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NOTE

A RADICAL PROCESS IN A REACTION OF A GRIGNARD COMPOUND

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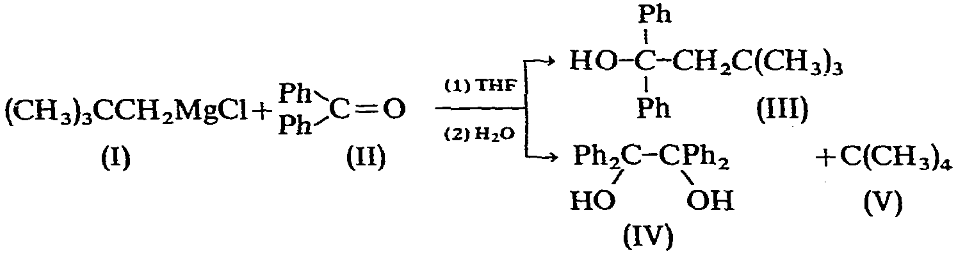
Although not common, there are several types of reactions of Grignard compounds which are recognized as having the characteristics of radical processes. Such reactions are ones which involve substrates or reagents which are widely associated with radical processes; for example, the reactions with oxygen[1], reactions in the presence of cobaltous chloride[2], reactions with electronegative substrates such as nitrosobenzene[3], azoxy compounds[4] and reactions of the triphenylmethyl Grignard reagent[5,6]. Such radical reactions of Grignard compounds have been discussed in the literature by several authors[1,4,7,8]. Recently radical formation during reactions of Grignard compounds has been detected with the aid of electron spin resonance (ESR) by several groups of workers[3,9,10,11]; the report of the presence of radicals during reactions of simple aliphatic Grignard compounds with benzophenone and with substituted benzophenones, as well as with acetophenone and substituted acetophenones[9,10], is particularly significant since these are processes in which radical products have not been found previously and would not be expected.

We wish to report both chemical and ESR evidence for the occurrence of radicals during the reaction of the Grignard reagent from neopentyl chloride (I) with benzophenone (II) in tetrahydrofuran (THF) as the solvent. Although the main reaction product is the expected but hitherto unknown 1,1-diphenyl-3,3-dimethylbutanol (III), benzopinacol (IV) was also isolated in approximately 20% yield and a corresponding amount of neopentane (V), although not isolated, was shown to be present from nuclear magnetic resonance (NMR) measurements on the unhydrolyzed reaction mixture. The latter two compounds are products characteristic of a radical process.



$$\underset{\text{(I)}}{(CH_3)_3CCH_2MgCl} + \underset{\text{(II)}}{Ph_2C{=}O} \xrightarrow[(2)\ H_2O]{(1)\ THF} \underset{\text{(III)}}{HO\text{-}C(Ph)_2\text{-}CH_2C(CH_3)_3} \text{ and } \underset{\text{(IV)}}{Ph_2C(OH)\text{-}C(OH)Ph_2} + \underset{\text{(V)}}{C(CH_3)_4}$$

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EXPERIMENTAL

The preparations of the reagents and their reactions were carried out in a glass-to-glass sealed high-vacuum apparatus under conditions which rigorously exclude oxygen and moisture as previously described[12]. Crystals of sublimed magnesium were used* to prepare perfectly clear and colorless solutions of Grignard reagents which contained no visible magnesium; there was no observable magnesium sediment in the ampoules after standing for several months**.

NMR spectra taken immediately after mixing benzophenone with the Grignard reagent from neopentyl chloride gave an increasing signal which was shown to be due to neopentane by its subsequent isolation from the unhydrolyzed reaction mixture and by comparison with the signal obtained from an authentic sample of neopentane, prepared by the reaction of neopentylmagnesium chloride with an alcohol in THF. The signals for bineopentyl could not be detected in the reaction mixture; an authentic sample of bineopentyl was isolated with the aid of preparative vapor phase chromatography from the distillate of a solution of neopentylmagnesium bromide in THF where it was formed in the reaction of neopentyl bromide with magnesium in *ca* 50% yield; its NMR spectrum was made. From the hydrolyzed reaction mixture there was isolated by crystallization from hexane a 20% yield of benzopinacol, m.p. 193° (dec.) which was identified by direct comparison of its IR spectrum with that of an authentic sample. The major reaction product was the previously unreported 1,1-diphenyl-3,3-dimethylbutanol, m.p. 76°, which was identified by its NMR and IR spectra and by carbon and hydrogen analyses. (Found: C, 85.10; H, 8.60. $C_{18}H_{22}O$ calcd.: C, 84.99; H, 8.72%.)

These reaction products were produced in the same amounts when the reaction was carried out in the absence of light.

The source of the hydrogen for the formation of the neopentane has not been determined but presumably is the THF solvent. Stevens[4] has isolated a tetrahydrofuran-containing product from another radical process in which a Grignard reagent is involved.

The presence of radicals during the process was also demonstrated by ESR measurements as follows. A solution of (I), about 0.5 *M* in THF, was prepared and transferred under the same rigorous conditions into the bottom of a Pyrex capillary tube (inner diameter *ca.* 1 mm). Benzophenone was distilled into the upper cooled portion (−78°) of this tube where it solidified. After the capillary was sealed, it was warmed to −20°, the contents mixed and the tube was immediately inserted into the cavity of a Varian 4500 ESR apparatus***. A weak but distinct and reproducible spectrum was recorded in which the features of the already published ESR spectrum for

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* We gratefully acknowledge the gift of sublimed magnesium from the Dow Chemical Company; it had the following maximum limits of elemental impurities in parts per million: Al, 1; Cu, 1; Fe, 4; Mn, 2; Ni, 4; Pb, 10; Si, 10; Zn, 100; Ba, 1; Ca, 18; K, 5; Na, 6; Sn, 1. The formation of benzopinacol during the reaction of ethylmagnesium bromide with benzophenone, previously reported by Lewis and Wright[13] was attributed to the presence of "impurities" in the metallic magnesium used by these authors for the preparation of the Grignard compound.

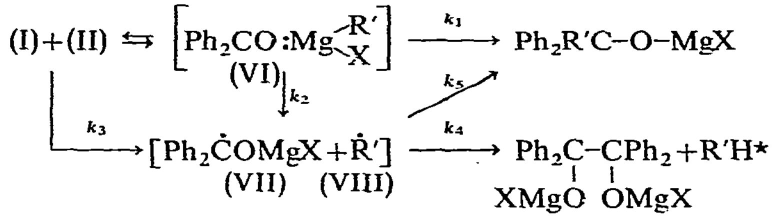
** Noller and coworkers[14,15] were unable to detect any benzopinacol when filtered Grignard solutions were used for reaction with benzophenone.

*** We wish to thank Prof. HARDEN MCCONNELL and Mr. R. OGATA for these measurements.

benzophenone-magnesium ketyl in dimethoxyethane[16] could be observed. The coupling constants obtained were 2.9, 1.1 and 3.4–3.5 gauss as compared to the reported values for *ortho*, *meta* and *para* signals of 2.87, 1.01 and 3.46 gauss respectively.

DISCUSSION

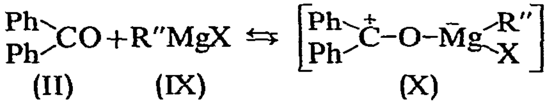
The chemical and ESR results provide strong evidence for the occurrence of a radical process during the reaction of the Grignard reagent from neopentyl chloride with benzophenone and require the postulation of a radical component in this particular reaction; the possibilities are represented by the following equations:



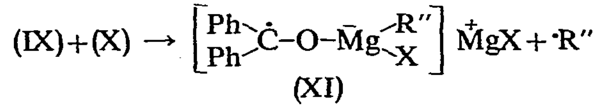
From the evidence it is not possible to make any firm, detailed mechanistic conclusion. It seems reasonable to postulate, however that the steric bulk of the neopentyl group (R′) so retards the normal addition reaction as represented by k_1 (which may be an oversimplification of a more complex process) that the radicals, formed in the process represented by k_2, are able to escape from the solvent cage. The neopentyl radical can then react with the solvent to give neopentane and the ketyl can dimerize to give the magnesium halide salt of benzopinacol. It is impossible to say to what extent the normal addition reaction might take place by recombination of radical (VII) with radical (VIII) within the solvent cage (via k_5).

Another case in which steric hindrance seemingly is responsible for causing a radical reaction was reported by Kharasch, Morrison and Urry[17] who postulated the two competing mechanisms (k_1 *vs.* k_2) in the reaction of mesitoyl chloride (2,4,6-trimethylbenzoyl chloride) with methylmagnesium iodide (but not with methylmagnesium chloride or bromide) to give the substituted benzil, $[2,4,6\text{-}(CH_3)_3C_6H_2CO]_2$.

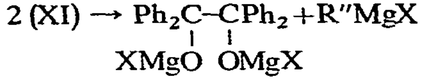
For the formation of benzopinacol during the reaction of triphenylmethylmagnesium halide with benzophenone, as reported both by Gilman[5] and Bachmann[6], Eicher recently proposed the following mechanism (where R″ represents the



$$\underset{(II)}{\begin{matrix}Ph\\Ph\end{matrix}\!\!>\!CO}+\underset{(IX)}{R''MgX} \rightleftarrows \underset{(X)}{\left[\begin{matrix}Ph\\Ph\end{matrix}\!\!>\!\overset{+}{C}-O-\overset{-}{Mg}\!<\!\begin{matrix}R''\\X\end{matrix}\right]} \qquad (1)$$



$$(IX)+(X) \rightarrow \underset{(XI)}{\left[\begin{matrix}Ph\\Ph\end{matrix}\!\!>\!\dot{C}-O-\overset{-}{Mg}\!<\!\begin{matrix}R''\\X\end{matrix}\right]} \overset{+}{M}gX+{\cdot}R'' \qquad (2)$$



$$2\,(XI) \rightarrow \begin{matrix}Ph_2C-CPh_2\\ | \quad\;\; | \\ XMgO\;\;OMgX\end{matrix}+R''MgX \qquad (3)$$

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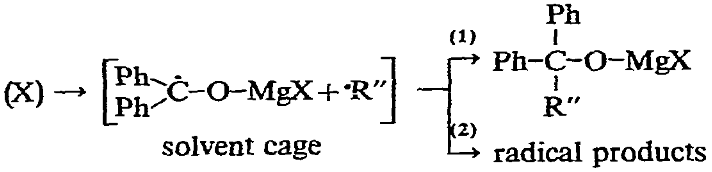
* The formation of neopentane occurs by an independent process presumably by reaction of the radical R′ with the solvent.

triphenylmethyl group)[7].

This mechanism is used by Eicher to rationalize Wittig and Herolds (unpublished) observation that triphenylmethylsodium alone does not react with benzophenone but that benzopinacol is produced after triphenylboron is added to the reaction mixture[8]. It is postulated by Eicher that the triphenylboron complex, similar to (X), reacts with triphenylmethyl carbanion leading to the transfer of one electron to give a radical anion*, similar to (XI) and triphenylmethyl radical.

In the case of the reaction of a Grignard compound with *e.g.* benzophenone, however, reaction (2), proposed by Eicher, is mechanistically not necessary to explain radical formation; the transfer of one electron can take place within complex (X) itself:



This may either lead to the formation of "normal" addition products (pathway 1) or to the formation of radical products (pathway 2).

In conclusion it seems possible that many reactions of Grignard compounds have the potential for such a radical course.

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* This is similar to the recent proposal by Eastham and Screttas[18,19] of single electron transfer (SET) processes during reactions of organolithium compounds.