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Preliminary communication

Electron transfer radical mechanism in reactions of Grignard reagents with organic halides*

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In spite of the tremendous synthetic importance of the reactions of Grignard reagents with various types of organic substrates, the mechanistic details of many of these reactions are still insufficiently understood. For example, a large number of reactions[2] of Grignard reagents with organic halides such as quoted in eqn. A[3b], are known to yield products attributable to free radical intermediates, but the mode of formation of the radical intermediates has not yet been explained any more clearly than that suggested by an 'oxidation–reduction' process pointed out by Kharasch and Fuchs[4]. Continuing our research interest in the electron transfer reaction mechanisms[5], we have studied the reactions of benzyl, benzhydryl and trityl chlorides with phenylmagnesium bromide and/or benzylmagnesium chloride, for which a new radical mechanism involving a single electron transfer from the Grignard reagent to the organic halide is presented in this communication.

$$PhCH_2Cl + CH_3MgI \longrightarrow PhCH_2{-}CH_2Ph + CH_4 + C_2H_6 + C_2H_4 + PhCH_2CH_3 \qquad (A)$$

When the Grignard reagents RMgX (prepared from 0.03 mol of bromobenzene or benzyl chloride) were treated with organic halides R′X′ (0.01 mol) in ethyl ether solutions at reflux temperature under nitrogen atmosphere in ordinary laboratory light, the reaction times for ca. 75% completion of the reactions and the product distributions listed in Table 1 were recorded.

That the coupling products R–R, R′–R′ and R–R′ do not arise from an interchange reaction of the type RMgX + R′X′ → R′MgX + RX′, followed by a nucleophilic attack by either of the Grignard reagents RMgX or R′MgX on the halide RX′ or R′X′, is confirmed by the results of Gilman and Jones[6]. On the other hand, it is noteworthy that the reactivity sequence of the halides with respect to their reaction with

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TABLE 1

PRODUCTS AND COMPARATIVE TIMES FOR REACTIONS OF GRIGNARD REAGENTS WITH MONO-, DI- AND TRI-PHENYLMETHYL HALIDES

Reactants		*Time for ca. 75% completion of the reaction (sec)*	*% Yield of the products*[a]			
R'X'	*RMgX*		*R–R'*	*R'–R'*	*R–R*[b]	*R–H*[b]
$C_6H_5CH_2Cl$	C_6H_5MgBr	172 800	56	6	4[c]	12[c]
$(C_6H_5)_2CHCl$	C_6H_5MgBr	28 800	60	6	6[c]	10[c]
$(C_6H_5)_3CCl$	C_6H_5MgBr	4 800	46	5	4[c]	10[c]
$(C_6H_5)_2CCl$	$C_6H_5CH_2MgCl$	3 600	55	5	15	–

[a] Yields of R–R', and R'–R' are based on the organic halide and those of R–R and R–H on the Grignard reagent.

[b] Yields of R–R and R–H have been corrected after taking into account the amounts of these products formed from the radical intermediates during the preparation of the Grignard reagents[7].

[c] Determined by VPC.

phenylmagnesium bromide (as reflected in the relative reaction times) *viz.* $(C_6H_5)_3CCl > (C_6H_5)_2CHCl > C_6H_5CH_2Cl$ is the same as the ease of formation of the corresponding free radicals. The relative reactivity of the two Grignard reagents with respect to trityl chloride *i.e.* $C_6H_5CH_2MgCl > C_6H_5MgBr$ also appears to be related to the ease of formation of the benzyl and phenyl radicals.

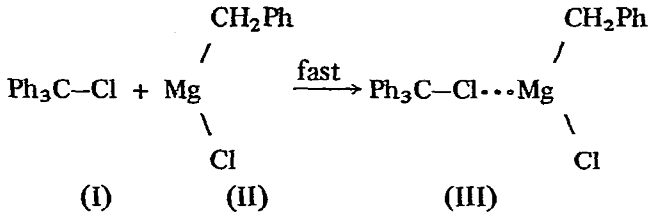
In a typical experiment, when benzhydryl chloride and phenylmagnesium bromide were reacted in complete darkness, the reaction was only 63% over in 28 800 sec; but when illuminated by a 100 watt lamp kept 1ft. away, the reaction was 84% complete within the same time. The product distribution in the two experiments remained essentially unaltered which indicates a common mechanism subject to photochemical catalysis.

Another observation was that on mixing the Grignard reagent with the organic halide, a characteristic colour developed immediately in each case. This colour deepened to start with but slowly faded to that of the solution of the products as the reaction proceeded.

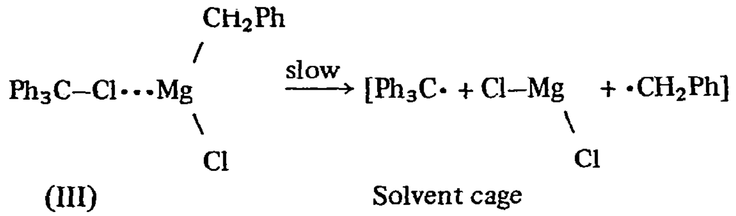
Finally, it was possible to observe an ESR signal which was shown conclusively to occur during the reaction of benzylmagnesium chloride with trityl chloride and which was not present in the ESR spectra of the reagents. The intensity of the signal was found to decrease with time.

The above observations and arguments strongly suggest that there is a radical component in the mechanism of the reactions studied in this work. As the formation of radical intermediates by unimolecular thermal homolytic dissociation is not likely[3a], we suggest the following mechanistic steps (1–5) for these reactions taking the reactants benzylmagnesium chloride and trityl chloride as specific examples.

The proposed pathway suggests that on mixing the two reactants, the organic halide (I) associates with the Grignard reagent (II) in a fast step as shown in (III), through



$$\underset{(I)}{Ph_3C{-}Cl} + \underset{(II)}{\overset{CH_2Ph}{\underset{Cl}{Mg}}} \xrightarrow{fast} \underset{(III)}{Ph_3C{-}Cl\cdots\overset{CH_2Ph}{\underset{Cl}{Mg}}} \qquad (1)$$



$$\underset{(III)}{Ph_3C{-}Cl\cdots\overset{CH_2Ph}{\underset{Cl}{Mg}}} \xrightarrow{slow} \underset{\text{Solvent cage}}{[Ph_3C\cdot + Cl{-}\underset{Cl}{Mg} + \cdot CH_2Ph]} \qquad (2)$$

$$Ph_3C\cdot + \cdot CH_2Ph \longrightarrow Ph_3C{-}CH_2Ph \qquad (3)$$

$$Ph_3C\cdot + \cdot CPh_3 \longrightarrow Ph_3C{-}CPh_3 \qquad (4)$$

$$PhCH_2\cdot + \cdot CH_2Ph \longrightarrow PhCH_2{-}CH_2Ph \qquad (5)$$

the partially negatively charged chlorine and partially positively charged magnesium atoms. This association should undoubtedly polarize the carbon–chlorine and magnesium–carbon bonds further, resulting in the increased anionic character of the benzyl group and decreased electron density on the α carbon of the organic halide. One of the possible pathways for the consumption of the complex (III) is the transfer of one electron from the incipient benzyl carbanion to the triphenylmethyl portion of the halide (I) in the complex, with formation of organic radicals corresponding to the two reagents. Indeed, the stability of the resultant radicals which is related to the ease of their formation, controls the speed of the reaction. We believe that the photochemical catalysis operates by aiding the electron transfer in step 2 and the characteristic colour changes are associated with the electronic transitions absorbing in the visible region of the spectrum. The two radicals formed in step 2 may couple with each other or with themselves to produce the corresponding products (steps 3–5).

The proposed reaction course suggests the formation of toluene and benzene in the reactions of benzylmagnesium chloride and phenylmagnesium bromide respectively via hydrogen atom abstraction by the radicals from the ether solvent. Although the more stable benzyl radical appears to prefer dimerization and coupling with another free radical, the more reactive and less selective phenyl radical does abstract hydrogen from diethyl ether to produce benzene. The intermolecular association of step 1 and single electron transfer as in step 2 are precedented[2,8].

In addition to providing a satisfactory explanation for the electron transfer radical mechanisms of Grignard reagents with carbonyl compounds[8,9], oxygen[10] and 7,7-dibromobicyclo [4.1.0] heptane[11], the proposed mechanism may also satisfactorily account for the reactions of adamantane-type bridgehead bromides[12] with Grignard reagents. The reaction between t-butyl bromide and t-butylmagnesium bromide in which the intermediacy of free radicals has been demonstrated[13] by using CIDNP★ phenomena, may also involve a similar mechanism.

A few more experiments designed to test the validity of this mechanism are in progress and will be reported subsequently.

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★Chemically induced dynamic nuclear polarization.