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Does The Reaction Between Fluorenone And Grignard Reagents Involve Free Fluorenone Anion Radicals?

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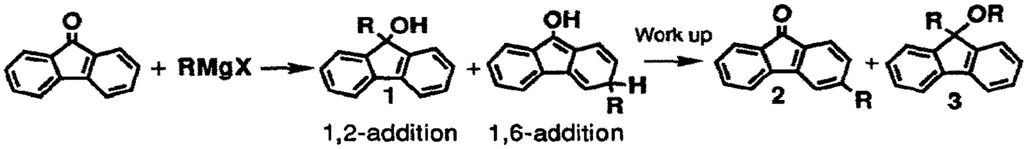
Abstract: The ratio between 1,6- and 1,2-addition in the reactions of electrogenerated fluorenone anion radicals with RX in THF were similar to the ratio obtained in the Grignard reaction of fluorenone with RMgX in THF. This indicates that the addition products in the Grignard reaction may be obtained via the coupling of freely diffusing fluorenone anion radicals with R radicals.

During the last 25 years the polar v.s. electron transfer (ET) nature of the Grignard reaction has been discussed intensively.[1-3] Formation of the so called "abnormal" 1,4- and 1,6-addition products together with the "normal" 1,2-addition main product in the Grignard reactions of fluorenone and benzophenone has been taken as evidence for an ET mechanism.[1-3]



1)

The question is whether the product composition of 1) can be explained by freely diffusing anion radicals and R· as suggested by Walling.[4] In an attempt to answer this question fluorenone anion radicals where generated electrochemically in THF in the presence of a halide RX. The reaction scheme of aromatic anion radicals with RX is shown below:[5]

$$A + e^- \rightleftharpoons A^{\bullet-} \qquad 2) \qquad\qquad A^{\bullet-} + R^\bullet \longrightarrow AR^- \xrightarrow{H^+} ARH \qquad 4)$$

$$A^{\bullet-} + RX \longrightarrow A + R^\bullet + X^- \qquad 3) \qquad\qquad AR^- \xrightarrow{RX} AR_2 + X^- \qquad 5)$$

Scheme1

In Table 1 the ratios between 1,6- and 1,2-addition products, **2/1**, obtained in the Grignard reactions are compared with the corresponding ratios from the electrolysis. In both the Grignard reactions and the electrolysis the 1,4-addition product is observed as a minor product, (less than 5 % of the 1,6-addition product in THF0). The dialkylation product **3** is observed in the electrolysis of fluorenone in presence of CH_3I and n-C_4H_7Br in 75% and 10% yields, respectively. The dialkylation product is obtained by O-alkylation of the 9-alkylfluorenolate AR^- (Scheme 1). The dialkylation product, **3** is included as a "normal" addition product.

From Table 1 it is seen that the ratio **2/1**, surprisingly, very much depends on the R group in the coupling reactions of electrochemically generated fluorenone anion radicals. From the coupling reaction in scheme 1 it might be anticipated that the ratio between **2** and **1** would be independent of the structure of R and would only have be determined by the relative electron spin densities of the fluorenone anion radical. However this is certainly not the case.

Table 1: The ratio between **2** and **1** in the reactions of fluorenone (E^0 = -1.20 V v.s. SCE) with RMgX in THF and in the electrolysis of fluorenone in THF and DMF in presence of RX. Total yields (%) of **1+2+3** are included.

	$E^0_{R\cdot}$/V	Grignard		Electrolysis		Electrolysis	
RX	v.s. SCE	THF	yield	THF	yield	DMF	yield
t-C_4H_7Br	-1.77[7]	0.325	41	0.153	67	0.077	93
s-C_4H_7Br	-1.72[7]	0.120	93	0.062	61	0.049	93
n-C_4H_7Br	-1.62[7]	0.085	73	0.000	45	0.027	52
$PhCH_2Cl$	-1.45[6]	0.006	94	0.022	93	0.001	62
$PhCH(CH_3)Br$	-1.57[6]	0.000	24	0.006	94	0.000	97
CH_3I	-1.19[8]	0.000	32	0.000	85	0.000	90

It can be seen from Table 1 that the ratio **2/1** in the Grignard reactions (and in the electrolyses) decrease with increasing value of the redox potential of the $R\cdot/R^-$ couple, $E^0_{R\cdot}$. While experimentally obtained reversible redox potentials of RMgX compounds are not known, it might be expected that the relative potential differences between $E^0RMgX^{+\cdot}/RMgX$ will parallel the differences between $E^0_{R\cdot}$. t-C_4H_7MgBr is therefore expected to be a much better ET donor than CH_3MgBr. The decrease in the ratio **2/1** with increasing $E^0_{R\cdot}$ might therefore be explained by a transition from an ET to a polar mechanism. However, the ESR and UV investigations by Maruyama et al.[3] suggest that an ET mechanism is followed even for the relatively poor ET donor CH_3MgX. Futhermore it is seen from Table 1 that the **2/1** ratios in the Grignard reaction parallel the ratios in the reactions of the electrogenerated fluorenone anion radicals. The only major difference is observed for n-C_4H_7Br in THF. The similarity in yield of abnormal to normal products between the Grignard reactions and the electrolysis suggests that both reactions proceed through common intermediates. In conclusion the results indicate that the addition product distribution in the reaction of RMgX with fluorenone may be explained by the coupling of freely diffusing fluorenone anion radicals with free R radicals. Further work with other ketones is in progress.

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