allylbenzene, *cis*- and *trans*-β-methylstyrene and dimeric products as found on VPC columns D and A. Purification was performed by adding 20 ml Grignard solution to 25 ml n-hexane. On cooling with Dry Ice—methanol a white precipitate (at first oily) fell out, which could be filtered. Then 20 ml ether was directly distilled onto the solid. Anal.: H^+, 0.11 *M*; Mg^{2+}, 0.15 *M*; Br^-, 0.18 *M*. VPC of the hydrolysate on column D at 100°C showed n-propylbenzene 0.107 *M* (100%) with impurities allylbenzene 0.37%, *cis*- (0.046%) and *trans*-β-methylstyrene (0.28%), and on column A at 155°C no coupling products could be detected. It was assumed by the difference in the H^+, Mg^{2+} and Br^-titres, that 0.03 *M* (27%) of excess $MgBr_2$ was present.

With this solution the absorption spectrum was recorded. Five concentrations were used ranging from 3.93×10^{-3} *M* to 1.42×10^{-2} *M*. The Lambert—Beer law was fulfilled. After hydrolysis the spectrum of n-propylbenzene appeared having considerably lower extinction coefficients. A 20% higher concentration, 1.79×10^{-2} *M*, was calculated using the extinction coefficient of n-propylbenzene. λ(nm)(ϵ): 350(10), 340(26), 330(52), 320(93), 310(164), 300(355), 290(690), 280(1090), 270(1490), 260(1720), 250(2060), 240(2480), 230(2850), 220(6260), 210(11530).

Quantitative VPC analyses after irradiation and hydrolysis on column D with ethylbenzene as standard gave results compiled in Table 2. The quantum yields of the photoproducts, allylbenzene and *cis*- and *trans*-β-methylstyrene, are $\Phi = 0.1$, 0.02, and 0.1 respectively. The decrease of III as measured by n-propylbenzene as well as the increase in photoproducts is linear with time. *cis*- and *trans*-β-methylstyrene were identified by comparison of VPC retention times with known samples, which had been characterized by NMR and IR. No coupling products were found by VPC with column A.

Benzylmagnesium chloride, IVa. The Grignard was prepared by reaction of 5.05 g (0.04 moles) benzyl chloride and 1.4 g (0.058 moles) magnesium in 200 ml ether. The absorption spectrum of IVa in diethyl ether had been recorded earlier [15], and exhibits a strong absorption at 266 nm ($\epsilon = 12600$). Anal.: H^+, 0.195 *M* (yield 97.5%); Mg^{2+}, 0.20 *M*; Cl^-, 0.195 *M*; hydrolysis and VPC on column D, toluene, 0.192 *M*, and on column C, 0.000784 *M* (0.4%) dibenzyl. Less than 1% benzyl alcohol was detected and is believed to have been formed on contact with air during hydrolysis. The only photoproducts, n-propylbenzene, ethanol and products having retention times slightly greater than ether, were found in very low yields (about 1%). On a preparative scale 50 ml (4.87 mmoles) was irradiated for 61.5 hours with the 254 nm low pressure lamp. After deuterolysis dibenzyl was separated by preparative VPC on column G at 175°C, and subsequently toluene on column H at 130°C. The NMR spectrum of this 1-deuteromethylbenzene was identical to a spectrum from a compound obtained by deuterolysis of a non-irradiated solution.

Benzylmagnesium bromide, IVb. Benzyl bromide, 8.6 g (0.05 moles) reacted with 1.4 g (0.0576 moles) magnesium in 220 ml ether. Anal.:H^+, 0.225 *M* (yield 99%); Mg^{2+}, 0.235 *M*. After dilution a 0.00758 *M* solution was irradiated for 68.5 hours with a medium pressure lamp. The solution was deuterolysed. GC—mass spectrometry was performed with columns E plus D with a temperature program from 55 to 160°C. The following substances were identified by comparison of their fragmentation patterns with those reported in the literature: (*m/e*): ethyl formate (74), ethyl acetate (80) ethyl alcohol (46), toluene-d_1 (93), n- propylbenzene (120), allylbenzene (118), and benzaldehyde (106).

Dibenzylmagnesium, IVc. Five ml dioxane was added to the solution of IVa. Filtration through a frit gave a clear solution with the analysis: H^+, 0.185 *M*; Mg^{2+}, 0.095 *M*; no halogen.

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