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REDUCTION POTENTIALS OF CAGE-STRUCTURE HALOGEN DERIVATIVES : A METHOD FOR PREDICTING YIELDS OF ORGANOLITHIUM COMPOUND FORMATION

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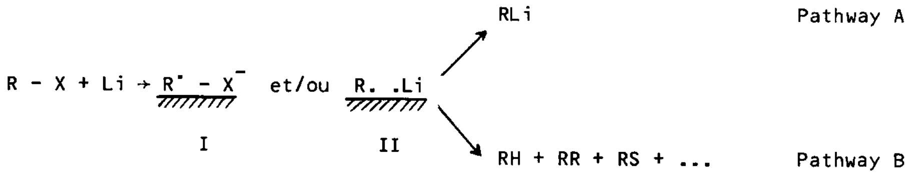
E_p reduction potentials for eight different cage structure RX halides have been measured by cyclic voltammetry between -2.25 and -3.00 V (± 0.02 V). These E_p are considered good approximations of the SET values. They correlate well with the relative stability of the corresponding halides expressed in terms of perester thermolysis constants. It is proposed to use these potentials to estimate and predict yields of organolithium compounds from cage-structure halide derivatives.

Previous studies from this institute[1,2] indicate that the formation of cage-structure organolithium compounds involves a multistep mechanism in which the first step, the formation of anion radical I or of radical pair II, determines the kinetics of the reaction. Transient species I and II, generated by <u>single electron transfer</u> (SET) between the metal and the halogenated derivative, are the precursors of all ensuing products (RLI, RH, RR, RS, ...).



Likewise, it has been shown that the competition between the formation of organometallic compounds (pathway A) and the formation of byproducts (pathway B) depends on the degree of adsorption[3] of the transient species ($R^{\bullet}X^-$, R..Li) at the metal surface. Although the degree of adsorption is thought to depend on the electronegativity of the halogen, on the geometry of the cage-structure radical, on the basicity of the solvent and on the nature of the metal, it remained to be measured quantitatively, thereby restricting any attempt at correlation.

The reduction potential of eight different cage-structure halogenated derivatives has been measured to see how this factor affects the degree of adsorption of the transient species.

I - REDUCTION POTENTIAL OF CAGE-STRUCTURE HALOGENS

The degree of adsorption related to the SET from a metal surface to a halogenated derivative is seemingly dependent on the energy involved in this SET. In a first approximation, this energy can be estimated from the reduction potentials of the halogenated derivatives ($\Delta G = -nFE$).

In measuring the reduction potential of eight cage-structure halogenated derivatives (3-Bromohomoadamantane, 1-Bromodiamantane, 1-Bromoadamantane, 3,5,7-Trimethyl-1-bromoadamantane, 1-Bromo bicyclo [2,2,2] octane, 2-Bromoadamantane, 7-Methyl-3-bromonoradamantane, 1-Bromonorbornane) by cyclic voltammetry, it was observed that the cathode peak potential ranges from -2.25 V for 3-Bromohomoadamantane to -3.00 V for 1-Bromonorbornane (Table).

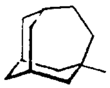
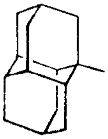
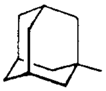
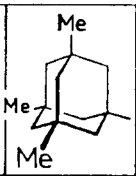
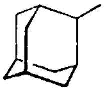
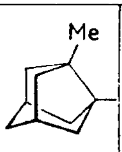
R-Br								
$E_{p}{}^{a}_{1}$	-2.25	-2.57	-2.67	-2.67	-2.79	-2.83	-2.86	-3

Table : Electroreduction of cage-structure bromide derivatives in THF.
a) Solutions contain 10^{-3}M bromides plus 0.2M NBu_4BF_4 using DME vs SCE at 0.2 VS^{-1} sweep rate.

Since it was previously propounded[3] that the yield of organolithium compound obtained from certain cage-structure halides is *inversely proportional to the stability of the corresponding cage-structure radicals*, we decided to test our hypothesis by correlating the reduction potentials of cage-structure halogenated derivatives with perester thermolysis rate constants.[4-6] These latter rate constants are commonly associated with the relative stability of the radicals.

Radical stability is highest for homoadamantane and lowest for norbornane (Fig. 1). The evolvement in stability is the same as the evolvement in reduction potential. The observed correlation tendency (0.97 correlation coefficient) is satisfactory in view of the experimental difficulties related to the various methods for measuring thermolysis reactivity.

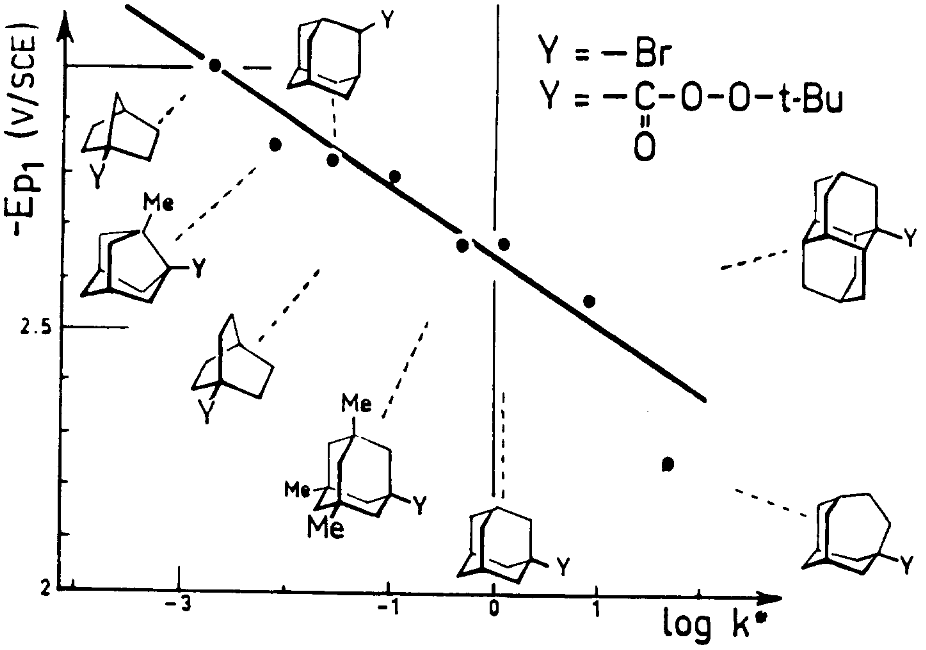


Figure 1 : Reduction potential (E_{p1}) of cage-structure halides vs. perester thermolysis rate constants (log. k*).

II - FORMATION OF ORGANOLITHIUM COMPOUNDS AND REDUCTION POTENTIAL

Our hypothesis on the reduction potential of cage-structure halides makes it plausible to correlate the reduction potential with the yield of organolithium compound, governed by the degree of adsorption. We tested this hypothesis by compared cathode peak potentials with the reaction output from the attack of the lithium by the halogenated derivative (Fig. 2).

These results indicate a rise in the yield of organolithium compound and a drop in the percentage of byproducts when the reduction potentials become more and more negative. The reduction potential, more readily accessible than perester thermolysis rate constants, seems to account satisfactorily for the degree of adsorption of transient species I and II at the lithium surface. By taking into account this type of relation between % RLi and E_p, it can be inferred that the output for syntheses involving various cage-structure organolithium compounds can be estimated by measuring potentials E_{p1} (a simple task).

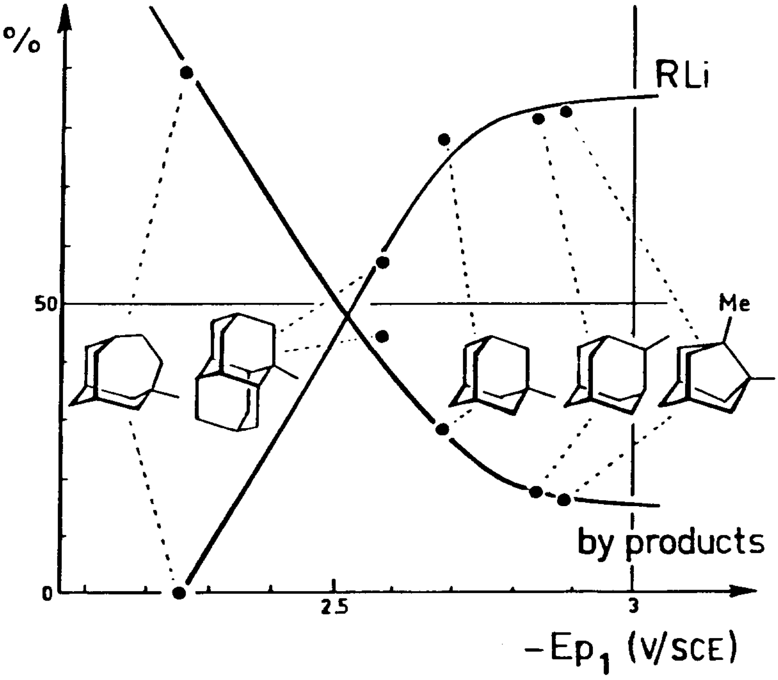


Figure 2 : Yield of organolithium compound vs. reduction potential (E_{p_1}) of cage-structure halides.

These initial results highlight the interest that lies in using measured reduction potentials as correlation data to predict reaction output. The generality of this conclusion should be tested by establishing similar correlations for other transient species generated by SET.

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