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

α_1 −0.66 α_2 −0.21 α_3 −0.10
            −0.18
β_1 +0.14
     +0.17
γ_1 −0.10 (Evans, Lee and Lee)
$\Delta pK_A/pK_{A(\text{subst.})}\alpha = -0.68$
β (Derick) $= -0.19$
γ $= -0.06$
δ $= -0.02$

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 ($\Delta pK_A/pK_{A(\text{substituted})}$ 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

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

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).

TABLE I

ACYL DERIVATIVES OF *o*-ANISIDINE

Acyl groups	Solvent used in crystn.	Yield, %	M. p., °C.	Formula	Nitrogen % Calcd.	Nitrogen % Found
Propionyl	Ether[a]	73	33.5–34.5	$C_{10}H_{13}NO_2$	7.82	7.80
Butyryl	Ether[a]	78	24.5–25.5	$C_{11}H_{15}NO_2$	7.25	7.11
Valeryl	Ether[a]	91	25.5–26.5	$C_{12}H_{17}NO_2$	6.76	6.45
Isovaleryl	Ether[a]	94	49–49.5	$C_{12}H_{17}NO_2$	6.76	6.59
Caproyl	Ether[a]	61	33–33.5	$C_{13}H_{19}NO_2$	6.33	6.38
Heptanoyl	Pet. ether	67	42–43	$C_{14}H_{21}NO_2$	5.96	5.73
Phenylacetyl[b]	Dilute alc.	88	82.5–83			
Hydrocinnamyl	Isopropyl ether or benzene and heptane	100	59.5–60	$C_{16}H_{17}NO_2$	5.49	5.50
m-Bromobenzoyl		86	112.5–113	$C_{14}H_{12}BrNO_2$	4.58	4.59
					Br, 26.11	25.60
p-Anisoyl		100	96.5–97.5	$C_{15}H_{15}NO_3$	5.45	5.42
Benzoyl[c]			66–67			
Acetyl[d]			85–85.5			
Dibenzoyl	Alc. or toluene	60	149.5–150	$C_{21}H_{17}NO_3$	4.23	4.25
Dipropionyl	Hexane	85	62.5–63.5	$C_{13}H_{17}NO_3$	5.96	5.98

[a] By cooling with solid carbon dioxide.

[b] Aggarwal, Das and Rây[2] prepared this compound from *o*-anisidine and phenylacetic acid and reported a melting point of 84°.

[c] Prepared by Mühlhäuser,[1] who reported a melting point of 59.5°.

[d] Mühlhäuser[1] reported a melting point of 78°. Our melting point agrees with the one given in Mulliken's "Identification of Pure Organic Compounds," Vol. II, p. 151.

soluble in ether, and almost insoluble in hexane. *o*-Dibenzoylanisidine is difficultly soluble in toluene and alcohol but readily soluble in chloroform. *o*-Dipropionylanisidine is soluble in practically all organic solvents.

One additional compound was prepared during this investigation. Its properties are given below.

o-Benzoylmethylaminophenyl Benzoate.—This compound was prepared by the Schotten–Baumann method in 40% yield. It was crystallized from alcohol. It is soluble in dioxane, acetone, chloroform and benzene; somewhat soluble in alcohol and ether; and almost insoluble in petroleum solvents, m. p. 114–115°.

Anal. Calcd. for $C_{21}H_{17}NO_3$: N, 4.25. Found: N, 4.12.

(2) Aggarwal, Das and Rây, *J. Ind. Chem. Soc.*, **6**, 717 (1929).

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Addition of Methyl Alcohol to Dialkylacetylenes

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The many well-known reactions of acetylene and its homologs with hydroxylated compounds (alcohols, carboxylic acids, etc.) are characterized by the fact that they proceed quite readily in an appropriate acid medium in the presence of a small amount of a suitable mercuric salt. The mechanism of this catalysis has engaged our attention for some time. There is little doubt but what the reaction of an acetylene with methyl alcohol, for example, produces first a vinyl ether which in turn immediately adds a second molecule of alcohol to form the ketal or acetal. There is evidence to indicate that the mercuric salts function only in the first of these reactions.

In attempting to determine whether the catalytic mercuric salt forms an intermediate with the acetylene by addition or substitution (or both) we have succeeded in adding methyl alcohol to two dialkylacetylenes in the usual way.[1] This indicates quite clearly that an intermediate of the mercury acetylide type is not essential to the mechanism of catalysis.

Preparation of 2-Octyne.—This compound was obtained by the action of methyl iodide on sodium amylacetylide in liquid ammonia: b. p. 132–136°; d^{32} 0.751; n^{32}_D 1.4227.

Reaction of 2-Octyne with Methyl Alcohol.—The catalyst was prepared by heating together momentarily 3 g. of red mercuric oxide, 1 ml. of $(C_2H_5)_2O{\cdot}BF_3$, 0.5 g. of trichloroacetic acid, and 3 ml. of methyl alcohol. The reaction was carried out and the product purified as previously described.[1] From 55 g. of 2-octyne there was obtained 48 g. of 3,3-dimethoxyoctane: yield, 55%; b. p. 90–92° at 26 mm.; d^{25} 0.8552; n^{25}_D 1.4171; MR calcd. 51.67, found 51.22.

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(1) Hennion, Killian, *et al.*, THIS JOURNAL, **56**, 1130 (1934), and subsequent papers.