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CARBANION STABILITIES - EXCHANGE REACTIONS BETWEEN ORGANOMERCURY AND ORGANOMAGNESIUM COMPOUNDS

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THE question of the relative stabilities of carbanions has been approached in several ways, with varying degrees of success. For aryl and benzylic carbanions, and anions of stronger acids, competitive metallation studies provided this information quite well[1]. For carbanions of weaker acids, such as aliphatic hydrocarbons which are not readily metallated, this method cannot be applied. Some studies of rates of H-D exchange in $C_6H_5CHR_1R_2$ systems[2] (where R_1 and R_2 are various alkyl groups), of the orientation in halogenation of ketones,[3] and of dealkylations of geminal alkylcyclohexadienes[4] have attempted to answer the carbanion stability question. However, the use of kinetics and/or irreversible

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[1] J.B. Conant and G.W. Wheland, J. Am. Chem. Soc. 54, 1212 (1932); W.K. McEwen, Ibid. 58, 1124 (1936).

[2] A. Streitwieser, Jr., D.E. Van Sickle, and L. Reif, Ibid. 84, 258 (1962) and preceding papers.

[3] H.M.E. Cardwell and A.E.H. Kilner, J. Chem. Soc. 2430 (1951).

[4] H. Pines and L.A. Schapp, "Advances in Catalysis", pp.124-130, Academic Press, New York (1960).

reactions to explore a thermodynamic phenomenon is fraught with danger. As an example, the enol content of cyclohexanone is greater than that of cyclopentanone, but the rate of base-catalyzed deuterium exchange is higher for the cyclopentanone.[5] Similarly, among a series of nitroparaffins ($R_1R_2CHNO_2$) the most highly acidic compound exhibits the slowest rate of proton exchange.[6]

Metathetical reactions of the type $R_2M + R'_2M' \rightleftharpoons R'_2M + R_2M'$ have been examined for a number of organometallic compounds; these provide a possible means of establishing a scale of carbanion stabilities for alkyl carbanions. Studies by Gilman,[7] and by others, have involved exchanges between organolithium reagents or Grignard reagents and less reactive organometallic compounds. The reaction mixtures were treated with carbon dioxide to allow characterization of the equilibrium mixture. It was assumed that the carbonation reaction is faster than any possible shift in equilibrium. In these equilibrium mixtures it appears that the more electropositive metal is linked to the more electronegative organic group.[8]

The relative stabilities of the products of these exchange

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[5] H. Schechter, M.J. Collis, R. Dessy, Y. Okuzumi, and A. Chen, *J. Am. Chem. Soc.* **84**, 2907 (1962); G. Schwarzenbach and C. Wittmer, *Helv. Chim. Acta* **30**, 656 (1947).

[6] H.M.E. Cardwell, *J. Chem. Soc.* 2442 (1951).

[7] H. Gilman and R.G. Jones, *J. Am. Chem. Soc.* **63**, 1443 (1941) and references cited therein.

[8] Kharasch[9] has proposed that the reaction of R_2Hg with HX would provide data concerning relative electronegativity of alkyl groups assuming that $R_2Hg \rightleftharpoons R:^- + RHg^+$. Subsequent work[10] has shown the system is not S_E1 in character and that the actual mechanism is solvent dependent.

reactions may be correlated with differences in bonding energies, which should be sensitive to small changes in the relative weights of the covalent and ionic resonance structure contributions that follow from changes in the electronegativities of R and M. This line of reasoning has been employed by Skinner[11] to account for the thermochemical effects in R_2Hg - HgX_2 exchanges, ionicity changes in the R-hg and X-hg bonds being used to explain "heats of redistribution".

Insofar as carbanion stability is the measure of the ability of a carbanion to accommodate a negative charge, this property might be determined from the positions of the organometallic exchange equilibria. Among organomercury-organomagnesium systems, the more electronegative group, or the more stable carbanion, should at equilibrium be linked to magnesium (the more electropositive metal), since the percent ionic character in R-mg bonds is higher than in R-hg bonds.[12]

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[9] M.S. Kharasch and A.L. Flenner, J. Am. Chem. Soc. 54, 674 (1932).

[10] R.E. Dessy, G.F. Reynolds, and J.Y. Kim, Ibid. 81, 2683 (1959) and references cited therein; M. Gielen, unpublished results, private communication.

[11] H.A. Skinner, Rec. trav. chim. 73, 991 (1954).

[12] Calingaert's[13] study of redistribution of alkyl groups in the system dimethylmercury-tetraethyllead gave a value for K = (Me-hg)(Et-pb)/(Et-hg)(Me-pb) = 4. The present study of the dimethylmercury-diethylmagnesium system showed that the reaction proceeded essentially to completion. That the magnesium-mercury system shows a much more pronounced preference for methyl versus ethyl groups than does the lead-mercury system indicates strongly that ionic bonding contributions, more important in magnesium than in lead compounds, are significant in these exchanges.

By the use of NMR spectroscopy, which has the advantage of giving rapid analyses without disturbing the system being studied, the present work investigated the metathetical reactions of a series of organomercury[14] and organomagnesium[16] compounds.

Table I shows the results of these studies. An order of relative carbanion stabilities of the organic groups studied, can be set up. In order of *decreasing carbanion stability* this is:

Phenylethynyl, phenyl, methyl, ethyl, *iso*propyl.

The order of the alkyl groups is that which would be expected from consideration of inductive (+I) effects. Calculations of orbital electronegativities by Hinze and Jaffé[18] show the same order for sp, sp^2 and sp^3 hybridized carbon atoms as was found in this study.

An attempt was made to include the *tert*-butyl group into the stability series. However, di-*t*-butylmagnesium would not exchange with either di-*iso*propylmercury or diphenylmercury in 5 hours at room temperature. Apparently steric factors prevent this type of exchange reaction with di-*t*-butylmagnesium.

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[13] G. Calingaert, H. Soroos, and H. Shapiro, *J. Am. Chem. Soc.* **63**, 947 (1941).

[14] $(CH_3)_2Hg$ prepared by Koton's method[15] using Na-Hg and CH_3I. Other dialkylmercury compounds prepared by Grignard reactions.

[15] M.M. Koton, *Zhur. Obscheii Khim.* **22**, 1136 (1952), *C.A.* **47**, 6341 (1953).

[16] $(CH_3)_2Mg$ prepared by exchange of $(CH_3)_2Hg$ with Mg. $(C_6H_5C{\equiv}C)_2Mg$ prepared from $C_6H_5C{\equiv}CH$ and $(C_2H_5)_2Mg$. Other dialkylmagnesium compounds prepared by dioxane precipitation of the appropriate Grignard reagent.[17]

[17] A.C. Cope, *J. Am. Chem. Soc.* **60**, 2215 (1938).

[18] J. Hinze and H.H. Jaffé, *Ibid* **84**, 540 (1962).

TABLE I EXCHANGE REACTIONS IN THE SYSTEM $R_2Hg + R'_2Mg \xrightarrow[25^o]{THF} R'_2Hg + R_2Mg$

$(Rhg + R'mg \overset{K}{\rightleftarrows} R'hg + Rmg)$

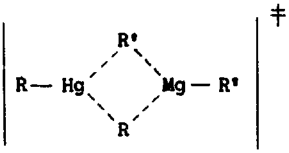
R_2Hg	Conc.(m./l.)	R'_2Mg	Conc.(m./l.)	Result of Reaction[a,f]	Half-life
$(C_6H_5)_2Hg$	0.45	$(C_6H_5C\equiv C)_2Mg$	0.45	K = *ca.* 0.3	Fast[b,c,d]
$(C_6H_5C\equiv C)_2Hg$	.3	$(CH_3)_2Mg$	.3	Complete Reaction	Fast[d]
$(C_6H_5)_2Hg$	.3	$(CH_3)_2Mg$	.3	K = *ca.* 40	0.4 hrs.[b]
$(C_6H_5)_2Hg$	.5	$(C_2H_5)_2Mg$	.5	Complete reaction	0.1 hrs.
$(C_6H_5)_2Hg$	.5	$[(CH_3)_2CH]_2Mg$	.5	Complete reaction	0.05 hrs.
$(C_6H_5)_2Hg$	.2	$[(CH_3)_3C]_2Mg$	.2	No reaction	-
$(C_2H_5)_2Hg$	.6	$[(CH_3)_2CH]_2Mg$	.6	Complete reaction	Slow[c]
$[(CH_3)_2CH]_2Hg$	.2	$[(CH_3)_3C]_2Mg$	.2	No reaction	-
$[(CH_3)_2CH]_2Hg$	.55	$(C_2H_5)_2Mg$	.55	No reaction	-
$(CH_3)_2Hg$	.9	$(C_2H_5)_2Mg$	.9	Complete reaction	3.5 hrs.
$(CD_3)_2Hg$	.9	$(CH_3)_2Mg$	.6	Statistical Exch.[e]	7 hrs.[e]

(a) Values for K are approx. equilibrium constants for reactions as written.
(b) These reactions reach an equilibrium; half-life taken as time required for 50% approach to equilibrium conc'ns. K = (Rmg)(R'hg)/(R'mg)(Rhg)
(c) Complexity of NMR spectrum precludes more accurate calculation.
(d) Too fast to measure.
(e) From mass spectral studies.[20]
(f) NMR spectra determined on a Varian A60 Spectrometer at 60 MC. and 32°. Relative concentrations of the various organometallic compounds were determined as a function of time by electronic integration of areas under their resonance peaks. All samples prepared in a nitrogen atmosphere and sealed into glass tubes.

The different chemical shifts of phenyl groups on Hg and on Mg facilitated studies of mixtures involving phenyl groups. For alkyl-alkyl exchanges the hydrogens of the R-mg compound were observed.

The data for those reactions proceeding in the forward direction show that the larger the separation in the stability scale of two groups, the greater is the rate of exchange, although the rates of the reactions between various alkylmagnesium compounds and diphenylmercury do not show a very large difference in reactivity (except for di-t-butylmagnesium which does not react).

If an ionic exchange pathway were involved ($R_2Mg \rightleftharpoons R{:}^- + MgR^+$, $R{:}^- + R'_2Hg \rightarrow$ product) it is difficult to explain the sharp break in exchange characteristics between isopropyl and t-butyl. A multicenter exchange process is suggested, involving a transition state complex such as



Similar transition states appear to be involved in exchanges in the Zn,Cd[19] and Hg,Hg[20] systems studied previously.

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[19] C.R. McCoy and A.L. Allred, Ibid 84, 912 (1962).

[20] R.E. Dessy and R.M. Salinger, Ibid in press, O.A. Reutov, Tet. Letters #19, p. 6, (1960); Angew. Chem 72, 198 (1960).