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REDUCTION POTENTIALS OF REAGENTS : II - A TOOL TO ANTICIPATE YIELDS OF ORGANOMETALLIC REACTIONS ?

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Reduction potentials of four cage-structure halogenated derivatives and five alicyclic and aromatic ketones have been determined by cyclic voltammetry. For the Barbier reaction these parameters are used to anticipate the behaviour of intermediates formed at the metal surface and on which the distribution product depends. Semiquantitative relationships are obtained between these potentials and yields of condensation products.

Recently, several papers have shown the existence of relationships between distribution products or reactivity in the reactions of organomagnesium[1,2] or organomercuric[3] compounds and reduction potentials of reagents.

In previous publications dealing with the synthesis of organolithium cage compounds[4], we have shown that product distribution, and especially the yields of organometallic compounds, depends on the behaviour of the precursors, anion radicals ($R^{\cdot} - X^{-}$) and tight pair radicals ($R^{\cdot}$ $^{\cdot}Li$) formed at the metal surface by single electron transfer between lithium and the halogenated derivative. Moreover, this behaviour can be anticipated from the reduction potentials of the reagents, determined by cyclic voltammetry[5]. For cage-structure halogenated derivatives the yield in organolithium increases when the reduction potential decreases[5].

In view of the importance of cage-structure compounds in major fields, such as Polymers[6], Pharmacology[7]... and of the difficulties in synthesizing some of them, it would be interesting to anticipate the yield of organometallic reactions involving halogenated cage compounds and some organic reagents.

In order to test this hypothesis, the condensation reactions between some cage-structure bromine derivatives (1-bromoadamantane 1, 1-bromo dimethyl-3,5-adamantane 2, 2-bromoadamantane 3, 3-bromo methyl-7 noradamantane 4) and some aliphatic or aromatic ketones (Adamantanone 5, Bicyclo (3.3.1) nona-9-one 6, Benzophénone 7, Xanthone 8, Fluorenone 9) were carried out according to the Barbier experimental procedure described previously[4].

Table 1 : List reduction potentials of 1 to 9

R-Br	E_p [a] V	Ketones	E_p [a] V
1	-2.67	5	-2.94
2	-2.74	6	-2.40
3	-2.83	7	-1.73
4	-2.86	8	-1.65
		9	-1.23

Table 1 : Reduction potentials of cage-structure bromide derivatives and ketones in THF. a) at 0.2 M; (nBu_4BF_4) = 0.2 M ; determined by using a SCE with a sweep rate of 0.2 V s^{-1}.

Table 2 lists the yields of condensation products formed in the Barbier reaction :

$$\text{R-Br} + \text{ketone} \xrightarrow{\text{Li}} \text{Products}$$

For each halide derivative the yield of condensation products increases when the reduction potential of the ketones decreases. The plots of the yield vs.Ep show almost linear straight lines.

R-Br \ Ketones [a]	5	6	7	8	9	Correl. Coeff. [b]
1	71	58	36	33	22	0.998
2	70	61	40	39	22	0.988
3	81	66	42	37	25	0.998
4	72	65	47	51	30	0.963

Table 2 : Yields of condensation products in the Barbier reaction.
(RX : 0.2M l^{-1}, ketones : 0.25M l^{-1}, 0.016 mol of alloy Li-Na, 1% Na, in Ether -25°C)
a) In the case of aromatic ketones, compounds formed by substitution on the aromatic ring predominate.
b) The last column gives the correlation coefficients of semi-quantitative relationships between these yields and the reduction potential of the ketones for each halogenated derivative.

These results confirm the existence of semiquantitative relationships between the reduction potentials of reactants and the yields of condensation products.

The observation is similar to that previously reported in the case of the synthesis of organolithium compounds[5].

The relationships between the yields observed for organolithium formation, or for the Barbier reaction and the reduction potentials, suggest that these parameters can be used to optimize the yields of organometallic reactions by choosing the better experimental process or to conceive new ones.

These first results will be completed and discussed in detail in a forthcoming paper.

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