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Electron Transfer from Alkylmagnesium Compounds to Organic Substrates

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The present article gives a survey over some mechanistic problems concerning the reactions of Grignard reagents, which have had the interest of the author since 1965. It is perceived from a rather personal point of view and does not pretend to be comprehensive in covering the many very recent contributions, which have appeared in the field.

Alkylmagnesium compounds are the most important representatives of organometallics; they are in everyday use in any chemical institution concerned with organic chemistry. Apart from their synthetic usefulness, the compounds are mechanistically interesting because of the wide spectrum of "normal", "abnormal" or even "paradoxical" products, which are found among the reaction products.[1]

Because of the polar nature of the carbon–magnesium bond the reactions of the Grignard reagents have usually been considered those of potential carbanions, but for many years the mechanistic suggestions in the area were not given a thorough kinetic foundation.[1] Many good reasons may be given for this situation. The reagents are difficult to handle, because contact with air and moisture must be rigorously avoided. The purity of the reagents is difficult to ascertain, since crystallization and sublimation and other separation procedures are usually not feasible. Metallic impurities in the magnesium are almost impossible to avoid and may alter the course of the reactions when present even in trace amounts. The reaction rates to be measured are often very high with half lives of the order of ms.

Even when kinetic measurements have been obtained in spite of the practical obstacles, their interpretation presents many problems. Since magnesium is a Lewis acid the reagents are at the same time electron rich and electron deficient. For this reason Grignard reagents enter into various coordination equilibria by, for example, self-association, reagent-solvent association, and reagent-substrate association. Because of the Schlenk equilibrium:

$$2\,RMgX \rightleftharpoons R_2Mg + MgX_2,$$

at least three types of electrophilic magnesium species may enter into all the coordination equilibria mentioned. All the equilibria are of importance for the kinetics and should be studied.

Progress in the understanding of the self-association of Grignard reagents has been obtained mainly by ebullioscopic measurements of the vapour pressure of the solvent.[2,3] Reagent-solvent equilibria were studied by the use of optically active solvents [4] and by calorimetric and spectrographic procedures.[5] The Schlenk equilibrium was investigated by thermometric titration [6] and by the NMR technique,[7] and the reagent-substrate equilibria were studied by UV and IR spectroscopy [8,9] as well as kinetic methods.[10]

Because of the complicated nature of Grignard reagent-substrate mixtures the most useful and reliable method to obtain kinetic results has been to use pseudo first-order conditions with the reagent present in very large excess. In this way the reagent is virtually unchanged during the

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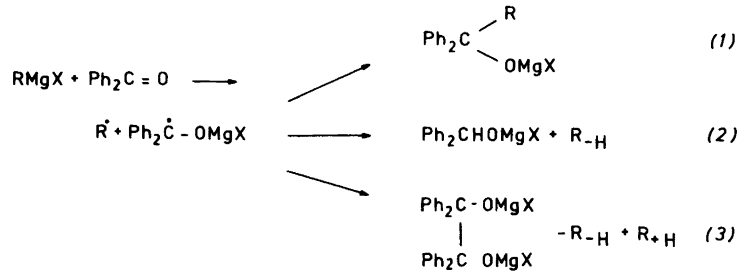


Scheme 1.

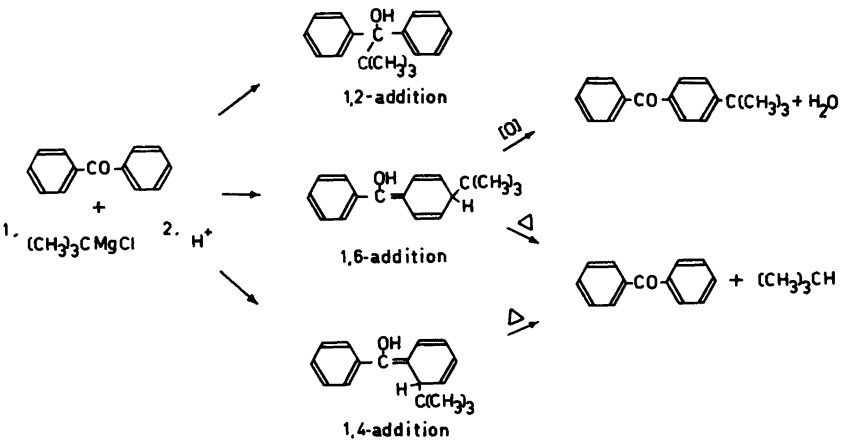
reaction. The kinetic procedures have been spectroscopic or thermographic, and flow techniques have often been required. The results obtained have given a few answers, while many questions are left open.

Grignard reagents+benzophenone. Electron transfer or polar mechanism? The problem which will be dealt with in the following is whether Grignard reagents behave primarily as anion precursors and react by concerted reaction mechanisms, or whether they are electron donors and therefore react by stepwise mechanisms. It is not to be expected that a simple answer may be given, which would cover all reagents reacting with any substrate. It seems, however, that if the question is limited to Grignard reagents reacting with benzophenone the answer is that the reactions are stepwise and are always initiated by the transfer of a single electron (ET) to benzophenone.

Blicke and Powers [11] in 1929 proposed that Grignard reagents are homolyzed in the reaction with benzophenone and loose magnesium subhalide to form an alkyl radical and the magnesium salt of benzophenone ketyl; Scheme 1.

The two radicals might combine to form the 1,2-addition product (1) or possibly, the ketyl would abstract hydrogen from the β-position of the alkyl radical, which would lead to the reduction product, benzhydrol and alkene (2). The authors also suggested that two ketyl radicals might combine to form benzopinacol and that the alkyl in this case would disproportionate to form alkene and alkane (3). At the time of its proposal, the theory was purely hypothetical, but today, after half a century, it seems that the mechanism in Scheme 1 is very close to being correct.

Evidence from by-products and ESR. Benzopinacol, which should be expected as a by-product according to the radical mechanism, was not observed by Blicke and Powers, but it was reported a few years later by Arbuzov and Arbuzova [12] in the reaction of cyclohexylmagne-



Scheme 2.

sium bromide with benzophenone. It would seem that the radical mechanism could then be established, but it was argued that metallic magnesium present in the Grignard reagent could be the reducing agent. Another serious problem arose when Kharash and Lambert [13] showed that trace amounts of transition metals added to methylmagnesium bromide would prevent the formation of addition product and lead to high yields of benzopinacol. The interest in the radical mechanism was renewed in 1968, when Blomberg and Mosher [14] using filtered solutions of neopentylmagnesium chloride prepared from sublimed magnesium obtained a 20 % yield of benzopinacol in the reaction of benzophenone. Also the ESR technique had shown the formation of ketyl during Grignard reactions with benzophenone.[14,15] A radical mechanism was no doubt in operation, but there were no means by which one could tell whether the benzopinacol was a by-product produced in an ET mechanism in competition with a polar mechanism, which might be alone responsible for the addition product.

Evidence from reaction rates and products distributions. The answer had to come from kinetic work. A study was made of the reaction of benzophenone with *t*-butylmagnesium chloride. This reaction was reported to give *ca.* 60 % 1,2-addition product and no reduction product.[16] It was found that when the reaction mixture was worked up cold and in the absence of air, NMR showed the presence of large amounts of the 1,6-addition product, a dihydrobenzophenone enol, Scheme 2.[17] The reaction mixture also contained the 1,2-addition product and benzopinacol. A series of substituted benzophenones was now tested for reactivity toward *t*-butylmagnesium chloride and for product distribution in the reaction. It showed that the overall reaction, *i.e.*, the rate at which the substituted benzophenone was consumed, followed the Hammett rate law, Fig. 1, but the product distribution was 0–55 % for the 1,2-addition product, 0–39 % for the 1,4-addition product, 0–100 % for the 1,6-addition product and 0–21 % for the benzopinacol, Table 1. It was obvious that the product distributions were extremely sensitive to steric factors, but the overall rate was not. This allowed the conclusion that the reaction had a discrete rate-determining step, and that the product distribution was determined in fast consecutive steps. ET was most likely as the rate-determining

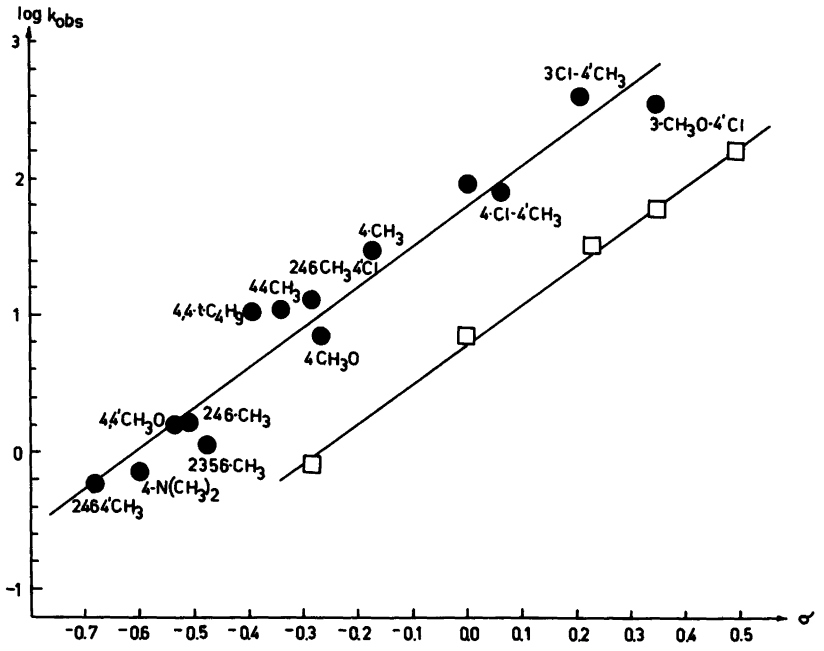


Fig. 1. Hammett plot for the reaction of *t*-butylmagnesium chloride 0.5 M with 0.02 M of substituted benzophenones. Temperature 20 °C (●) and −30 °C (□).

Table 1. Product distributions in the reaction of *t*-butylmagnesium chloride in excess with substituted benzophenones in diethyl ether.

Benzophenone	% Benzopinacol	% Addition		
		1,2-	1,4-	1,6-
Unsubstituted	6	44	0	50
4,4'-dimethyl-	12	55	0	33
4,4'-di-*t*-butyl-	21	40	39	0
4,4'-dichloro-	0	50	21	29
2,4,6-trimethyl-	0	0	0	100
2,3,5,6-tetramethyl-	0	0	0	100

step and the *t*-butyl radical would combine with sterically accessible carbon atoms of the ketyl molecule, which shared the spin density by resonance.

Evidence from the correlation of reaction rates with the anodic oxidation potentials for Grignard reagents. The establishment of ET as the only important reaction mechanism for a typical tertiary Grignard reagent reacting with benzophenone in diethyl ether under normal conditions was very welcome after several decades of suggestive, but non-conclusive evidence. It obviously created an urge to reach conclusions also concerning the reaction mechanisms for primary and secondary Grignard reagents with benzophenone. Several differences in the reaction pattern were *a priori* to be expected. Secondary and especially primary radicals are much less stable than tertiary, and the lifetime of a radical pair (alkyl and ketyl, after ET and homolysis) would be expected to be extremely short. If ET and radical combination follow each other with almost no separation it would seem impossible to distinguish between the two-step ET mechanism and the one-step concerted anionic mechanism. One thing would, however, be different: The predicted relative rates for reaction of alkylmagnesium reagents with the ketone. For a concerted reaction a reactivity series tertiary<secondary<primary would be expected for steric reasons, while for ET the series would be reversed. Since ET involves the transfer of an electron from the different reagents to one and the same acceptor, *e.g.*, benzophenone, it should be possible to relate the reaction rate to the anodic oxidation potential of the individual Grignard reagents.

As early as 1935, Evans, Lee and Lee determined values for the "decomposition potentials" of Grignard reagents using an electrolysis set-up with large platinum electrodes and rather concentrated ethereal solutions of Grignard reagents.[18] From the simple plots of current *versus* potential was chosen a value "where the curve showed a distinct break" and this potential was given as the decomposition potential.

In an attempt to repeat the work of Evans *et al.*, it was found that the plots of current density *versus* potential are, as would be expected, exponential, and do not show any distinct breaks.[19] If, however, corrections were made for ohmic potential drops and for concentration

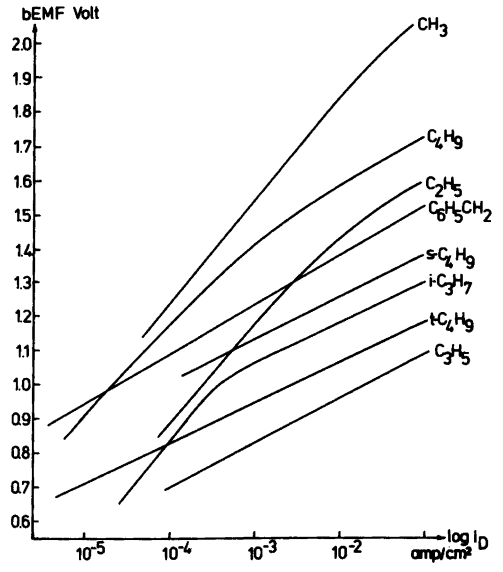


Fig. 2. Tafel plots for the electrolysis of *ca.* 1 M ethereal alkylmagnesium bromides showing the anodic overvoltage at platinum relative to the Pt|Mg|MgBr cathode.

potentials, *etc.* linear Tafel plots were obtained for many Grignard reagents, Fig. 2. The Tafel plots for some of the alkylmagnesium bromides show a change in slope as the current density is varied. While the plots for *t*-butyl, allyl and benzyl (which form stable radicals) have a constant slope of 0.15, plots for reagents, which form more reactive radicals show a break from a slope of ~0.30 at low current densities of ~0.15 at high values of I_D. The break occurs at higher currents the more reactive the corresponding radical is in the sequence $CH_3>C_2H_5>C_4H_9>i\text{-}C_3H_7$. A comparison of the electrochemical reactivity is only possible at a current density at which the slopes are identical and for this reason the overpotentials at $I_D=0.06$ A cm^{-2} were taken as being representative for the anodic oxidation potential and given in Table 2 as $\eta_{0.06}$.

The values of $\eta_{0.06}$ are not standard oxidation potentials, since they are measured at a working electrode and relative to the Pt|Mg|$MgBr_2$ electrode. Relative to this standard a Pt|H_2|HBr electrode is found at 1.92 V and a Pt|*t*-Bu·|*t*-BuMgBr electrode at 0.85 V. On this basis the $\eta_{0.06}$ values may be tentatively converted to standard oxidation potentials relative to SHE by substraction of 2.23 V. In order to see if the electron transfer process at the anode is related to the reaction of Grignard reagents with benzophenone, a correlation was made between log *k* for the chemical reaction and $\eta_{0.06}$ for the electrode process, Fig. 3. The correlation was found to be linear provided the reaction constants were obtained for the reaction of the

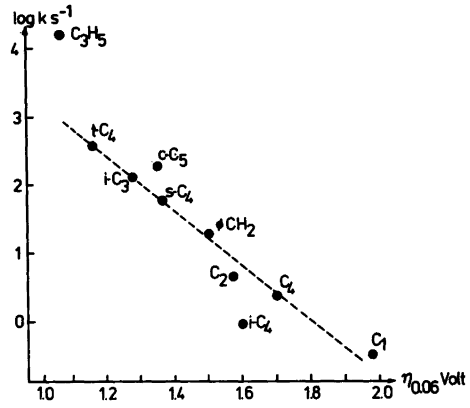


Fig. 3. Log pseudo first-order rate constants for the reaction at 20 °C of alkylmagnesium bromide 0.02 M in diethyl ether with 0.25 M benzophenone.

Grignard reagent with an excess of benzophenone, Table 3. When the reaction takes place in this way the kinetics is first order in benzophenone and first order in Grignard reagent, which is not the case if the relative concentrations are reversed. *t*-Butylmagnesium chloride in ether is, for example, just as reactive toward 0.02 M benzophenone at 0.1 M as when the concentration is 1.0 M. This rate-levelling effect is well known for any Grignard reagent reacting in ether solution with aliphatic ketones like acetone, [20] while with aromatic ketones it only applies to tertiary and secondary reagents. The effect probably is steric and is a consequence of complex

Table 2. Anodic overvoltage at a platinum electrode relative to the reference electrode Pt|Mg|$MgBr_2$ at a current density $I_D=0.06$ amp cm^{-2} for Grignard reagents in diethyl ether at the concentration given, with an excess magnesium bromide given as % Br^-. Also shown are tentative values for E_o for alkylmagnesium bromides relative to SHE.

R	% Br^-	[RMgBr] M	$\eta_{0.06}$ V	E_o V
CH_3	0.8	1.00	1.98	−0.25
C_2H_5	2.8	0.87	1.57	−0.66
i-C_3H_7	13.0	0.99	1.28	−0.95
C_4H_9	4.4	1.09	1.70	−0.53
i-C_4H_9	9.5	1.00	1.60	−0.63
s-C_4H_9	19.6	0.98	1.36	−0.87
t-C_4H_9	30.0	0.69	1.16	−1.07
C_3H_5	19.7	0.68	1.07	−1.16
$C_6H_5CH_2$	15.0	1.02	1.50	−0.73
c-C_5H_9	9.9	0.98	1.35	−0.88

Table 3. Pseudo first-order rate constants, k_{obs}, in s^{-1} for the reaction of 0.02 M alkylmagnesium bromide with 0.25 M benzophenone in diethyl ether at 20 °C. Anodic overvoltage $\eta_{0.06}$ (see text) is given in V.

Grignard reagent	k_{obs}	$\eta_{0.06}$
CH_3MgBr	0.3	1.98
C_2H_5MgBr	2.8	1.57
i-C_3H_7MgBr	133	1.28
C_4H_9MgBr	2.6	1.70
i-C_4H_9MgBr	0.9	1.60
s-C_4H_9MgBr	64	1.36
t-C_4H_9MgBr	400	1.16
$CH_2=CHCH_2MgBr$	16 000	1.07
$C_6H_5CH_2MgBr$	21	1.50
cyclo-C_5H_9MgBr	214	1.35

formation in ether solution between the electrophilic magnesium compounds and ketones with donor properties. The rate constants obtained under the two sets of conditions cannot be compared because the Grignard reagents are different: The ligands bound to magnesium are in the first case (large excess of Grignard reagent) predominantly ether, but in the second case (large excess of benzophenone) supposedly ether and benzophenone.

That the possibility exists to correlate the reactivity of the Grignard reagents with the anodic oxidation potential is very good evidence for a rate-limiting electron transfer. At the same time it indicates that with excess benzophenone the ET mechanism is not sensitive to steric hindrance since *t*-butylmagnesium bromide is 1330 times more reactive than methylmagnesium bromide.

Evidence from kinetic isotope effects, etc. The possibility of discerning a rate-limiting step different from the product-determining step, which was used to prove the stepwise nature of the reaction of *t*-butylmagnesium chloride with benzophenone is also present, for primary and secondary reagents, although the picture is a little less clear-cut. Secondary and primary Grignard reagents react with benzophenone to form the 1,2-addition product and large amounts of the reduction product benzhydrol formed by transfer of a β-hydrogen from the Grignard reagent to the carbonyl carbon, Scheme 1. The product distribution was changed when the β-hydrogens were exchanged with deuterium so that more addition and less reduction took place. If the partial rates for the addition and the reduction were calculated on the basis of the overall rate and the product distributions, it was found that the reduction was slowed down, while the addition was accelerated.[21] The simplest way to interpret the result is to assume rate-limiting ET, which has a rather low deuterium isotope effect and a product-determining radical combination step. Since the abstraction of a β-deuterium is rather much slower than abstraction of hydrogen, the recombination to form addition product is favoured leading to an increase in the rate of formation of addition product.

Substituents in the benzophenone also affect the ratio of addition/reduction in the reaction with primary Grignard reagents. With isobutylmagnesium bromide the ratio is 100 times lower with *p,p'*-dichloro substituted benzophenone than with *p,p'*-dimethylamino substitution and an irregular Hammett plot, Fig. 4, is obtained for $\log(k_{red}/k_{add})$ *versus* σ. The overall reaction also obeys the Hammett rate law although somewhat irregularly, Fig. 5. A comparison of *p,p'*-dimethylbenzophenone (3) with *p,p'*-di-*t*-butylbenzophenone (4) is interesting. These ketones have the same overall reactivity toward isobutylmagnesium bromide. This is in keeping with the almost identical σ-values for methyl and *t*-butyl. The ratio reduction/addition is, however, 4.26 for methyl and 1.44 for *t*-butyl in the para positions, which means that the addition taken as a partial reaction is much faster for *t*-butyl- than for methyl substituted benzophenone.[22] It is impossi-

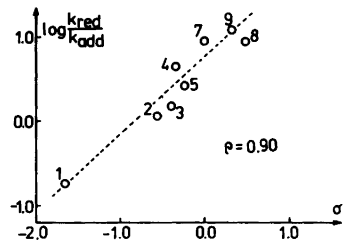


Fig. 4. Logarithm to the ratio reduction: addition in the reaction of isobutylmagnesium bromide in diethyl ether with substituted benzophenones *versus* Hammett σ constants. 1=*p,p'*-dimethylamino, 2=*p,p'*-dimethoxy, 3=*p,p'*-di-*t*-butyl, 4=*p,p'*-dimethyl, 5=*p*-methoxy, 7=unsubstituted, 8=*m*-methoxy-*m'*-chloro, 9=*m*-fluoro.

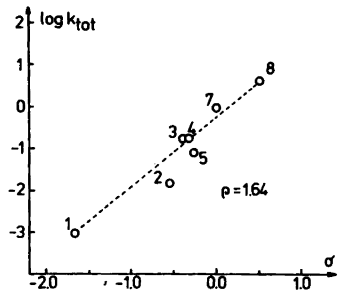


Fig. 5. Log relative rate for the overall reaction of isobutylmagnesium bromide in diethyl ether with substituted benzophenones (see Fig. 4) *versus* Hammett σ constants.

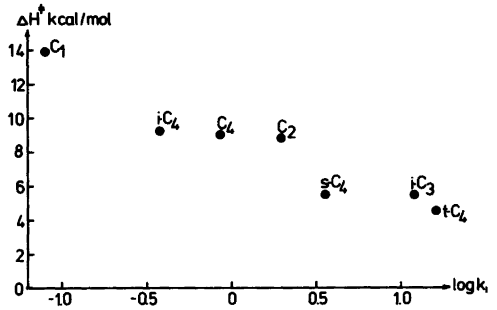


Fig. 6. Enthalpy of activation for the reaction of 0.1 M alkylmagnesium bromide with 0.02 M benzophenone in diethyl ether *versus* log pseudo first-order rate constant for the reaction at 20 °C.

ble that the substitution of methyl with the bulkier *t*-butyl should cause a significant increase in the rate of an independent addition reaction of whichever mechanism, and the only possible explanation is, therefore, that the addition is not independent but that an SET with low steric requirements is rate-limiting for the overall reaction, and that the bulk of the *t*-butyl groups impedes the facile collapse to reduction product and a larger fraction of the radical pairs, therefore, collapses in the 1,2-fashion.

Evidence from an isokinetic relation between activation parameters. In the search for a reaction mechanism for primary and secondary Grignard reagents reacting with benzophenone, it was found of interest to compare the activation parameters. Rate measurements for the reaction of seven alkylmagnesium bromides (0.1 M) with 0.02 M benzophenone in ether were performed at 20 °C and at 40 °C, which allowed estimates of the enthalpy of activation and the entropy of activation.[23] It was found that low reactivity of a reagent like methylmagnesium bromide was the result of a high enthalpy of activation (13.7 kcal mol^{-1}) with a rather favourable entropy of activation (−12.2 e.u.), while a highly reactive reagent like *t*-butylmagnesium bromide had a low enthalpy of activation (4.5 kcal mol^{-1}) combined with an unfavourable $\Delta S^{\ddagger}$ (−33.3 e.u.). The relation between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ tended to be linear. This isokinetic relationship is an indication to similarity in mechanism within the reaction series.[24]

It has been shown that because of the way in which the parameters are calculated they are not quite independent, but if there is linear correlation between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ the same should apply to $\Delta G^{\ddagger}$ and $\Delta H^{\ddagger}$ and therefore to log *k* and $\Delta H^{\ddagger}$, which are derived independently.[25] In Fig. 6 the values of log *k* *versus* $\Delta H^{\ddagger}$ for the seven alkylmagnesium bromides are shown. While the isokinetic plot of $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ (not shown) yields a linear correlation with a correlation coefficient of 0.986, the plot of $\Delta H^{\ddagger}$ *versus* log k_{20} has a correlation coefficient of 0.94.

As mentioned in the previous sections, the observed rate of a Grignard reaction is dependent on equilibria of several types between reagent and substrate and within the reagent itself. The measured enthalpy of activation therefore includes *e.g.* the enthalpy of the Schlenk equilibrium and of the equilibrium reagent-substrate. To make the true test for isokinetic correlation, it will be necessary to determine all the relevant contributions since one or more of them may not be isokinetically correlated.

Concerted electrophilic displacement of magnesium. (a) Reactivity series. As pointed out above, Grignard reagents are both electron donors and potential anions, and toward benzophenone or a platinum anode they play the role as electron donors. It would be of interest to find substrates toward which Grignard reagents do not react by electron transfer, but rather in a truly concerted fashion. The property in the substrate, which would be of importance would be the relative ease with which a single electron is accepted, as compared with the ease with which a nucleophile is accepted. The reduction potential of Grignard substrates may be measured as the polarographic

half wave potential, $E_{1/2}$ (*versus* SCE), and half wave potentials for substituted benzophenones have been correlated with the Hammett σ constants, but no direct correlation has been obtained between reaction rates for Grignard substrates of different types of compounds and the measured reduction potentials. This shows that even if the electron transfer reaction is simple in principle, its mechanism is nevertheless highly individual for each type of substrate, and this fact will be discussed later.

True nucleophilic behaviour of Grignard reagents should be expected toward substrates, which have a polar carbonyl group but a relatively high reduction potential, since they lack the ability to stabilize a radical anion by resonance. Purely aliphatic ketones like acetone fill this description, and a strong indication of a concerted course of the reactions of acetone with Grignard reagents is the reactivity series, Table 4, found by flow stream thermographic kinetics

Table 4. Pseudo first-order rate constants for the overall reaction of 0.05 M of ketone with 0.5 M of alkylmagnesium bromide in diethyl ether at 20 °C.

RMgX	k_1 s^{-1} (acetone)	k_1 s^{-1} (benzophenone)
CH_3MgBr	3.8	0.30
C_2H_5MgBr	7.5	7.2
C_3H_7MgBr		3.2
$(CH_3)_2CHMgBr$	1.6	21
C_4H_9MgBr	2.2	3.2
i-C_4H_9MgBr	0.1	27
C_3H_5MgBr	momentary	momentary
$C_6H_5CH_2MgBr$	150	91
p-$CH_3C_6H_4MgBr$	69	1.0
C_6H_6MgBr	42	0.3
p-ClC_6H_4MgBr	14	0.17
c-C_5H_9MgBr		2.6
C_4H_9MgCl	36	
t-C_4H_9MgCl		94
p-$CH_3C_6H_4MgCl$		700
$C_6H_5CH_2MgCl$		350
p-ClC_6H_4MgCl		200
$(CH_3)_2Mg$	15	1.9
$(C_2H_5)_2Mg$	110	
$(i\text{-}C_4H_9)_2Mg$		30
$(s\text{-}C_4H_9)_2Mg$		630
$(t\text{-}C_4H_9)_2Mg$		110
$(C_4H_9)_2Mg$	120	64
C_4H_9MgI	0.6	

and showing phenyl ≫ethyl>methyl>i-propyl>*t*-butyl.[26] As seen from Table 4, this is the reverse order which is valid for the ET reaction with benzophenone. The reactivity series is not a direct proof for a concerted mechanism, but it clearly shows that a mechanism is operating in which the steric effects are extremely important.

The high rates obtained with acetone reacting with aromatic Grignard reagents deserve comment. In diethyl ether Grignard reagents and ketones momentarily form complexes and the coordinated ketone is much less reactive than is the small amount of free uncoordinated ketone, which is present according to the equilibrium. This "self inhibition" of the reaction is common for all aliphatic Grignard reagents and is responsible for the fact that Grignard reagents have an extremely high reactivity toward an excess of aliphatic ketone, while the reaction of ketone of a low concentration with an excess of Grignard reagent tends to be very low order or even zero order with respect to Grignard reagent.[20] The conclusion was reached that ketone-Grignard reagent complexes may represent "blind alleys" in the reaction. The complexes do not rearrange to products, but as the reaction goes on they supply by dissociation reactive uncoordinated ketone in a very fast equilibrium.

In contrast to the aliphatic Grignard reagents, aromatic reagents seem to form complexes with acetone which are capable of rearrangement and this may be one of the reasons for the high reactivities observed. The normal reactivity series for nucleophilic substitution is methyl>ethyl>i-propyl>*t*-butyl≫phenyl. That phenyl is at the top instead of at the bottom, when the substitution is electrophilic, is explainable from the fact that S_N2 requires attack from the rear (impossible in bromobenzene), while S_E2 requires frontal attack, which is very facile in phenylmagnesium bromide.

A further example of an electrophilic substrate, which reacts with Grignard reagents by a concerted electrophilic substitution, is carbon dioxide, for which the same reactivity series applies as was found for acetone.[22]

(b) Stereochemistry. The investigation of the steric course of nucleophilic substitution has been of crucial importance for the distinction between the concerted and the stepwise mechanisms S_N2 and S_N1. Grignard reagents usually have a very low barrier for inversion and the stereochemical

course is therefore impossible to follow. Only one example is known of a Grignard reagent which is chiral and has magnesium at the asymmetric carbon. The reagent is 1-methyl-2,2-diphenylcyclopropylmagnesium bromide and was prepared by Walborsky and Young.[27] With this reagent the reaction with carbon dioxide was found to take place with full retention at carbon. The reaction with benzophenone, however, was found to take place predominantly with retention, but with a 20 % loss of optical activity.[22] While a concerted reaction is indicated with electrophilic CO_2, the partial loss of optical activity in the reaction with benzophenone indicates a finite lifetime of a cyclopropyl radical on the reaction path. It should be remembered that the strained cyclopropyl radical has a rather high barrier for inversion.

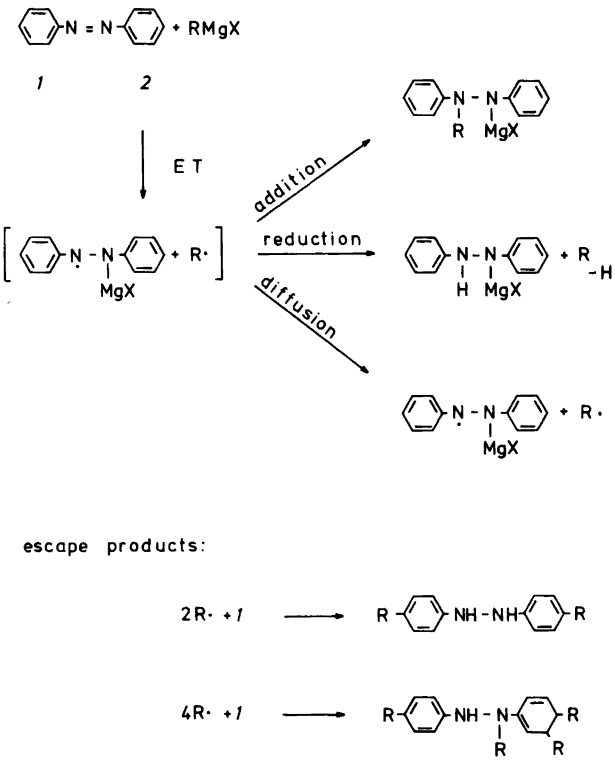
Carbon dioxide and acetone are then obviously electrophiles toward Grignard reagents, while benzophenone, azobenzene and other highly conjugated substrates are electron acceptors. No doubt it will be possible to find substrates in which the concerted mechanism and the stepwise are of comparable efficiency and will therefore compete. One might, for example, expect to find substrates reacting by ET with *t*-butylmagnesium halide, but by concerted mechanism with methyl- or phenylmagnesium reagents. Most likely, however, the two competing mechanisms would lead to the same product(s) and only special kinetic investigations would reveal how large the individual contributions had been.

The evidence for concerted electrophilic displacement of magnesium which has been presented, *e.g.*, the reactivity series and the steric outcome, although very persuasive is not definitive, since it would be indistinguishable from a very "tight" ET mechanism. The subject of the review is, however, ET reactions in which the two steps are clearly distinguishable. It seems that more than one type of ET from a Grignard reagent is possible, dependent on which type of substrate is the acceptor.

Four-center and six-center ET. Primary and secondary cage product. For the ET reaction of benzophenone with Grignard reagents several examples have been given of changes in the product distribution without changes in the overall reaction rate. This may have left the impression, that ET is an extremely unselective process with no steric or conformational restrictions and requirements. This is probably an incorrect picture, and it is likely that a number of ET types may be distinguished, each characterized by a specific geometry of the transition state. Often the radical recombination will occur extremely fast to form a product with a structure closely related to the ET transition state. This product may be named the primary cage product. Sometimes, when the immediate collapse of the radicals fails to take place, an alternative secondary cage product is formed after a reorientation of the radicals. The third possibility is that the radicals diffuse from each other to form escape products. The concept of different types of ET emerged from work with azobenzene as the substrate for reactions with Grignard reagents.

Reactions of azobenzene with Grignard reagents. Azobenzene has been known to react with Grignard reagents with formation of hydrazobenzene and the hydrocarbons, which result from coupling or disproportionation of the alkyl of the Grignard reagent.[28] During a reinvestigation of the reaction it was found, however, that addition to form monoalkylhydrazobenzene was important; in the 1,2- as well as the 1,6-fashion, and that also *p,p'*-dialkylated hydrazobenzenes, and even tetraalkylated products, were sometimes formed,[29] Scheme 3.

A study of the reaction rates as well as the product distributions when using different Grignard reagents revealed that allylic reagents reacted very fast to give addition product exclusively; benzyl and *t*-butyl both gave more than 50 % addition, but benzyl was 100 times slower than *t*-butyl. Primary and secondary reagents all gave between 10 and 20 % addition, but the rates increased by a factor 10 for each hydrogen in the β-position, Table 5. Isopropylmagnesium bromide therefore reacted 10 000 times faster than isobutylmagnesium bromide. In spite of these exceedingly large variations in rate, the fraction of addition product was the same within narrow limits. This indicates that the factors which determine the rate are common for the two reactions, which must therefore have closely related reaction mechanisms. Because of the analogy with benzophenone, this mechanism was assumed to be ET. To test this theory the plot of log rate *versus* the anodic oxidation potential was made and a nice linear relation was observed except for *t*-butyl and benzyl, which were both too slow, Fig. 7.



Scheme 3.

The best interpretation must be that the rate controlling step is ET. Since benzyl reacts several hundred times more slowly than expected from the value of its anodic oxidation potential, an important role has to be assigned to the β-hydrogens. A six-center transition state seems indicated in which the β-hydrogen is very close to an azo-nitrogen, Fig. 8a. After the ET the tendency is high for the hydrazyl radical to abstract the close-by hydrogen atom and thereby

Table 5. Pseudo first-order rate constants and product distributions (see text) for the reaction of 0.1 M azobenzene with 0.5 M alkylmagnesium bromide in diethyl ether at 20 °C. Number of experiments given in parantheses.

Alkyl	% Addition product	k_{obs} s^{-1}
CH_3	14	0.5×10^{-5} (3)
C_2H_5	10	1×10^{-2} (3)
i-C_3H_7	14	1 (1)
C_4H_9	15	2×10^{-3} (3)
i-C_4H_9	22	1×10^{-4} (3)
s-C_4H_9	12	6×10^{-1} (1)
t-C_4H_9	55	5×10^{-2} (1)
C_3H_5 (allyl)	100	120 (1)
$C_6H_5CH_2$	57	3×10^{-4} (3)
C_6H_5		1×10^{-5} (1)
$CH_3CH{=}CHCH_2MgBr$	100	13 (1)
$CH_3CH{=}CH{-}CH(MgBr)CH_3$	100	50 (1)

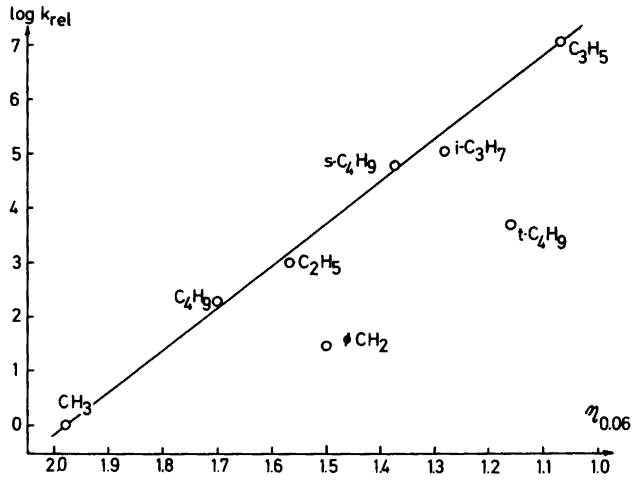


Fig. 7. Log (k_{RMgBr}/k_{CH_3MgBr}) for the reaction of Grignard reagents with azobenzene (Table 5) *versus* the anodic oxidation potential of the Grignard reagent. See text.

producing the primary cage product. But in spite of the proximity of the hydrogen, the immediate collapse may fail and a collapse to form addition product is then possible, leading to a secondary cage product. Because of a rather low affinity of the hydrazyl radical for alkyl radicals, the latter may also diffuse out of the cage and attack unreacted azobenzene, which may lead to the various escape products.

The geometry for the transition state for the ET taking place with benzophenone and Grignard reagents must be different from that of the azobenzene-ET, since benzyl has the expected reactivity in the first-mentioned reaction. A four-center transition state is therefore indicated, in which case the 1,2-addition product is the primary cage product, Fig. 8b. A study of the kinetic isotope effect of deuterium in the β-positions of the Grignard reagent, however, seems to indicate that reactions in which reduction product is formed have a higher value of k_H/k_D than reactions in which addition predominates, Table 6. It seems that six-center and four-center ET are of almost the same efficiency toward benzophenone and that one may substitute the other according to the steric require-

Table 6. Relative yield (%) of benzhydrol in the reaction of Grignard reagents with benzophenone in diethyl ether at 20 °C. Kinetic isotope effect k_H/k_D for the overall reaction by the introduction of deuterium in the β-position(s) of the Grignard reagent. The effect given is the estimated value for 100 % substitution based on rate measurements with a reagent of the stated degree of deuteration.

Grignard reagent	[Benzophenone] M	k_H/k_D	% benzhydrol	% deuteration
0.50 M C_2H_5MgBr	0.02	1.01	6	95
0.20 M C_4H_9MgBr	0.02	1.28	55	97
0.50 i-C_3H_7MgBr	0.02	1.16	20	92
0.25 i-C_4H_9MgBr	0.02	1.46	91	95
0.26 M *t*-C_4H_9MgCl	0.02	1.0	0	64
0.02 M i-C_3H_7MgBr	0.25	2.5		92
0.02 M i-C_4H_9MgBr	0.25	2.5	95.5	95
0.02 M *t*-C_4H_9MgCl	0.25	1.0		64
0.10 M c-C_5H_9MgBr	0.02	1.67	100	75
0.02 M c-C_5H_9MgBr	0.25	2.8	100	75

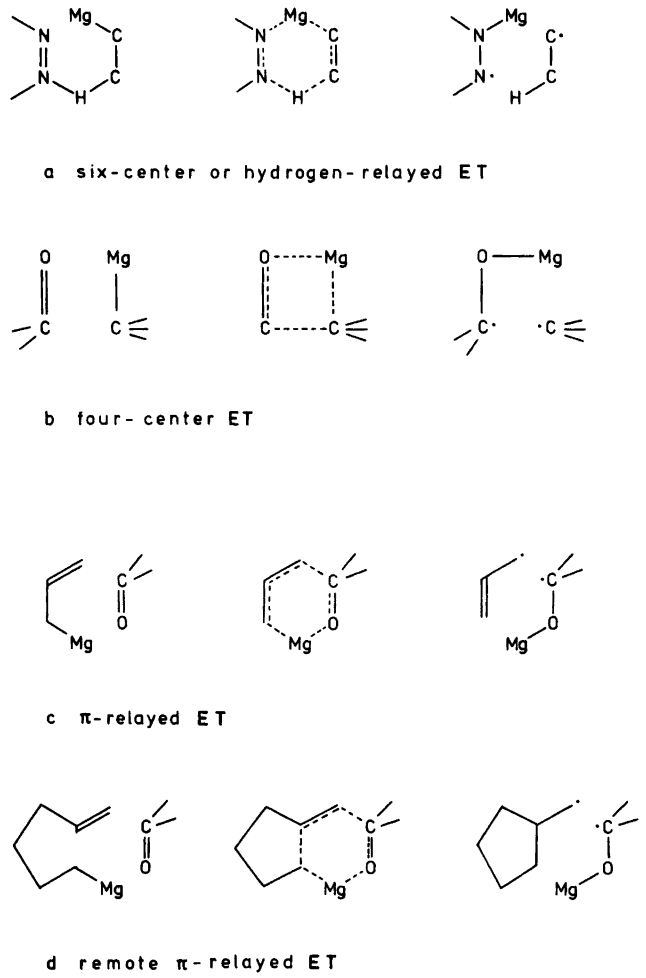


Fig. 8. Geometry of the transition states for electron transfer from Grignard reagents to various substrates.

ments without any significant effect on the rate. The six-center ET is not possible in the case of methyl- benzyl-, or *t*-butylmagnesium halide reacting with either benzophenone or azobenzene. For this reason methyl, benzyl, and *t*-butyl are out of line in the reactions with azobenzene, which is not well-suited for the four-center ET. With benzophenone these reagents have the expected reactivities reacting by a four-center ET. Both with azobenzene and benzophenone the primary cage products for methyl, benzyl and *t*-butyl reagent are 1,2-addition products. Isobutylmagnesium bromide is not suited for a four-center ET, but has a β-hydrogen. It is therefore well-behaved in the reaction with azobenzene (six-center ET) and the six-center ET in the reaction with benzophenone is only slightly less effective than required according to its oxidation potential. A less hindered primary Grignard reagent reacts by four-center ET with benzophenone and by six-center ET with azobenzene yielding 1,2-addition product and reduction product, respectively, as the primary cage product.

Four-center and six-center reaction mechanisms for Grignard reagents are not new. Especially a six-center concerted mechanism for the Grignard reduction, Fig. 9, has been widely

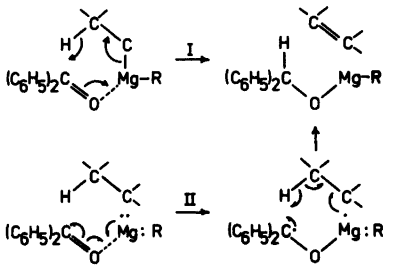


Fig. 9. I. Cyclic concerted mechanism for the reduction of benzophenone with isobutylmagnesium bromide. II. Stepwise electron transfer mechanism for the same reaction.

accepted after being suggested by Whitmore.[30] Many observations of asymmetric induction, when reduction of ketones is performed using an asymmetric reagent have been rationalized on the basis of the Whitmore mechanism.[31] Also rather refined experiments have shown that a *cis* planar arrangement of magnesium, α- and β-carbon, and β-hydrogen of the reducing Grignard reagent is favourable, or even necessary for the reaction.[32] It seems, however, that the *cis* planar arrangement may just as well be a requirement for the six-center ET, Fig. 8a, as for the Whitmore mechanism.

One may wonder why a stepwise ET should be preferred to a six-center concerted reaction. The question probably should be answered by a consideration of orbital symmetry rules for compounds with highly polar bonds. The simple Whitmore reduction mechanism may just not be allowed. A closely related question would be: why do we so often get secondary cage products as *e.g.* 1,6-addition with benzophenone or 1,2-addition with azobenzene? It might be a result of the geometry of the transition state not being optimal for bonding. Possibly the one electron transfer does not require an approach nearly as close as does actual C–C or C–H bonding.

The possibility that spin correlation in the radical pair is a factor of importance for the product distribution has been considered. According to the theory developed for the CIDNP phenomena it has been argued that combination of radical pairs may be under the influence of magnetic fields,[33] and that the product distribution in the reaction of benzyl chloride and butyllithium may be changed by the application of a magnetic field.[34] The reaction between azobenzene and butylmagnesium bromide was performed in a 15 000 G magnetic field with no clear-cut effect on the product distribution.[29] Attempts to reproduce the results obtained with benzyl chloride and butyllithium were, however, also unsuccessful, since the magnetic field did not change the product distribution significantly.[29]

Reaction of ethyl cinnamate with t-butylmagnesium chloride. Escape products. The "normal" reaction products from the addition of a Grignard reagent to an α,β-unsaturated ester are the 1,4- and the 1,2-adducts. When reacting ethyl cinnamate with *t*-butylmagnesium chloride, Crossland,[35] however, obtained the 1,3-adduct in very significant yields, Fig. 10.

In a study of the mechanism of this reaction, free *t*-butyl radicals were found to play an important role.[36] It was found possible to suppress the 1,3-addition by the addition of α-methylstyrene, which acted as a free radical scavenger. The formation of 1,4-adduct was not influenced by the addition of scavenger. It was concluded that the reaction is initiated by ET from the Grignard reagent to the ester and that because of low affinity between the *t*-butyl radical and the ester anion radical, a large fraction of the radicals diffuses out of the cage, Scheme 4. The affinity of the *t*-butyl radical toward ethyl cinnamate is higher than that toward other species in the reaction mixture, and addition takes place with formation of a neutral benzylic radical. This radical accepts an electron from the ester anion radical, and after transfer of the magnesium ion, the 1,3-adduct is formed. Since the adduct is an ester and a Grignard reagent, it undergoes cyclization and a cyclopropanone hemiketal salt is produced.

Factors which influence the ratios between primary/secondary cage products and escape products. From the experience obtained with

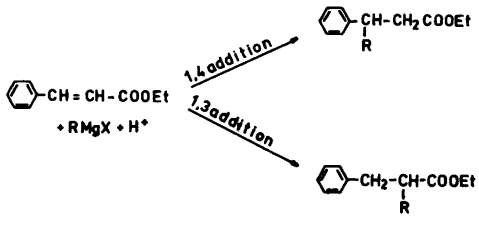
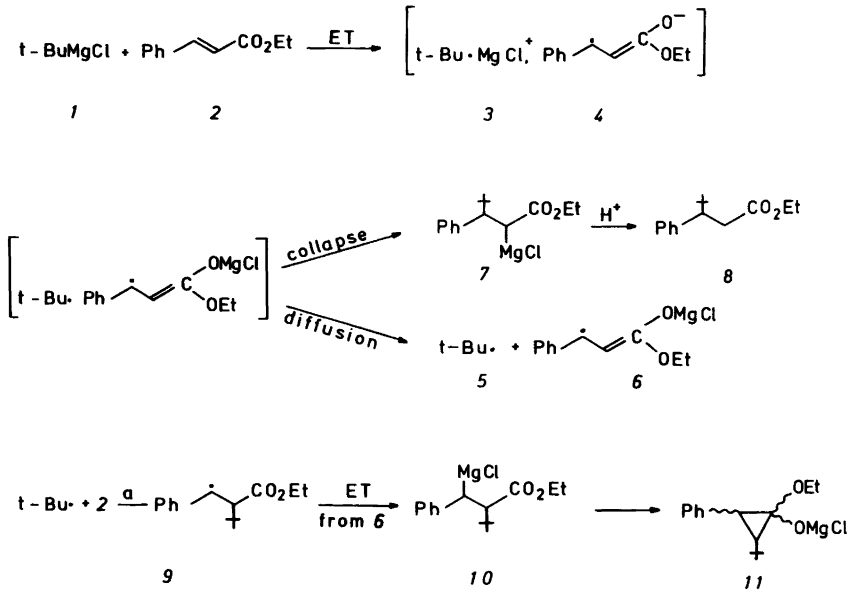


Fig. 10. Products obtained in the reaction of *t*-butylmagnesium chloride with ethyl cinnamate.



Scheme 4.

benzophenone, azobenzene and ethyl cinnamate, one is left with the impression that the most important factor ruling the distribution of products in an ET reaction of a Grignard reagent is the affinity of the substrate anion radical toward the alkyl radical. The benzophenone ketyl has a rather high affinity for the free radicals and the amount of escape products is usually below 10 % for *t*-butyl reagents, and much lower for less hindered alkylmagnesium halides. On the other hand, with varying substitution in the benzophenone the ratio between the primary and the secondary cage product may vary almost between 0 and 100 %, Table 1.

Anion radicals of ethyl cinnamate and azobenzene are much less reactive and escape products account for large fractions of the reaction products. At the same time secondary cage products have been of little importance in the examples investigated.

Important for which type of escape products is formed is, for instance, the affinity of the unreacted substrate toward alkyl radicals. The reactivity series is here α-methylstyrene>ethyl cinnamate>azobenzene≫benzophenone. Anion radical dimerization is fast in benzophenone ketyl, and very slow with the anion radicals from azobenzene and ethyl cinnamate.

Dimesityl ketone is highly hindered and the primary cage product, the 1,2-adduct, is not formed. The caged radical pairs, however, predominantly collapse in a 1,6-fashion to form the secondary cage product when the Grignard reagent is secondary or tertiary, or the reduction product if the alkyl is primary.[37] A smaller fraction diffuses out of the cage and since the ketyl is sterically hindered toward pinacol formation, the stable magnesium ketyl free radical is the escape product.

In a recent publication,[38] dimesityl ketone was reported to yield with Grignard reagents stable pairs of anion radical/cation radical. The evidence was ESR spectra and reactivity series based on observation of the rate of formation of absorption at 579 mm. It was shown, however, that this absorbtion is due to the ketyl and that if transition metal impurities are avoided no colour is developed in the reaction with primary Grignard reagents.[37]

Radical probes in electron reactions of Grignard reagents. The ET mechanism requires a finite lifetime as a free radical for the alkyl of the Grignard reagent. ESR experiments have shown beyond any doubt the presence of ketyl radicals, while only very vague indications have been obtained by this method as evidence for the

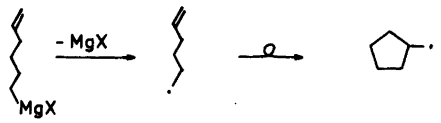


Fig. 11. Cyclization of the 5-hexenyl radical as obtained by homolysis of 5-hexenylmagnesium halide.

existence of alkyl radicals in the reaction mixture. Although the evidence from free radical by-products and from rate correlations proves that Grignard reactions with benzophenone and azobenzene run *via* ET, an analysis is required of the details of the ET and the fate of the ion radicals, which are the immediate products of the electron transfer.

A promising approach to the problem seems to be the use of radical probes in the form of Grignard reagents, in which the alkyl is capable of very fast rearrangement, if it is released in its free state with an unpaired electron. The 5-hexenyl radical has been shown to cyclize to cyclopentylmethyl radical with a rate constant of 10^5 s^{-1},[39] Fig. 11. In the reaction of the stable 5-hexenylmagnesium bromide with oxygen, Lamb *et al.*[40] obtained significant amounts of cyclopentanemethanol, which indicated a free radical chain mechanism. Ashby and Bowers [41] used this probe in the reaction with benzophenone. With the simple 5-hexenylmagnesium bromide they obtained equal amounts of benzhydrol and uncyclized, 1,2-addition product, but with a tertiary reagent, 1,1-dimethyl-5-hexenylmagnesium bromide, they obtained a cyclized 1,6-addition product and a 1,2-addition product, which was practically uncyclized, when ether was the solvent, but which was up to 40 % cyclized in THF, Fig. 12. With azobenzene in ether, even the primary 5-hexenylmagnesium bromide gave a cyclized 1,2-addition product and also a cyclized 1,6-addition product.[29] Ashby and Bowers also prepared a neopentyl-like reagent, 2,2-dimethyl-5-hexenylmagnesium bromide, and with this primary Grignard reagent they obtained a 10 % yield of cyclized 1,2-addition product in the reaction with benzophenone in ether.

In order to interpret these results, Ashby and Bowers suggest that the alkyl radicals when formed by ET are still bound to the magnesium ion. These magnesium cation radicals are supposed to be stable in the open chain state. They may in time either collapse to form uncyclized 1,2-addition product or they may by dissociation from magnesium form genuine free radicals, which rearrange and add to the ketyl in the 1,6- or the 1,2-fashion.

A serious objection may be raised against this interpretation. It is known that the rate constant of cyclization of the hexenyl radical is $\simeq 10^5$ s^{-1}. This does not leave time for the radical to rearrange while in the cage. In reactions, which like the autoxidation of Grignard reagents have a chain mechanism, the radicals live long enough for the rearrangement to take place, especially if the concentration of oxygen is kept low, but in the reaction with benzophenone both 1,2- and 1,6-addition products are formed within the cage, since scavengers like α-methylstyrene or fluorenone ketyl fail to interfere with the normal product distribution or reaction rate. It is difficult to give an explanation why the cage in this reaction should live several thousands times longer than normal caged radical pairs.[42]

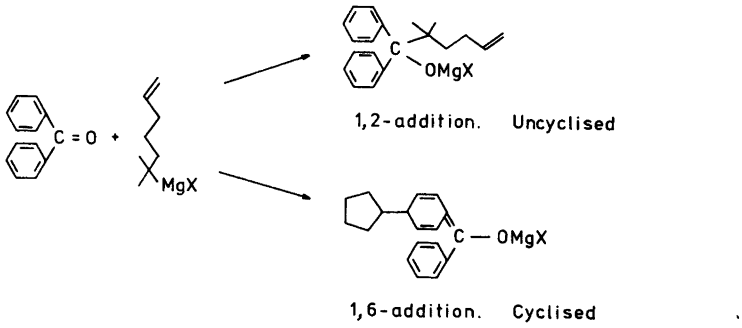


Fig. 12. Products obtained in the reaction of benzophenone with 1,1-dimethyl-5-hexenylmagnesium halide.

Since an alternative interpretation seems needed, one might imagine a "ring closing ET", Fig. 8d, which becomes a possible alternative when the more 'normal' ET types are blocked by steric hindrance. The electron donating ability of the Grignard reagent is caused by the high electron density at the α-carbon. By means of resonance this excess charge may be relayed either to the β-hydrogen, Fig. 8a, or to the γ-carbon of an allylic reagent, Fig. 8c. It seems possible that the electron pressure might also be relayed to the π bond of a remote double bond if a suitable conformation is obtainable, Fig. 8d.

A factor which would favour the relayed ET mechanisms is the low steric requirements, since the voluminous magnesium atom does not have to approach the substrate very closely. The collapse of the ketyl and the cyclized radical would be possible in a 1,2- or 1,6-fashion within the cage.

Transfer coefficients for ET from Grignard reagents. In the preceeding sections several examples have been described in which $\Delta G^{\neq}$ for the reaction of a Grignard reagent has been linearly correlated with ΔG for the reaction, the last quantity being measured as the anodic oxidation potential. The slope of the plot:

$$\Delta G^{\neq} = \alpha \Delta G + \text{constant}$$

is the symmetry or transfer coefficient, which for processes at electrodes is often between 0.3 and 0.7.

For oxidation of Grignard reagents at a platinum anode the Tafel plots [19] showed two different values for α since at low current densities and with alkyls, corresponding to unstable radicals, the value was 0.20, while at higher current densities and with alkyls forming stable radicals (benzylic, tertiary, secondary), the value was 0.45. The changeover from the lower value to the higher was seen with isopropyl at 5×10^{-4} amp cm^{-2} and with ethyl at 10^{-2} amp cm^{-2}. The change in the value of the transfer coefficient indicates a change in the mechanism of the electrode process.

For the reaction of benzophenone and azobenzene [29] the plots of log rate *versus* anodic oxidation potential for the various Grignard reagents have very different slopes, since the transfer coefficient for the reaction of azobenzene is 0.45, Fig. 7, while for the reaction of benzophenone, the transfer coefficient is only 0.23. Fig. 3. That the two values result from dissimilar reaction mechanisms seems obvious. A more difficult problem is whether the finding can give any support to the assignment of the six-center SET to the reaction with azobenzene and the four-center SET to the reaction with benzophenone. Electron transfer in organic chemistry and organometallic chemistry has been the object of much activity and theories have developed which allow predictions concerning the relations between the activation energy for a reaction and the difference in electrochemical potentials of the reactants.

The Marcus theory of ET reactions. The theory developed by Marcus and others for reactions having an ET as the rate determining step has in recent years successfully been applied to organic reactions and organometallic reactions.[44] The theory relates the reaction rate to two variables of which λ is the reorganization free energy on going from the ground state to the transition state and $\Delta G^{\circ\prime}$ is the driving force for the reaction. In a simplified form the theory requires that:

$$\Delta G^{\neq} = \frac{\lambda}{4}\left(1+\frac{\Delta G^{\circ\prime}}{\lambda}\right) \qquad (1)$$

$\Delta G^{\circ\prime}$ is available from measurements of standard oxidation potentials of Grignard reagents as described earlier in this review combined with the standard reduction potentials for the substrates,

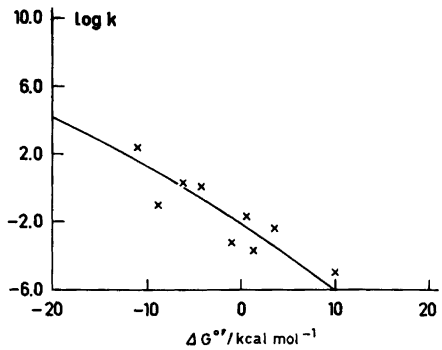


Fig. 13. Marcus plot (eqn. (1)) of rate data for the reaction between azobenzene and alkylmagnesium bromides (Table 5), using an electrostatic term of -10 kcal mol^{-1} to correct ΔG° values. The reduction potential of azobenzene was taken to be -1.12 V and approximate E° values of alkylmagnesium bromides were from Table 2.

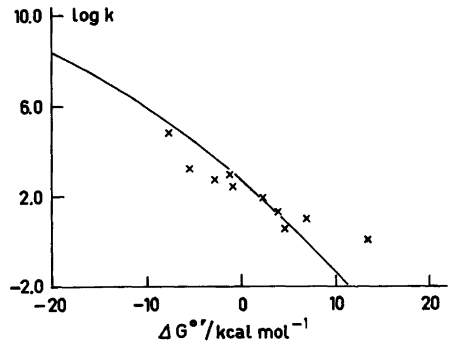


Fig. 14. Marcus plot (eqn. (1)) of rate data for the reaction between benzophenone and alkylmagnesium bromides (Table 3), using an electrostatic term of -15 kcal mol^{-1} to correct $\Delta G°$ values. The reduction potential of benzophenone was set equal to -1.48 V and approximate $E°$ values of alkylmagnesium bromides were from Table 2.

e.g. $E_o = -1.48$ V for benzophenone and -1.12 V for azobenzene. Using the rate data in Table 3 and Table 5, Professor L. Eberson has kindly performed a series of calculations to find the λ values which give the best possible fit of the rate data to the Marcus parabolae (1). Because of the low dielectric constant of the ether solvent, a correction in $\Delta G°'$ had to be added for the change in electrostatic energy at the moment of electron transfer. For azobenzene the correction used was -10 kcal mol^{-1} and the best fit of the data was obtained for a λ value of 70(5) kcal mol^{-1}, Fig. 13. For benzophenone an electrostatic term of -15 kcal mol^{-1} was used and the best fit was obtained for a λ of 44(5) kcal mol^{-1}, Fig. 14.

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