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(20) $E_{1/2}$ values vs. SHE at 25 °C determined by normal pulse polarography and cyclic voltammetry (J. P. Gisselbrecht and M. Gross, unpublished results): (a) propylene carbonate solutions, μ = 0.1, $(n\text{-hexyl})_4ClO_4$ (in the same conditions copper(II) perchlorate shows a potential of +494 mV/SHE for the copper(II)/copper(0) couple); (b) aqueous solutions, μ = 0.1, KCl, copper(II)/copper(0) +334 mV (in propylene carbonate solution the bis copper(II) complex of **1** shows a reversible transfer of two electrons at +545 mV).
(21) Solvent: propylene carbonate/chloroform 1:1. Owing to the spontaneous partial reduction of copper(II) to copper(I) when [18]-N_2S_4 subunits are present, the ϵ values for the copper(II) complexes of **2** and **3** are approximate.
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(26) Chemistry Department, TNO, Croesestraat, Utrecht, Netherlands.
(27) Chemistry Department, Università di Milano, Via C. Golgi, 19, 20133 Milano, Italy.
(28) ERA No. 265 of the CNRS.

Albert H. Alberts,[26] Rita Annunziata,[27] Jean-Marie Lehn*
Institut Le Bel, Université Louis Pasteur
67070 Strasbourg, France[28]
Received August 8, 1977

Nature of Alkyl Transfer in Reactions of Grignard Reagents with Ketones[1]

Sir:

Now that the mechanisms of formation of hydrol and pinacol[2] in Grignard reactions with ketones have been determined, the description of the alkyl transfer from the Grignard reagent to the carbonyl carbon atom is the most significant question that remains to be answered. With respect to the nature of this alkyl transfer, Holm and Crossland[3] have presented convincing evidence for a rate-determining single-electron transfer (SET) step (eq 1) in the reaction of *t*-C_4H_9MgCl with benzophenone in diethyl ether involving the intermediate formation of a "free" radical and radical anion. The ability to "trap" or "observe" the intermediate radical or the radical anion would be instrumental in establishing the integrity of the proposed mechanism.

$$\text{"RMgX"} + Ph_2C{=}O \rightarrow [R\cdot + Ph_2\dot{C}{-}O^{-+}MgX] \rightarrow \text{products} \quad (1)$$

With this in mind, radical probes were incorporated into the R group of Grignard reagents such that free-radical character would be observed as isomerization or cyclization of the particular probe. The radical probes studied are illustrated in Table I.

The absence of isomerization or cyclization in the 1,2-addition products of "*cis*-propenylmagnesium bromide" (a vinylic Grignard) and "5-hexenylmagnesium bromide" (a primary Grignard), respectively, with benzophenone indicates that either the reaction is polar or, if SET, no "free" radical character is exhibited. On the other hand, when 1,1-dimethyl-5-hexenylmagnesium chloride (a tertiary Grignard) was allowed to react with benzophenone, the resulting products consisted of 62% 1,6 addition and 38% 1,2 addition. Although no cyclization of the probe was observed in the 1,2-addition product, cyclization was observed for 74% of the 1,6-addition product.

The ratio of cyclized to uncyclized 1,6-addition products (74:26) established the radical nature of the 1,6-addition process and also indicates that the rate of probe cyclization is comparable with the rate of 1,6-addition product formation ($R_{cyc} \simeq 10^5\ s^{-1}$).[4] It is important to note that the ratio of 1,6-addition to 1,2-addition products (62:38) indicates that the rate of formation of 1,6-addition product is faster than the rate of 1,2-addition product formation. Thus, 1,2-addition product is being formed at a rate slower than that of cyclization of the probe but no cyclization was observed in the 1,2-addition product. Since Holm's results eliminate the possibility of a polar 1,2-addition reaction, the only reasonable rationalization of these findings is that, after the transfer of the electron from the Grignard reagent to the benzophenone, R· of the Grignard is still tightly bound to the magnesium as a radical cation ($RMgX^{+}\cdot$). Collapse of the radical anion–radical cation pair to form 1,2-addition product would preclude cyclization.

We have also found that the radical anion as well does not appear to be a "free ketyl" in reactions of either primary or tertiary Grignard reagents with benzophenone. We have found that the radical anion scavenger (*p*-dinitrobenzene[5]) completely eliminates pinacol formation in the reaction of "CH_3MgBr" and "*t*-C_4H_9MgCl" with 2-methylbenzophenone, but has no effect on the ratio or rate of formation of 1,2- and 1,6-addition products. The pathway to pinacol formation has been shown to involve a "free ketyl" [6] which is susceptible to electron transfer to *p*-dinitrobenzene.[7] Thus formation of 1,2- and 1,6-addition products must not involve a "free ketyl" (eq 2–4).

$$RMgX + Ph_2C{=}O \rightarrow [RMgX]^{+}\cdot[Ph_2\dot{C}{-}O^{-}] \quad (2)$$

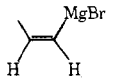
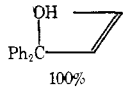
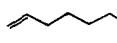
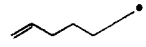
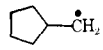
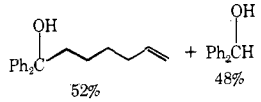
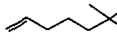
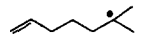
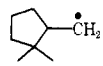
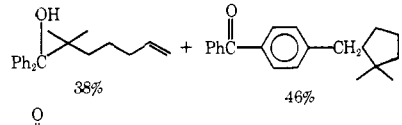
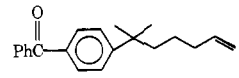
$$p\text{-DNB} + [Ph_2\dot{C}{-}O^{-}] \rightarrow [p\text{-DNB}]^{-}\cdot + Ph_2C{=}O \quad (3)$$

$$[p\text{-DNB}]^{-}\cdot + [RMgX]^{+}\cdot \rightarrow p\text{-DNB} + RMgX \quad (4)$$

In light of the "bound" nature of the R-group radical and ketyl, it seems necessary for the mechanism of *t*-C_4H_9MgCl with benzophenone to involve a radical anion–radical cation pair which can (a) collapse to 1,2-addition product or (b) dissociate to from a radical anion and a free radical within the solvent cage which in turn can collapse to conjugate addition products or escape the solvent cage to form benzopinacol, as shown in the proposed mechanism (eq 5).

It is possible that all Grignard reactions with ketones proceed through a SET pathway by the proposed mechanism. However, the stability of the radical-cation complex should be determined by the stabilities of the incipient radical (R·) and

Table I. Grignard Reagent Radical Probe Results

Grignard reagent	Expected intermediate	Isomerized or cyclized radical	Product of intermediate with benzophenone
			 100%
			 52% 48%
			 38% 46%  16%

$$RMgX + Ph_2C{=}O \rightleftharpoons \underset{\sigma\ \text{complex}}{Ph_2C{=}O{\cdots}Mg(X)X} \rightarrow \underset{\text{I (SET intermediate)}}{Ph_2\dot{C}{-}\bar{O}{\cdots}\overset{+}{M}g(\dot{R})X} \quad (5)$$

$$\text{I} \xrightarrow{a} \text{1,2-addition product}$$

$$\text{I} \xrightarrow{b} [Ph_2\dot{C}{-}\bar{O}\overset{+}{M}gX + R\cdot] \rightarrow \text{1,6-addition product}$$

$$[Ph_2\dot{C}{-}\bar{O}\overset{+}{M}gX + R\cdot] \xrightarrow[\text{solvent cage}]{\text{escape from}} \text{pinacol} + RH$$

the ketyl ($R_2\dot{C}{-}O^-$) which in turn would determine the amount of SET character observed in the reaction. With tertiary Grignard reagents, the intermediate complex would be unstable owing to the stability of the *tert*-alkyl radical, thus making path b competitive with path a or even the predominant reaction pathway. On the other hand, vinylic Grignards (*cis*-C_3H_5MgBr) and primary alkyl Grignards ($C_6H_{11}MgBr$) may react by a polar mechanism or if, by SET, form a more stable complex which would collapse via path a to give only 1,2-addition product with no SET character observed (as in the cases reported here).

The possibility that polar and SET mechanisms are competitive, depending principally on the reduction potential of the ketone and the oxidation potential of the Grignard reagents, seems quite clear. At the two ends of the spectrum, all evidence indicates that the reaction of *t*-C_4H_9MgCl with benzophenone is SET in nature, whereas the reaction of CH_3MgBr with acetone is polar in nature. Since no isomerization of the *cis*-C_3H_5MgBr or cyclization of the $C_6H_{11}MgBr$ probes were observed it is not clear whether these reactions proceed by a polar or SET pathway (or both). However, it is clear from this work that, if these reactions proceed by a SET pathway, a "free radical" is not involved. It is also clear that the mechanism initially proposed by Blomberg-Mosher[8] and Fauvarque[9] and later supported by Holm-Crossland[1] for the reaction of *t*-C_4H_9MgCl with benzophenone needs some modification. A "free radical" and "free ketyl" cannot form in the SET step as was proposed. Apparently an intermediate radical anion-radical cation pair is formed which can collapse to give 1,2-addition product or dissociate to form a radical anion and a free radical within the solvent cage which in turn can collapse to conjugate addition products or escape the solvent cage to form pinacol.

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E. C. Ashby,* Joseph S. Bowers, Jr.

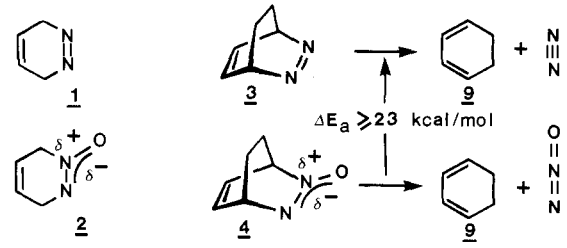
Department of Chemistry, Georgia Institute of Technology
Atlanta, Georgia 30332

Received July 30, 1977

Energetics of Heteroextrusion Reactions. N_2 vs. N_2O[1]

Sir:

1,2-Diazacyclohexa-1,4-dienes **1** are known as exceptionally labile intermediates expelling nitrogen at −78 °C with a half-life of 30 s or less.[2,3] *N*-Oxides **2**, on the other hand, are shelf-stable substances which lose N_2O at a comparable rate some 300 °C higher. Although it has been established that fragmentation of both the cyclic unsaturated azo system[3] and the corresponding azo *N*-oxide[1,4] is concerted, the origin of the great difference between the two energy barriers has remained obscure. The gap amounts to $\Delta E_a = E_a(\text{azoxy}) - E_a(\text{azo}) \geq 23$ kcal/mol, and, assuming that $\Delta E_a = \Delta\Delta G^*$, $k_{azo}/k_{azoxy} \geq 10^{17}$ at 25 °C.[4,5]



In the present contribution we report thermochemical data for the azo *N*-oxide retrocycloaddition which permits the relative azo/azoxy hypersurfaces to be compared quantitatively. New light is shed on the origin of the large difference between