NOTES

The Decomposition Voltage of Grignard Reagents in Ether Solution

By Elliot Q. Adams

Evans, Lee and Lee[1] have found decomposition voltages of Grignard reagents ranging from 0.86 volt for allylmagnesium bromide, to 2.17 volts for phenylmagnesium bromide. If the *differences* in the decomposition voltages of the saturated aliphatic derivatives produced by the introduction of one methyl group are taken, it is

$$\begin{array}{llllll} \alpha_1 & -0.66 & \alpha_2 & -0.21 & \alpha_3 & -0.10 \\ & & & -0.18 & & \\ \beta_1 & +0.14 & & & & \\ & +0.17 & & & & \\ \gamma_1 & -0.10 \text{ (Evans, Lee and Lee)} & & & & \end{array}$$

$$\begin{array}{lcl} \Delta pK_{\mathrm{A}}/pK_{\mathrm{A(subst.)}}\alpha & = & -0.68 \\ \beta \quad \text{(Derick)} & = & -0.19 \\ \gamma & = & -0.06 \\ \delta & = & -0.02 \end{array}$$

α_1, α_2, α_3 represent the changes *in volts* in the decomposition potential of Grignard reagents in ether solution, produced by replacing, respectively, the first, second, and third α-hydrogen by methyl; β_1 and γ_1 represent similarly the changes *in volts* produced by the first methyl group in, respectively, the β and γ positions. α, β, γ and δ are the changes in Derick's function[3] produced by substituting chlorine for, respectively, the α-, β-, γ- or δ-hydrogens in butyric or valeric acid, or their chlorinated derivatives.

found that successive substitutions in the alpha position produce diminishing decreases in the decomposition potential, and that the effect of substitution in the beta position is opposite in sign to that of alpha or gamma substitution. Conant[2] has found that irreversible oxidation–reduction potentials are represented by equations similar in form to those for oxidation–reduction equilibrium potentials. Derick[3] has pointed out that the relative effects of substituents on the logarithms of the ionization constants of organic acids ($\Delta pK_{\mathrm{A}}/pK_{\mathrm{A(substituted)}}$ in present-day notation) are reduced approximately 3-fold by each additional carbon atom between the carboxyl and the substituent, without change in sign. The results of Evans, Lee and Lee agree within the error of measurement with the series

$$-0.63{:}\mp 0.21{:}-0.07 = 9{:}\pm 3{:}1$$

that is, 3-fold reduction in the effect of successive alpha replacements, as well as with increasing distance from the MgBr radical. In the latter case, there is also an alternation in sign of the effect.

The results for phenyl- and allylmagnesium bromides indicate an effect of unsaturation alternating in sign, and less for the more distant double bond, in qualitative agreement with the rule for methyl groups.

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(1) W. V. Evans, F. H. Lee and C. H. Lee, This Journal, **57**, 489–490 (1935).

(2) J. B. Conant and M. F. Pratt, *ibid.* **48**, 3178–3192 (1926).

(3) C. G. Derick, *ibid.* **33**, 1182 (1911). The approximate numerical agreement between Evans, Lee and Lee's results in volts, and Derick's is, of course, a coincidence. Since pK_{A} for unsubstituted aliphatic acids is of the order of 5 and with a single strongly negative α-substituent becomes about 3, the unit of Derick's function for singly substituted acids will range from 3 to 5 pK units. (1 volt $\simeq$ 17 pK units.) The form of Derick's function provides for a diminishing effect on pK_{A} with successive substitutions, but the decrease even in the case of α-substitution is not as great as that shown in the results of Evans, Lee and Lee. Since the acid hydrogen in substituted acetic acids is separated by a carbon and an oxygen atom from the α-carbon of the chain, while in tbe Grignard reagents the magnesium atom is directly attached, a factor of the order of 9 is to be expected. There is, to be sure, no reason to expect the effect of a methyl group on the irreversible breaking of the bonding of magnesium to carbon in ether solution to be identical with the effect of chlorine on the equilibrium of the bonding of hydrogen to oxygen in aqueous solution.

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Some Acyl Derivatives of *o*-Anisidine

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We have prepared a number of acyl derivatives of *o*-anisidine, the majority of which have not been described in the literature. The monoacyl derivatives were prepared by the action of the corresponding acyl chlorides upon 2 molecular proportions of *o*-anisidine.[1]

The diacyl derivatives were prepared by boiling a toluene solution of *o*-anisidine with 2.5 molecular proportions of acyl chlorides under reflux for twelve to eighteen hours. The dibenzoyl derivative precipitated upon cooling the solution and the dipropionyl derivative was obtained by evaporation of the toluene.

The first six compounds are very soluble in most organic solvents but only moderately soluble in pentane, hexane, etc. The next four compounds are very soluble in chloroform, dioxane and acetone, fairly soluble in alcohol, slightly

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(1) Mühlhäuser, *Ann.*, **207**, 235 (1881); *Ber.*, **13**, 919 (1880).