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# Aryliminodimagnesium Reagents. VII. The Moderate Electron-donating Ability Estimated by Oxidation Peak Potentials

Masao Ōkubo,* Toshiki Tsutsumi, Akio Ichimura,† and Toyokichi Kitagawa†
*Department of Chemistry, Faculty of Science and Engineering, Saga University, Honjō-machi, Saga 840*
†*Department of Chemistry, Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka 558*

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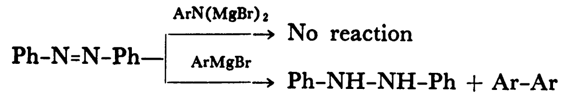
**Synopsis.** Oxidation peak potentials of *p*-$RC_6H_4N(MgBr)_2$ and *p*-$RC_6H_4MgBr$ ($R=CH_3O, CH_3, F$) were determined by cyclic voltammetry with a platinum disk electrode in tetrahydrofuran. The potentials obtained proved to be a semiquantitative measure of electron-donating abilities of organomagnesium reagents.

It was proposed very recently that aryliminodimagnesium reagent ($ArN(MgBr)_2$, aryl-IDMg) was less reactive—less "electron-donating"—than arylmagnesium reagent (ArMgBr): The proposal remained entirely qualitative because it was based on comparison of the distribution of major and minor products formed in the reactions with carbonyl and nitro compounds.[1] Even the clearly different behavior of azobenzene toward $ArN(MgBr)_2$ and ArMgBr (Scheme 1)[2] suggests strongly but still qualitatively that the latter reagent is much more electron-donating than the former, and determination of oxidation potentials as a quantitative measure of electron-donating abilities is needed. The electrochemical reduction of a wide variety of electron-accepting organic compounds were studied extensively: The correlation of reduction potentials with Hammett's substituent constants were reviewed.[3] The study of electrochemical oxidation potentials of carbanions[4,5] and amide anions[6] as well as their correlation with substituent constants[7] are now in progress. In the field of electrochemistry of organomagnesium reagents, an important result was provided by the measurement of anodic overvoltages of some alkyl Grignard reagent at constant current density.[8] In this paper, the result of a voltammetric study for estimating semiquantitatively the oxidation potentials of *p*-$RC_6H_4N(MgBr)_2$ and *p*-$RC_6H_4$-MgBr ($R=CH_3O, CH_3, F$) will be described.



Scheme 1.

*Procedures.* Cyclic voltammograms were recorded on a Yanaco P-1000 Voltammetric Analyzer having electrolysis cell equipped with three electrodes: working electrode (Pt-disk), reference electrode (Ag-wire), and counter electrode (Pt-wire). Tetrahydrofuran, which has been used as the reaction solvent, was used also for electrolysis: Tetrabutylammonium perchlorate (TBAP, 0.2M) was used as the supporting electrolyte. The concentration of organomagnesium reagents was 1.0—$2.0\times10^{-3}$M (1 M=1 mol $dm^{-3}$), and all the measurements were carried out under nitrogen atmosphere. Contamination of the surface of working electrode was unavoidable, and the surface was polished by use of alumina powder prior to the individual measurements.

The typical voltammogram with a scan rate of 50 mV/s is shown in Fig. 1. Two oxidation peaks were observed in every case, the first peak(I) being assigned to the initial oxidation of the magnesium reagent and the second peak(II) to the further oxidation of the initially formed radical species. Even when the faster scan rate(500 mV/s) was applied, a very small reduction peak was observed only in two cases: The electrode process is almost completely irreversible and the redox potential was not determined by this method. For comparison of the values of oxidation peak potentials[9] with each other, the observed potentials of I were normalized by use of the redox potential of ferrocenium/ferrocene couple added as internal standard: 0.400 V *vs.* NHE.[10]

*ArN(MgBr)₂ and ArMgBr.* The normalized oxidation peak potentials of individual reagents were plot-

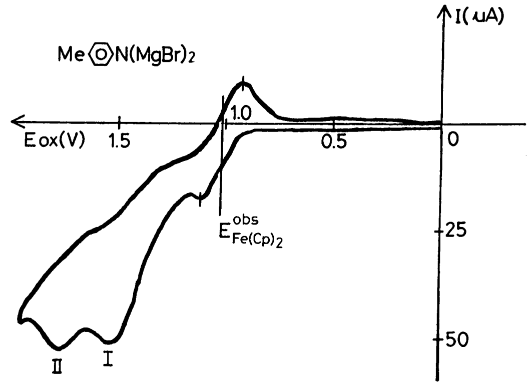


Fig. 1. Cyclic voltammogram of *p*-methylphenyl-IDMg reagent using Ag-wire as reference electrode.

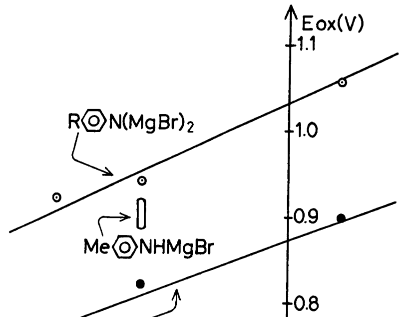


Fig. 2. Plot of oxidation peak potentials *vs.* substituent constants $\sigma_p$. The values of potentials are normalized using the redox potential of ferrocenium/ferrocene couple as internal standard.

ted against substituent constants ($\sigma_p$, Fig. 2): The difference between the potentials of two kinds of reagent was 120—170 mV. The higher oxidation peak potentials of IDMg in comparison with those of ArMgBr support the previous suggestion of the lower electron-donating ability of the former reagent than that of the latter.[1,2,11] The substituent effect on the oxidation peak potentials ($CH_3O<CH_3<F$) of the respective kinds of reagent is in accord with the effect on the electron-donating ability suggested previously.[2] The reaction constants($\rho$) were not determined since the potentials obtained are not the redox potentials but the oxidation peak potentials which, however, proved to be at least a semiquantitative measure of electron-donating abilities of organomagnesium reagents.

*ArNHMgBr and ArN(MgBr)₂.* The oxidation peak potentials of *p*-$CH_3$-substituted PhNHMgBr, $PhN(MgBr)_2$, and PhMgBr were also compared (Fig. 2). The potential of the anilinomagnesium reagent was difficult to be determined precisely, however, the medium potential compared with those of ArMgBr and IDMg was established.

The higher ability of ArNHMgBr than that of $ArN(MgBr)_2$ as electron donors is suggested from the result of an experiment, which, however, is performed in an unadvisable manner. When the IDMg reagent[12] containing a small amount (*ca.* 5%) of anilinomagnesium species was allowed to react with a nitroarene, a large amount of unidentifiable dark brown materials was formed with a heavy loss of the expected azoxyarene:[13] The result is due to the preferential electron-transfer from the anilinomagnesium species, the process being followed by decomposition and/or polymerization of nitroarene anion radical.[14] The reactivity of different types of magnesium reagents, *i.e.*, ArMgBr, ArSMgBr, ArNHMgBr, $ArN(MgBr)_2$, and ArOMgBr, in the replacement reaction of $\beta$-methoxy $\alpha,\beta$-enones is discussed elsewhere.[15]

The lower electron-donating ability of $ArN(MgBr)_2$ than that of ArNHMgBr is ascribable to the presence of two positive Mg atoms attached to the anionic nitrogen atom.

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