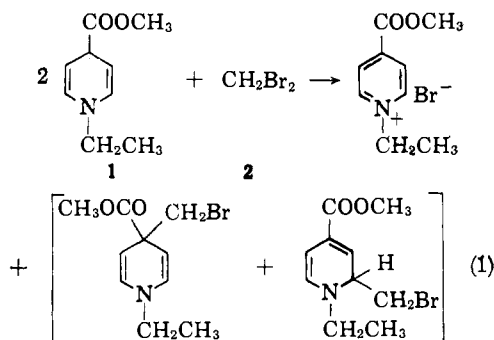
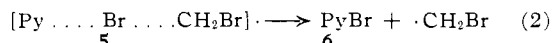


Fig. 1.—A free-energy vs. reaction coordinate diagram for halogen abstraction by pyridinyl radical. $\text{Py}\cdot$ is pyridinyl free radical, PyX is the adduct of halide ion and pyridinium ion, $\text{Py}^+ \text{X}^-$ is pyridinium halide, PyC is the dihydropyridine formed from the radical, $\cdot\text{C}$, left by halogen abstraction and the pyridinyl radical, and F_1^\ddagger , F_2^\ddagger , and F_3^\ddagger represent the transition-state free energies for the transformations indicated in the diagram.

acetonitrile ($Z = 71.3$) and isopropyl alcohol ($Z = 76.3$)⁵ to ethanol ($Z = 79.6$).⁵ The absence of a solvent effect upon the reaction rate demonstrates that the transition state for the reaction has approximately the same degree of charge separation as the initial state. The net dipole moments of the reactants,



1 and **2**, cannot be large since both are soluble in hexane, *ca.* 0.02 *M* solutions being possible for the radical **1**. The transition state, **5**, cannot be highly charged and must decompose into the uncharged species, PyBr (**6**), the covalently bonded adduct of bromide ion, and the pyridinium ion⁶ and a bromomethyl radical (eq. 2).



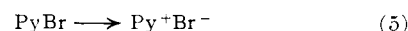
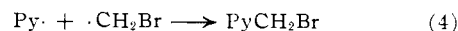
Both products disappear quickly, **6** by ionization to pyridinium bromide and $\cdot\text{CH}_2\text{Br}$ by reaction with another molecule of **1**. The mechanism is summarized

(4) E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253 (1958).

(5) The *Z*-values of the halocarbon-alcohol mixtures are actually somewhat lower than those values cited for the pure alcohols, as noted in Table I.

(6) *Cf.* K. Wallenfels and H. Schüly, *Ann.*, **621**, 111 (1959).

in eq. 3, 4, and 5 and the free-energy diagram which is a necessary concomitant of these facts is shown in Fig. 1.

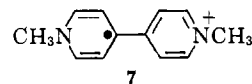


The "carbonium ion stabilization" for transition states of reactions between radicals and halocarbons or hydrocarbons proposed by Huyser,^{7,8} Walling,⁹ and Bamford^{10a} cannot be significant in the case of pyridinyl radicals in spite of the fact that it would be expected that the pyridinyl radical would be unusually effective in accumulating positive charge in the transition state because of the stability of the pyridinium ion.

No spectroscopic change attributable to a charge-transfer band^{10b} was observed for the radical **1** in dichloromethane in the visible region, although such absorption may well occur at shorter wave lengths. Visible light (irradiation with a tungsten lamp) or ultraviolet light (small amounts from the spectrophotometer) had no apparent effect on the course of the reaction. Strong ultraviolet irradiation led to a photochemical reaction with a halocarbon in one case.¹¹

The radical **1** discriminates between different halogen-carbon bonds far more effectively than sodium¹² or 1-phenylethyl radicals.¹³ It is also noteworthy that there is so little difference between chlorine and bromine with regard to stabilization of the transition state for formation of $\cdot\text{CH}_2\text{X}$.

Disulfides react with **1**. Less reactive pyridinyl radicals like methyl viologen cation radical (**7**) do not react appreciably with **2** at room temperature but do react with more reactive halocarbons like tetrachloro- and tetrabromomethane.¹³



Further studies with pyridinyl radicals are continuing and promise much fundamental information on radical reactions.

(7) E. S. Huyser, *J. Am. Chem. Soc.*, **82**, 394 (1960).

(8) E. S. Huyser, H. Schimke, and R. L. Burham, *J. Org. Chem.*, **28**, 2141 (1963).

(9) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 158.

(10) (a) C. H. Bamford, A. D. Jenkins, and R. Johnston, *Trans. Faraday Soc.*, **55**, 418 (1959); (b) D. P. Stevenson and G. M. Coppinger, *J. Am. Chem. Soc.*, **84**, 149 (1962).

(11) E. J. Poziomek, unpublished results. A photochemical reaction between **7** and ethyl iodide has been observed.

(12) J. N. Haresnape, J. M. Stevels, and E. Warhurst, *Trans. Faraday Soc.*, **36**, 465 (1940).

(13) *Cf.* ref. 9, p. 152.

(14) Alfred P. Sloan Fellow, 1960-1964.

(15) The authors are grateful to the National Science Foundation for financial support through Grant GP-251.

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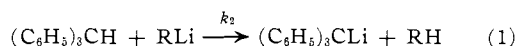
RECEIVED MAY 12, 1964

Metalation of Triphenylmethane by Organolithium Compounds

Sir:

The rate of metalation of triphenylmethane, *i.e.*, reaction 1, by different organolithium reagents varies

markedly (250-fold) with the structure of RLi. In



tetrahydrofuran (THF) solution, the following order of decreasing reactivity is obtained: benzyllithium > allyllithium > *n*-butyllithium > phenyllithium > vinylithium > methylithium. Kinetic data comparing metalating abilities of organolithium compounds have not been reported previously. In metalations with organolithium compounds carried out heretofore the emphasis has been on preparing particular compounds or on determining the position of metalation. The only prior information relating structure and metalating ability of organolithium reagents is based on product yields and results in a different reactivity order than that communicated here.¹

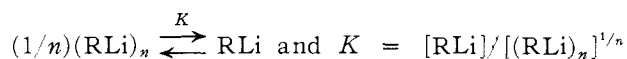
In this study the progress of reaction I was followed spectroscopically using an absorption cell described previously.² Triphenylmethane proved to be a suitable acid, because the electronic spectrum of its conjugate base triphenylmethylithium is well-defined² and its acidity provides experimentally acceptable reaction rates. A 40-fold excess of organolithium reagent relative to triphenylmethane was used. Consequently, in the initial stage all the reactions were kinetically pseudo first order in triphenylmethane. The reaction temperature was 22° and the solvent at least 90% (vol.) THF with diethyl ether or *n*-hexane making up the remainder.

Rate data for reaction 1 are given in Table I. Rates of formation of $(\text{C}_6\text{H}_5)_3\text{CLi}$ are illustrated in Fig. 1. The only reaction deviating strongly from first-order behavior prior to achieving 50% reaction is that with *n*-butyllithium, this being caused by the simultaneous consumption of *n*-butyllithium by reaction with THF. Rate constants determined from the initial slopes of optical density *vs.* time curves are identical, within

TABLE I
RATES OF METALATION OF TRIPHENYLMETHANE
BY ORGANOLITHIUM REAGENTS

| RLi | Initial concentration | | | Relative Reactivities | Key to Fig. 1 |
|------------------------|---------------------------------|---|--------------------------|-----------------------|---------------|
| | $\{RLi\}_i$ $\times 10^2, M$ | $\{(\text{C}_6\text{H}_5)_3\text{CH}\}_i$ $\times 10^2, M$ | $k_1, \text{min.}^{-1b}$ | | |
| Benzyllithium | 7.2 | 2.2 | 2.1 | 250 | ○ |
| Allyllithium | 6.5 | 1.6 | 0.35 | 51 | ● |
| <i>n</i> -Butyllithium | 7.1 | 1.7 | 0.10 | 13 | ● |
| Phenyllithium | 6.8 | 1.5 | 0.043 | 5.5 | ○ |
| Vinylithium | 6.9 | 1.9 | 0.020 | 2.5 | ○ |
| Methylithium | 5.3 | 1.4 | 0.008 | 1 | ● |

^a $\{RLi\}_i$ = the initial formal concentration of organolithium compound as determined by titration. ^b For $(\text{C}_6\text{H}_5)_3\text{CLi}$ in THF, $\log \epsilon_{500} m\mu = 4.52$. Allowance for clustering was made as follows



Thus for reaction 1

$$d[(\text{C}_6\text{H}_5)_3\text{CLi}]/dt = k_2[\text{RLi}][(\text{C}_6\text{H}_5)_3\text{CH}] = k_2K[(\text{RLi})_n]^{1/n}[(\text{C}_6\text{H}_5)_3\text{CH}] = k_1[(\text{C}_6\text{H}_5)_3\text{CH}]$$

(1) H. Gilman and H. A. McNinch, *J. Org. Chem.*, **27**, 1889 (1962). Decreasing metalation activity based on yields of acid obtained from the metalation of dibenzofuran and subsequent carbonation is reported to be *n*-butyllithium > phenyllithium > methylithium > benzyllithium.

(2) R. Waack and M. A. Doran, *J. Am. Chem. Soc.*, **85**, 1651 (1963).

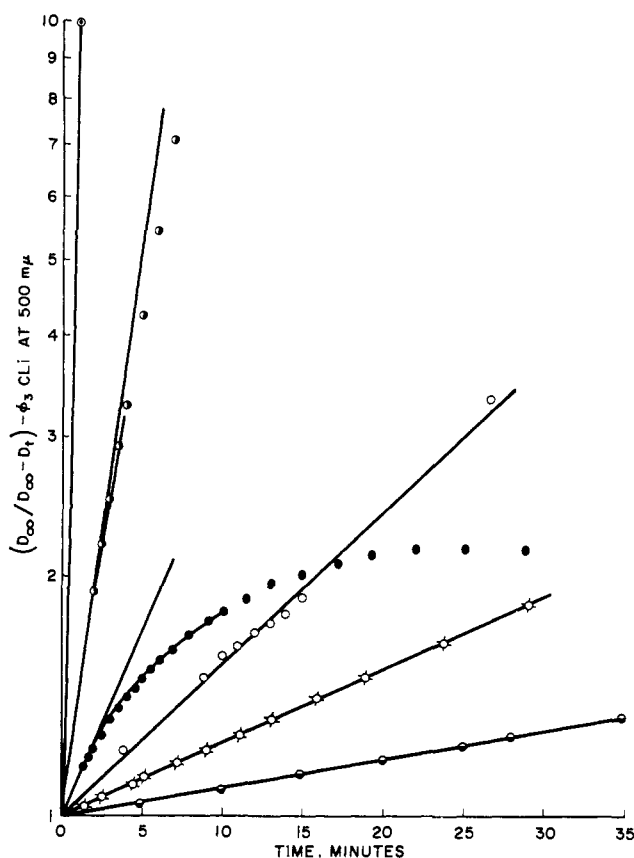


Fig. 1.—Rate of formation of $(\text{C}_6\text{H}_5)_3\text{CLi}$ in THF via $(\text{C}_6\text{H}_5)_3\text{CH} + \text{RLi} \rightarrow (\text{C}_6\text{H}_5)_3\text{CLi}$, where RLi = ○ benzyllithium, ● allyllithium, ● *n*-butyllithium, ○ phenyllithium, ○ vinylithium, ● methylithium. See Table I for details.

experimental error, with those derived from first-order treatment.

On the basis of structure similarities, the organolithium compounds in Table I may be divided into three classifications: (1) charge delocalized, *e.g.*, benzyllithium and allyllithium; (2) alkyl, *e.g.*, *n*-butyllithium and methylithium; and (3) sp^2 -hybridized, nondelocalized, *e.g.*, phenyllithium and vinylithium. Methylithium, the first member of the alkylithium series, is appreciably less reactive than *n*-butyllithium, which agrees with previous findings for this species.³ The most reactive metalating species are the resonance-stabilized organolithium compounds which are also believed to be the most thermodynamically stable. Thus, no correlation between rate of metalation and expected thermodynamic equilibrium constants exists.

The relative reactivities found for reaction 1 suggest that over-all nucleophilicity⁴ of the metalating species is rate controlling, supporting the presumption that the mechanism of metalation of compounds such as triphenylmethane is nucleophilic attack on hydrogen.⁵ Since both basicity and polarizability contribute to over-all nucleophilicity,⁴ the high reactivity of resonance-stabilized organolithium compounds is attributed to high polarizability despite low inherent basicity. A similar high relative reactivity was observed for the resonance-stabilized organolithium com-

(3) G. E. Coates, "Organometallic Compounds," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1960, p. 19; H. Gilman and B. J. Gaj, *J. Org. Chem.*, **22**, 1165 (1957).

(4) J. O. Edwards and R. G. Pearson, *J. Am. Chem. Soc.*, **84**, 16 (1962).

(5) H. Gilman, *Org. Reactions*, **8**, 262 (1954); J. D. Roberts and D. Y. Curtin, *J. Am. Chem. Soc.*, **68**, 1658 (1946).

pounds when used as initiators of vinyl polymerization.⁶ The high reactivity of benzyl lithium in halogen-substitution reactions⁷ is also in agreement with a high nucleophilicity for this species.

The rates of reaction 1 do not follow the expected order of relative organolithium basicities,⁸ although correlations between rate constants and equilibrium constants within a series of like reactions are known.⁹ A well-studied example is that rates of metalation by a given base are proportional to the acidity of the hydrogen which is replaced.¹⁰ In contrast, rates of metalation of RH by different organolithium bases presumably are not controlled solely by the base strength of the metalating reagent. Other nucleophilic displacement reactions on hydrogen also fail to obey the general rate-equilibrium parallelism.¹¹

A factor also anticipated to be important in regulating the relative reactivity of organolithium compounds is their degree of clustering in solution.¹² The existence of *n*-butyllithium as hexamers in benzene solution¹³ results in a kinetic dependence for metalation¹⁴ or initiation of polymerization¹⁵ of [*n*-butyllithium]^{1/6} in this solvent. Measurements of the order of reaction 1 with respect to organolithium reagent, within the concentration range 10⁻² to 10⁻¹ M total RLi reagent, indicate that benzyl lithium, allyllithium, and phenyllithium are reacting as monomeric species, whereas clustering appears to be dominant with *n*-butyllithium, methyl lithium, and vinyl lithium.¹⁶ Styryllithium, which should behave similarly to benzyl lithium, is reported to react as a monomeric species in the presence of THF.¹⁷ That the reactivity of an organolithium compound may vary with concentration, which in turn may depend on its propensity to self-associate, is indicated by the observation that 0.1–0.5 M benzyl lithium is stable in THF solution, whereas at 10⁻² M it decomposes, presumably by reaction with THF.

Since there are only small differences in organolithium concentrations used in the kinetic experiments reported here and those used by Gilman and McNinch,¹ it is unlikely that varying degrees of aggregation are responsible for the differences in the orders of relative reactivities of the RLi reagents. A possible explanation for the differing reactivity scales is that the product yields of Gilman and McNinch¹ reflect the equilibrium situation and are not a measure of the rate of metalation.

(6) R. Waack and M. A. Doran, *Polymers*, **2**, 365 (1961).

(7) H. Gilman and G. L. Schwebke, *J. Org. Chem.*, **27**, 4259 (1962).

(8) Decreasing relative basicities are indicated to be $n\text{-C}_6\text{H}_5\text{Li} > \text{C}_6\text{H}_5\text{Li} > \text{C}_6\text{H}_5\text{CH}_2\text{Li}$ (i.e., alkyl > sp² > charge delocalized): H. Gilman, *ibid.*, **27**, 1260 (1962), and references therein; G. E. Coates, "Organometallic Compounds," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1960, p. 25.

(9) (a) R. G. Pearson and R. L. Dillon, *J. Am. Chem. Soc.*, **75**, 2439 (1953); (b) N. Deno, G. Saines, and M. Spangler, *ibid.*, **84**, 3295 (1962); (c) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill, Book Co., Inc., New York, N. Y., 1940, pp. 136–138.

(10) A. Streitwieser, D. E. Van Sickle, and W. C. Langworth, *J. Am. Chem. Soc.*, **84**, 244 (1962), and subsequent papers; D. Bryce-Smith, *J. Chem. Soc.*, 1079 (1954).

(11) Ref. 9c, p. 209.

(12) R. Waack and M. A. Doran, *Chem. Ind. (London)*, 496 (1964).

(13) D. Margerison and J. P. Newport, *Trans. Faraday Soc.*, **59**, 2058 (1963).

(14) A. G. Evans and N. H. Rees, *J. Chem. Soc.*, 6039 (1963).

(15) D. J. Worsfold and S. Bywater, *Can. J. Chem.*, **38**, 1891 (1960).

(16) The rate of addition of vinyl lithium to 1,1-diphenylethylene in THF solution is one-third order in vinyl lithium, showing it is clustered in this solvent. The vinyl lithium concentration range was 5×10^{-3} to 1×10^{-1} M. R. Waack and P. Stevenson, to be published.

(17) S. Bywater and D. J. Worsfold, *Can. J. Chem.*, **40**, 1564 (1962).

More detailed kinetic studies will be reported soon.

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RECEIVED AUGUST 24, 1964

Zero-Charge Potentials of Solid Metals

Sir:

A new method has been devised for measuring zero-charge potentials (z.c.p.) of solid metals. The principle of this method is the same as that of the streaming mercury electrode; a transitory fresh metal surface is produced over the entire electrode, and the open circuit potential is measured before subsequent reactions can appreciably change the electrode charge.¹ The method of getting zero charge on the electrode is possible because the high activation energy for transfer of charge across the inner Helmholtz double layer enables one to measure the pre-existing potential. The simple inorganic ions are under equilibrium conditions during the entire process.

The method of producing fresh metal surface is that of scraping away the entire old metal surface. The apparatus consists essentially of a very high speed rotary scraper.

For the open circuit electrode we write

$$\frac{dq_m}{dt} + i_{\text{cath}} - i_{\text{anod}} = 0 \quad (1)$$

where q_m is the charge on the electrode, and i_{cath} and i_{anod} are the cathodic and anodic Faradaic processes occurring at the electrode-solution interface. The condition at the transient peak for the electrode potential, E , to be equal to z.c.p. is that

$$|(i_{\text{cath}} - i_{\text{anod}})\Delta t| < \Delta q_m \quad (2)$$

where Δq_m is the accuracy to which q_m is being measured and Δt is the shortest measurable time increment over which E should not change appreciably. This means that the new surface must be completely produced and potential recordings made in times less than Δt . Thus, the limitation of the method depends on the relative values of the velocity of the experimental procedures and of $(i_{\text{cath}} - i_{\text{anod}})$.

Zero-charge potentials have been obtained for several noble metals in 0.1 N KCl (cf. Table I). These values are in general agreement with values reported in the literature.

TABLE I

| Metal | Z.c.p. (vs. n.h.e.) |
|-------|----------------------|
| Pt | -0.40 ± 0.05 (pH 12) |
| Ag | -0.80 ± 0.05 (pH 7) |
| Cu | -0.35 ± 0.05 (pH 7) |
| Au | -0.09 ± 0.05 (pH 7) |

Acknowledgment.—We wish to acknowledge the AEC under Contract No. AT(11-1)1144 for financial support of this work.

(1) This method should be distinguished from the Billiter method.

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