

hydride (0.86 g.) in ether (50 ml.). The ether was decanted and the residue dissolved in diglyme. The resulting solution was added dropwise to a stirred solution of the above acid chloride (5.0 g.) in dry diglyme cooled to -70° in a Dry Ice-acetone-bath. The mixture was allowed to warm slowly to room temperature, then poured onto cracked ice and extracted with benzene. Removal of the benzene and recrystallization of the residue from ethanol gave 1-anthraldehyde (0.5 g., yellow needles from ethanol; m.p. 125–128°).

Anal. Calcd. for $C_{15}H_{10}O$: C, 87.30; H, 4.85. Found: C, 87.27; H, 4.71.

1-Acetylanthracene.—A solution of methylolithium (about 2.0 g.) in ether (150 ml.) was added to a stirred suspension of 1-anthracenecarboxylic acid in ether. After the addition, the mixture was heated under reflux for 30 minutes, then cooled and water and dilute HCl added. The ether layer was washed with Na_2CO_3 solution, dried over $MgSO_4$ and the solvent then removed. The 1-acetylanthracene (2.8 g., 56 g.) was recrystallized from ethanol; m.p. 105–108°.

Anal. Calcd. for $C_{16}H_{12}O$: C, 87.27; H, 5.45. Found: C, 87.09; H, 5.60.

The 2,4-dinitrophenylhydrazones formed orange needles from ethyl acetate; m.p. 265–267°.

Anal. Calcd. for $C_{22}H_{16}O_4N_4$: C, 65.99; H, 4.03; N, 14.00. Found: C, 65.61; H, 4.29; N, 14.23.

Measurement of pK_{BH^+} Values.—The procedure used is outlined in detail by Hammett and co-workers.² Weighed samples of the carbonyl compounds were dissolved in varying strength aqueous sulfuric acid solutions and the ultraviolet spectra taken on a Beckman model DB spectrophotometer. Corrections for spectral shifts due to solvent changes were made utilizing the "isosbestic point" method outlined by Hammett and co-workers. The pK_{BH^+} values were determined from the equation $H_0 = pK_{BH^+} - \log ([R^+]/[ROH])$, the H_0 values being taken from a large scale plot of the H_0 acidity function. A more detailed discussion of the method, as applied to the present series of compounds, is available elsewhere.⁷

Acknowledgment.—We thank the Robert A. Welch Foundation and the Alfred P. Sloan Foundation for financial assistance.

(7) Ph.D. Thesis of George S. Culbertson, Univ. of Texas, 1962.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILL.]

Equilibria in Halogen-Lithium Interconversions

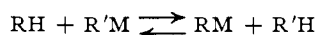
BY DOUGLAS E. APPLEQUIST AND DAVID F. O BRIEN

RECEIVED OCTOBER 27, 1962

Several halogen-lithium interchange equilibria have been measured to obtain the relative stabilities of various alkyl-, cycloalkyl-, alkenyl- and aryllithium reagents. Data and arguments are presented to show that the equilibrium constants are primarily affected by some structural parameter of the simple organolithium reagent, and it is concluded that the data may serve as a quantitative or semiquantitative measure of carbanion stability.

Introduction

Despite the interest there would obviously be in a knowledge of relative stabilities of carbanions, surprisingly little is known about the simple hydrocarbon anions. Semiquantitative measurements of "acidity" of hydrocarbons have been carried out in a few pioneering studies,¹ restricted necessarily to cases where the carbanions enjoy conjugative stabilization. The equilibria studied were exchange reactions of the type

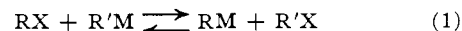


where M was sodium or potassium. Because of the non-polar media required and because of possible covalent character in the RM bonds, it was not possible to derive K_a 's which could be compared quantitatively with K_a 's of stronger acids in aqueous media, but the equilibria were of the same basic type as acid-base equilibria and were probably just as valid as the latter in establishing an order of anion stability. More recently, kinetic (rather than equilibrium) measurements of proton availability have provided promising approaches to stabilities of conjugated and acetylenic carbanions.²

(1) (a) J. B. Conant and G. W. Wheland, *J. Am. Chem. Soc.*, **54**, 1212 (1932); (b) W. K. McEwen, *ibid.*, **58**, 1124 (1936); (c) R. D. Kleene and G. W. Wheland, *ibid.*, **63**, 3321 (1941); (d) N. S. Wooding and W. C. E. Higginson, *J. Chem. Soc.*, 774 (1952).

(2) (a) D. Bryce-Smith, *ibid.*, 1079 (1954); (b) D. Bryce-Smith, V. Gold and D. P. N. Satchell, *ibid.*, 2743 (1954); (c) A. I. Shatenshtein, *Doklady Akad. Nauk S.S.S.R.*, **70**, 1029 (1950) (*C. A.*, **44**, 5194 (1950)); (d) A. I. Shatenshtein, N. M. Dykhno, E. A. Izraelievich, L. N. Vasil'eva and M. Faivush, *ibid.*, **79**, 479 (1951); (e) A. I. Shatenshtein and E. A. Izraelievich, *Zhur. Fiz. Khim.*, **32**, 2711 (1958); (f) A. I. Shatenshtein, *ibid.*, **26**, 1206 (1951); (g) A. I. Shatenshtein, L. N. Vasil'eva, N. M. Dykhno and E. A. Izraelievich, *Doklady Akad. Nauk S.S.S.R.*, **85**, 381 (1952); (h) F. S. Yabushin, U. G. Dubinskii, E. A. Yakovleva and A. I. Shatenshtein, *Zhur. Fiz. Khim.*, **33**, 2821 (1959); (i) N. M. Dykhno and A. I. Shatenshtein, *ibid.*, **28**, 11 (1954); *C. A.*, **48**, 10413d (1954); (j) H. Hart and R. E. Crocker, *J. Am. Chem. Soc.*, **82**, 418 (1960); (k) A. Streitwieser, Jr., D. E. Van Sickle and W. C. Langworthy, *ibid.*, **84**, 244 (1962); (l) A. Streitwieser, Jr. and D. E. Van Sickle, *ibid.*, **84**, 249 (1962); (m) A. Streitwieser, Jr., W. C. Langworthy and D. E. Van Sickle, *ibid.*, **84**, 251 (1962); (n) A. Streitwieser, Jr., and D. E. Van Sickle, *ibid.*, **84**, 254 (1962); (o) A. Streitwieser, Jr., D. E. Van Sickle and L. Reif, *ibid.*, **84**, 258 (1962); (p) R. E. Dessy, Y. Okuzumi and A. Chen, *ibid.*, **84**, 2899 (1962).

None of the techniques thus far described have been generally applicable to the less acidic (non-benzylic and non-allylic) hydrogens found in simple hydrocarbons. The present research was undertaken to see whether the halogen-metal interchange reaction (1) could be used to obtain quantitative data in the region of very low acidities. This reaction is formally similar to the acid-base equilibria traditionally used except



that the two bases compete for a halogen atom rather than a hydrogen atom. Examples of halogen-metal interchange are known in which the metal is sodium,³ magnesium,⁴ barium,^{4b} aluminum^{4c} and lithium,⁵ but the last metal is the most generally useful. For the purpose of obtaining carbanion stabilities, it would be desirable to maximize the ionic character of the R-M bond by the use of sodium or potassium, but lithium was nevertheless chosen for our initial studies because of anticipated difficulties with solubilities and with side reactions (such as Wurtz coupling and ether cleavage) to be expected from the other alkali metal alkyls. The halogen may normally be either bromine or iodine,⁵ and both are examined in the present work.

It is known qualitatively that halogen-lithium exchanges favor alkenyl or aryllithiums over alkyl-lithiums⁵ and cyclopropyllithiums over alkyl-lithiums,⁶ and it is known that exchanges involving very similar alkyl or aryl groups lead to equilibrium mixtures containing the four possible components in comparable amounts.⁷ However, systematic, quantitative determinations of the equilibrium constants do not appear to have been attempted.

(3) H. Gilman, F. W. Moore and O. Baine, *ibid.*, **63**, 2479 (1941).

(4) (a) H. Gilman and S. M. Spatz, *ibid.*, **63**, 1553 (1941); (b) H. Gilman, A. H. Haubein, G. O'Donnell and L. A. Woods, *ibid.*, **67**, 922 (1945); (c) H. Gilman and A. H. Haubein, *ibid.*, **67**, 1033 (1945).

(5) R. G. Jones and H. Gilman, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 339.

(6) (a) H. M. Walborsky and F. J. Impastato, *J. Am. Chem. Soc.*, **81**, 5835 (1959); (b) D. E. Applequist and A. H. Peterson, *ibid.*, **83**, 862 (1961).

(7) H. Gilman and R. G. Jones, *ibid.*, **63**, 1441 (1941).

Experimental⁸

Materials.—Argon and nitrogen were Matheson prepurified grades, and were dried by passage through phosphorus pentoxide.

The alkyl and aryl halides whose preparations are not described below were commercial materials. The chlorides and bromides were washed with sulfuric acid and water, dried over calcium chloride, and distilled from calcium hydride. All appeared by gas chromatographic analysis to be 99% pure. The commercial iodides were washed with aqueous sodium thiosulfate and water, dried over calcium chloride, and distilled. Gas chromatography indicated 99% purity. The iodides were stored in the dark over mercury.

Ether (Mallinckrodt reagent grade) was distilled from lithium aluminum hydride before use. *n*-Pentane was washed with sulfuric acid and water, dried over calcium chloride, and distilled from calcium hydride through a 60-cm. Vigreux column.

Neopentyl Iodide.—Neopentylmercuric chloride, m.p. 117–119°, was prepared by the method of Whitmore⁹ from neopentyl chloride. Iodination of neopentylmercuric chloride⁹ gave neopentyl iodide in 48% yield, b.p. 67–69° at 92–96 mm., n_D^{25} 1.4866 (lit.⁹ b.p. 70° at 100 mm., n_D^{20} 1.4887). The n.m.r. spectrum showed two singlets at τ 6.93 and 8.97, relative areas 2 and 9, respectively.

Cyclopentyl Iodide.—Cyclopentanol was treated with 47% hydriodic acid to give a 49% yield of cyclopentyl iodide, b.p. 58–60° at 20 mm., n_D^{25} 1.5448 (lit.¹⁰ b.p. 78–79° at 46 mm., n_D^{20} 1.5447).

Cyclobutyl chloride was prepared in 40% yield by the method of Roberts and Mazur (see ref. 17); (b.p. 81–83°, n_D^{25} 1.4332). Gas chromatographic analysis on diisodecyl phthalate indicated that the sample was 99% one component.

Cyclobutyl Iodide.—Cyclobutyl bromide¹¹ was converted to cyclobutyl lithium by reaction with a stoichiometric amount of lithium, into which copper powder has been pounded,¹³ in refluxing *n*-pentane overnight under an argon atmosphere. The filtered solution was found by the Gilman double titration¹⁴ to be 0.556 *N* in alkyl lithium (48% yield) and 0.605 *N* in total base. A solution of iodine (25.4 g., 0.10 mole) in 140 ml. of diethyl ether was added dropwise to a stirred solution of cyclobutyl lithium in pentane (0.095 mole). The reaction was conducted under an argon atmosphere at –70° (Dry Ice–isopropyl alcohol bath). The iodine solution was decolorized immediately upon addition to the alkyl lithium and formed a white precipitate. The last few ml. of iodine solution did not react and the mixture took on a reddish color. It was warmed to room temperature, treated with water, and then washed with aqueous sodium thiosulfate solution. The layers were separated and the organic layer was washed with water, then dried over anhydrous calcium chloride under a nitrogen atmosphere in a light-tight container at –20° (freezer). The major part of the pentane–ether was removed by distillation through a Holzman semimicro column¹⁵ under nitrogen atmosphere. The product was collected after separation on an F and M model 300 gas chromatograph, using an 8-foot preparative Carbowax 20M column at 90°. Approximately 12.0 g. of cyclobutyl iodide (99% pure) was collected, a yield of 70% based on the cyclobutyl lithium. Some alkyl iodide was

undoubtedly lost during the collection. The liquid had a micro b.p. 134–135°, n_D^{25} 1.5427. The major product was identified as cyclobutyl iodide by its n.m.r. spectrum, which is very similar to those of cyclobutyl bromide and chloride. The spectrum consists of a quintet (area 1) centered at 5.48, with peak separations of 7.9 c.p.s., and two groups of multiplets (areas 4 and 2) centered at 7.35 and 7.90, respectively. The infrared spectrum is similar to that of cyclobutyl bromide.¹²

Anal. Calcd. for C₄H₇I: C, 26.40; H, 3.88. Found: C, 26.68; H, 3.89.

Cyclopropyl Iodide.—Cyclopropyl chloride^{12,16} was prepared in 37% yield by a modification of the procedure of Roberts and Mazur¹⁷ for the chlorination of cyclobutane. A solution of dry ethylene dibromide (22.8 g., 0.118 mole) in 60 ml. of diethyl ether was added dropwise to a stirred, ice-cooled mixture of cyclopropyl chloride (10.3 g., 0.118 mole) and magnesium (5.8 g., 0.236 g. atom) in 225 ml. of ether. The addition took 8 hours. The reaction was vigorous with evolution of a gas, probably ethylene, and formation of magnesium halide. Following the initiation of the reaction, the cooling bath was removed. When the addition was completed the mixture was warmed to reflux and stirred for 24 hr. The reaction mixture had two phases. By titrating an aliquot from each phase and estimation of their respective volumes, the total base was found to be 0.084 mole. This represents a maximum yield of 71% (based on cyclopropyl chloride). An attempt to prepare the Grignard from the chloride without the use of ethylene dibromide failed.

Cyclopropylmagnesium halide (125 ml., 0.034 mole) was added dropwise to mercuric chloride (27.0 g., 0.10 mole) in 100 ml. of diethyl ether. The reaction was rapid and the ether refluxed gently. Following the addition, the white mixture was stirred for 3 hours and then the ether was distilled. The remaining solid was treated with 350 ml. of water to destroy any excess Grignard reagent and dissolve some of the magnesium salts. The mixture was filtered with suction and the residue was recrystallized from 95% ethanol. The product was a white crystalline material, plates m.p. 184–186°, 3.6 g., 35% yield. This material was a mixture of cyclopropylmercuric chloride and bromide, as indicated by analysis.

Anal. Calcd. for C₃H₅HgCl: C, 13.00; H, 1.82; Cl, 12.83. Calcd. for C₃H₅HgBr: C, 11.20; H, 1.57; Br, 24.85. Found for C₃H₅HgX: C, 11.73; H, 1.82; H, 1.61, 1.66; X, 23.58. Calcd. for 80% C₃H₅HgBr–20% C₃H₅HgCl: C, 11.56; H, 1.62; X, 23.46.

An analytical sample of cyclopropylmercuric chloride was obtained from the mixed halides by treatment with Dowex-1-X2 ion exchange resin in ethanol, followed by recrystallization from ethanol; m.p. 188–190°.

Anal. Calcd. for C₃H₅HgCl: C 13.00; H, 1.82. Found: C, 13.33; H, 1.79.

A solution of iodine (15.0 g., 0.059 mole), potassium iodide (20.5 g., 0.128 mole) and 150 ml. of water was added to cyclopropylmercuric halide (10.0 g., 0.03 mole). The mixture was shaken periodically to dissolve the reactants and then allowed to stand overnight. The excess iodine was destroyed with aqueous sodium thiosulfate solution. The resulting colorless two-layer mixture was extracted with ether to remove the organic materials. The ether extract was washed successively with sodium bisulfite solution, sodium carbonate solution and water. It was dried with anhydrous sodium sulfate overnight. Most of the ether was removed by distillation through a Holzman semimicro column; b.p. 36–36.5°, flask temperature 45–58°. The residue was stored under nitrogen in a light-tight flask at –20° (freezer). The cyclopropyl iodide was collected by separation on an F and M model 300 gas chromatograph, 8-foot preparative Carbowax 20 M column at 70°, block temperature 175°, injection port 165°, and flow 275 cc./min. The yield was 1.3 g. (26%), b.p. (micro) 92–93°, n_D^{25} 1.5362. The n.m.r. spectrum was closely similar to those of cyclopropyl chloride and cyclopropyl bromide⁸ and consisted of a multiplet centered at τ 7.72 (area 1) and another at τ 8.85–9.40 (area 4). The infrared spectrum was also similar to those of the chloride and bromide.

Anal. Calcd. for C₃H₅I: C, 21.45; H, 3.00. Found: C, 21.72; H, 3.07.

Vinyl Iodide.—To a solution prepared from 5.5 g. (0.14 g. atom) of potassium in 130 g. of *t*-amyl alcohol was added 40.0 g. (0.142 mole) of 1,2-diiodoethane (Aldrich). The mixture became milky and after an hour, it was neutral. The vinyl iodide was distilled out of the reaction mixture at 65 mm. and collected in 90% purity in a Dry Ice trap. The yield was 11.2 g.

The product was purified with an F and M model 300 gas chromatograph, using an 8-foot preparative Carbowax 20M column at 55°. The pure liquid boiled at 55–56° (micro), n_D^{25} 1.5286 (lit.¹⁸ b.p. 56°, n_D^{20} 1.5384.) The infrared spectrum

(16) J. D. Roberts and P. H. Dirstine, *J. Am. Chem. Soc.*, **67**, 1281 (1945).

(17) J. D. Roberts and R. H. Mazur, *ibid.*, **73**, 2509 (1951).

(8) All melting and boiling points are uncorrected. Nuclear magnetic resonance spectra were measured with Varian 60 Mc. high resolution spectrometers (model V-4300 B; serial 343 with super stabilizer or model A-60). Chemical shifts are expressed as τ , parts per million relative to tetramethylsilane internal standard (taken as τ 10) in carbon tetrachloride. The audio beat sideband method of calibration was used. Infrared spectra were obtained with Perkin–Elmer model 21 or Infracord double beam recording spectrophotometers with sodium chloride optics. Vapor phase chromatography was accomplished with a Perkin–Elmer model 154-B vapor fractometer, and F and M models 202, 300 or 500 linearly programmed gas chromatographs, using helium as carrier gas. Peak areas were measured either with a Keuffel and Esser compensating polar planimeter No. 4236 or with a disk integrator operating with the recorder.

Complete experimental details and data are available in the Ph.D. Thesis of D. F. O'Brien, University of Illinois, 1962.

The authors wish to acknowledge the aid of the following staff members: Mr. Josef Nemeth and associates who performed the microanalyses; Messrs. Paul McMahon and Dick Johnson and their associates who determined some of the infrared spectra; and Messrs. O. W. Norton and Dick Johnson and their associates who determined the nuclear magnetic resonance spectra.

(9) F. C. Whitmore, E. L. Whittle and B. R. Harriman, *J. Am. Chem. Soc.*, **61**, 1585 (1939).

(10) N. A. Rosanov, *Zhur. Russ. Fiz. Khim. Obshchestva*, **47**, 591 (1915).

(11) Prepared by a modification of the procedure of J. D. Roberts and V. C. Chambers, *J. Am. Chem. Soc.*, **73**, 3176 (1951), for cyclopropyl bromide, and identified by comparison of the infrared spectrum with the published spectrum.¹²

(12) J. D. Roberts and V. C. Chambers, *ibid.*, **73**, 5030 (1951).

(13) D. Y. Curtin and W. J. Koehl, Jr., *ibid.*, **84**, 1967 (1962).

(14) H. Gilman and A. H. Haubein, *ibid.*, **66**, 1515 (1944).

(15) C. W. Gould, Jr., G. Holzman and C. Niemann, *Anal. Chem.*, **20**, 361 (1948).

was identical with that in the literature,¹⁹ and the n.m.r. spectrum⁸ showed twelve peaks between 363 and 405 c.p.s. from tetramethylsilane.

Dicyclopropyl Mercury.—To 250 ml. of 1.47 *N*, filtered, ice-cold cyclopropylmagnesium chloride was added 42.0 g. (0.155 mole) of granular mercuric chloride. The addition required 2 hr., and the ice-bath was removed after one-fourth of the mercuric chloride had been added. The stirrer was stopped and the mixture refluxed overnight. A titration showed some unreacted base present, but a further treatment with mercuric chloride did not diminish it. The reaction mixture was mixed with 100 ml. of water and extracted with ether. The ether extract was washed with aqueous sodium thiosulfate and water and dried over calcium chloride. After removal of ether, the solid residue (4.7 g.) was distilled in a Hickman still²⁰ to give a liquid distillate, b.p. 50–55° at 0.15 mm. Efforts to obtain a carbon-hydrogen analysis gave high values, possibly due to elemental mercury in the water and carbon dioxide traps. However, a sample of the distillate reacted with concentrated hydrochloric acid to give an immediate precipitate of cyclopropylmercuric chloride (same m.p. and infrared spectrum as the authentic material described above), and the n.m.r. spectrum of the distillate showed a multiplet with area 4 at 36–78 c.p.s. and another multiplet, area 1, with one major peak, at 3 c.p.s. from tetramethylsilane.

Alkylolithium in *n*-Pentane.—Except for cyclopropylolithium, solutions of alkylolithiums in *n*-pentane were prepared from the corresponding chlorides by the method of Gilman.²¹ For example, 7.85 g. (0.101 mole) of isopropyl chloride in 50 ml. of pentane was added dropwise over 4 hr. to 1.39 g. (0.20 g. atom) of freshly cut lithium in 70 ml. of stirred, refluxing pentane under an argon atmosphere, and the mixture was stirred and refluxed overnight. The solution was filtered and stored at 5°. Titrations¹⁴ gave a base concentration of 0.57 *N* and a lithium reagent concentration of 0.48 *N* (52% yield).

Yields obtained by this method from other chlorides were: *n*-propyl, 80–82%; isobutyl, 62–67%; neopentyl, 63%; *sec*-butyl, 76–79%; cyclopentyl, 51%; and cyclobutyl, 50%. The last two were prepared with lithium treated with copper powder as described above.

Cyclopropylolithium in *n*-Pentane.—Dicyclopropyl mercury (4.0 g., 0.014 mole) in 130 ml. of stirred *n*-pentane was allowed to react with freshly cut lithium metal (1.2 g., 0.15 g. atom) at room temperature. The mixture rapidly became dark, and was allowed to react for 15 hours. An aliquot indicated the solution was 0.163 *N* in base. Fresh lithium metal was added, and after 8 hours the base was 0.179 *N*. Subsequent addition of lithium did not change the base appreciably. The mixture was filtered through a glass frit and stored at 5°. Analysis¹⁴ indicated a base concentration of 0.195 *N*, alkylolithium 0.098 *N*, volume 100 ml., 32% yield. Analysis of a hydrolyzed aliquot by v.p.c. indicated a solvent peak (*n*-pentane), and a smaller second peak, boiling range 60 to 80° (estimated from retention time) probably bicyclopropyl.

Alkylolithium in Diethyl Ether.—Ethyl, *n*-propyl, isobutyl, neopentyl and *n*-butyllithiums were prepared in ether from the chlorides by the method of Gilman.²² The respective yields were 85–88%, 77–82%, 76%, 76% and 89%.

Cyclopropylolithium in diethyl ether was prepared by the method of Hart.²³ Lithium dispersion (1.6 g. of metal, 0.23 g. atom) packed in mineral oil (30% Li by weight) was washed clean with *n*-pentane in a dry bag under a nitrogen atmosphere. The dispersion was then washed with ether and transferred to a flask. The flask was stoppered, removed from the bag, and connected to an argon source. Cyclopropyl chloride (7.6 g., 0.10 mole) in 30 ml. of ether was added dropwise to the stirred dispersion at 0°. The gray dispersion slowly became brown as the reaction progressed. After 3 hours the mixture was filtered and stored at –20°. The yield was 31%.

Phenylolithium in Diethyl Ether.—Redistilled bromobenzene (18.9 g., 0.12 mole) in 50 ml. of ether was added dropwise to a stirred mixture of freshly cut lithium (2.67 g., 0.38 g. atom) in 100 ml. of ether. The reaction was conducted under a nitrogen atmosphere at 0° for 20 hours. An excess of lithium was used to prevent any unreacted bromobenzene from being carried into the exchange reactions. The phenylolithium was filtered and stored at 0° and was 0.449 *N* (45% yield). An aliquot was hydrolyzed and analyzed by v.p.c. An ether peak, a small benzene peak and a smaller unknown peak (not bromobenzene)

were detected. The benzene presumably arose from ether cleavage and phenyllithium hydrolysis.

Vinylolithium in Diethyl Ether.—Tetravinyltin (Metal and Thermit Corporation; 1.9494 g., 0.00859 mole) in 10 ml. of stirred ether was treated rapidly with an ether solution of phenyllithium (75.54 ml., 0.455 *N*, 0.03437 mole) under an argon atmosphere.²⁴ It was stirred for 30 minutes and then the insoluble tetraphenyltin was filtered off. The product was found to be 0.393 *N* in vinylolithium (69% yield). Some of the product was oxidized in the filtration.

Exchanges of Alkylolithiums and Iodides.—A solution of the lithium reagent was added to a stirred solution of the iodide under nitrogen. Samples were removed immediately and at various intervals with a calibrated volumetric pipet equipped with a three-way stopcock at the cut-off line. The pipet entered the reaction flask through an opening sealed by a diaphragm under inert-gas pressure. The concentration of alkylolithium was determined by the double titration technique¹⁴ with allyl bromide (discussed below). The extent of exchange was determined by quenching an aliquot in water and analyzing the resulting organic layer by vapor chromatography for the two iodides involved. The presence of any Wurtz coupling product was also detected in this analysis, but reactions which gave appreciable coupling were not used to evaluate exchange equilibrium constants.

It was found that reactions at –70° in ether or 40% ether–60% pentane gave exclusively exchange. Reactions of *n*-propylolithium with ethyl iodide in ether at 2° or –25° gave too much coupling to permit evaluation of the exchange equilibria. A tentative value for the *n*-propyl–isobutyl equilibrium was obtained in 40% ether–60% pentane at –23°.

The reactions in pentane solvent were much slower, so a modified procedure was used: After the reactants had been mixed at –70°, samples were withdrawn for initial analyses of base, alkylolithium and alkyl iodide concentrations, and then 5-ml. aliquots were sealed in ampoules under argon. The ampoules were stored in an insulated vessel and stored in a freezer. The temperature in the ampoules was –22 ± 2°. They were removed periodically for analysis until equilibrium had been clearly reached.

Temperatures of –70 ± 1° and –23 ± 1° were maintained for short reaction times with Dry Ice–isopropyl alcohol and Dry Ice–carbon tetrachloride baths, respectively.

In several runs, the last iodide analysis was done by quenching the reaction mixture in the cold flask with water, followed by gas chromatography. Agreement of the points thus obtained with the others from the same reaction served to verify that the equilibrium was not shifted significantly in the pipet used for sample withdrawal (which operation normally required 10 seconds).

Attempted Exchange of *sec*-Butyllithium with Isopropyl Bromide.—A solution of 0.2 mole of *sec*-butyllithium and 0.2 mole of isopropyl bromide in 250 ml. of pentane was allowed to stand at 25° for 20 hr. The reaction was quenched with water and the organic layer concentrated on a spiral-wire fractionating column. The residue was further separated by gas chromatography on an F and M model 202 gas chromatograph, using a 4-foot dodecyl phthalate column, linearly programmed from 60 to 110°, block temperature 175°, injection port 195°, flow 20.6 cc./min., and 50 λ sample. The chromatograph showed, in order, peaks for pentane, first unknown, isopropyl bromide (still a major peak), second unknown and third unknown. The unknowns were collected and rechromatographed to determine their purity (98% or better). They were identified by comparing their infrared spectra with those of the known hydrocarbons^{25a} to be 2,3-dimethylbutane, b.p. 56–57°, lit.^{25b} 58°; 2,3-dimethylpentane, b.p. 89°, lit.^{25b} 89.7°; and, 4-dimethylhexane, b.p. 115–116°, lit.^{25b} 117.7°, respectively. No *sec*-butyl bromide was detected. The three coupling products were formed in comparable amounts, though 2,3-dimethylpentane was clearly the major product.²⁶ Careful analysis of this mixture was not undertaken. Similar attempted reactions of *sec*-butyl bromide with isopropylolithium gave similar mixtures of coupling products but no isopropyl bromide.

(24) (a) D. Seyferth and M. A. Weiner, *Chem. Ind.* (London), 402 (1959); (b) D. Seyferth and M. A. Weiner, *J. Am. Chem. Soc.*, **84**, 361 (1962).

(25) (a) F. D. Rossini, "Infrared Spectral Data," American Petroleum Institute Research Project 44, Carnegie Press, Pittsburgh, Pa., 1958; (b) F. D. Rossini, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," American Petroleum Institute Research Project 44, Carnegie Press, Pittsburgh, Pa., 1953.

(26) The observation of a roughly statistical array of coupling products in the absence of any exchange reaction has important implications for the mechanism of Wurtz coupling. Specifically, a direct displacement of a bromide ion by an alkylolithium is out of the question. The most simple explanation is that alkylolithium and alkyl bromide react to form lithium bromide and two free alkyl radicals, which diffuse apart and recombine randomly. A discussion of other evidence bearing upon these mechanistic possibilities is presented by J. Hine, "Physical Organic Chemistry," 2nd Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 245.

(18) J. Spence, *J. Am. Chem. Soc.*, **55**, 1290 (1933).

(19) P. Torkington and H. W. Thompson, *J. Chem. Soc.*, 303 (1944).

(20) (a) K. C. D. Hickman, *Chem. Rev.*, **34**, 51 (1944); (b) K. B. Wiberg, "Laboratory Technique in Organic Chemistry," McGraw-Hill Book Co. Inc., New York, N. Y., 1960, p. 65.

(21) H. Gilman, F. W. Moore and O. Baine, *J. Am. Chem. Soc.*, **63**, 2479 (1941).

(22) H. Gilman, J. A. Beel, G. G. Brannen, M. W. Bullock, G. E. Dunn and L. S. Miller, *ibid.*, **71**, 1499 (1949).

(23) H. Hart, private communication.

Attempted exchanges of *n*-propyllithium with ethyl bromide in ether were studied at 20°, 5°, -8°, -20° and -27°. The exchange product, *n*-propyl bromide, was not detected in any of the runs. At -27° there was no apparent decrease in the base concentration over 13 hours, while a very slight decrease of the base accompanied by a decrease in the ratio of ethyl bromide to *n*-hexane, coupling product, was observed at -20° over 46 hours. As the temperature was changed from -8° to 5° and to 20° the rate of decrease of base increased. An attempt to catalyze the exchange was conducted by adding a small amount of *n*-propyl iodide to the reaction mixture at -8°. Exchange was not observed after 5 hr., but the rate of base decrease was accelerated. The half-life of the decrease in base concentration at -8° without *n*-propyl iodide was about 540 min.; with the iodide it was about 135 min. It was felt that the iodide might also be catalyzing the interconversion, but the coupling occurred so rapidly that the exchange could not be detected. Therefore, a catalytic amount of *n*-propyl iodide was added to a reaction at -27°, at which temperature coupling does not occur, but again the desired interconversion was not observed.

Evaluation of the Double Titration for Alkylolithium.¹⁴—In an alkylolithium analysis, one aliquot of alkylolithium solution was quenched with water and titrated with acid to determine the total base. A second aliquot was allowed to react with a moderate excess of allyl bromide in ether for a few minutes and the resulting solution was quenched and titrated as before. The accuracy of the analysis has been tested by others²⁷ under conditions somewhat different from those employed in this work. (Benzyl chloride has usually been used, rather than allyl bromide.)

It was observed that a suspension of lithium ethoxide in ether, containing some ethanol, did not react with allyl bromide under the conditions of the analysis, as judged by titration of base present. It was further observed that when a solution of heptyllithium (0.0146 mole) was added to a solution of 0.03 mole of allyl bromide in ether and the resulting mixture decomposed with 99.5% deuterium oxide, that the *n*-heptane isolated from the reaction mixture contained less than 0.03 atom per cent deuterium, whereas when the *n*-heptyllithium was treated directly with deuterium oxide, *n*-heptane containing 5.08 atom per cent deuterium was obtained. These experiments established that the reaction with allyl bromide is quantitative and selective for lithium reagent in the cases indicated, and the method was therefore used for all analyses of lithium reagents.

Gas Chromatographic Analysis for Alkyl Iodides.—The determination of equilibrium constants required the accurate determination of the ratio of concentrations of the two iodides involved in each reaction. Empirical determinations of relative peak areas as functions of mole fractions were made for each pair of iodides. Excellent straight-line correlations were generally obtained. Known mixtures of ethyllithium and ethyl iodide in ether containing an *n*-heptane internal standard were hydrolyzed and analyzed as described above to give ethyl iodide analyses 0.5 and 1.5% in error. A similar check in pentane solution gave 2.5 and 1.4% errors.

An *n*-heptane standard was included in many of the exchange reaction mixtures, and served as a check on the constancy of the concentrations of individual iodides (otherwise indicated only by the constancy of the alkylolithium determinations). Since only the ratio of iodides was required for calculation of equilibrium constants and since the latter were calculated only when alkylolithium determinations and total iodide determinations (when *n*-heptane was present) were essentially constant, detailed data from iodide/*n*-heptane determinations will not be reported here, but may be found elsewhere.⁸

Peak areas were measured in part with an integrator on the recorder, which gave average deviations of 1.0–1.3%, and in part with a planimeter, which gave average deviations of 2.7%.

Sample Run with Calculations.—An exchange reaction of *n*-propyllithium with ethyl iodide in ether at -65° was run as described above, with an added *n*-heptane internal standard. The results are shown in Table I. That the data of this run are suitable for an equilibrium constant determination is shown by the absence of drifts in the values of total base, total lithium reagent, ratio of iodides and ratios of iodides to *n*-heptane. The average value obtained for total base was 0.192 *N*, whereas the stock solution of *n*-propyllithium used had a base concentration of 0.879 *N*. Since 10.57 ml. of the stock solution was used, the volume of the reaction solution was 48.3 ml. The total lithium reagent concentration was taken to be 0.144 *N*, the average of the determinations in Table I, and the total iodide concentration was obtained from the weighed amount of ethyl iodide used (1.23 g.) and the volume calculated above. The ratio of *n*-propyl iodide and ethyl iodide concentrations was obtained from the v.p.c. peak areas and the empirical thermal conductivity corrections (mole fraction of ethyl iodide was about 1.5% larger than the v.p.c. peak area fraction). The concentrations of

TABLE I

EXCHANGE DATA FOR *n*-PROPYLLITHIUM-ETHYL IODIDE

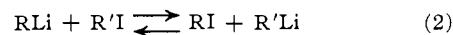
Time, min.	Base, <i>N</i>	RLi, <i>N</i>	—Peak areas (v.p.c.)—			<i>K</i> _{obsd} ^a
			EtI	<i>n</i> -PrI	<i>n</i> -C ₇ H ₁₆	
2.5	0.183		38	52	90	2.43
5.5		0.135				
28.0	.198		33	44	68	2.30
30.5		.155				
60.0	.194		54	78	112	2.75
62.5		.144				
90.0	.186		57	76	115	2.30
92.0		.140				
133.0	.189		60	86	139	2.69
135.0		.141				
208.5	.198		56	80	136	2.67
211.0		.149				
266.5	.196		59	83	127	2.57
269.0		.151				

$$^a K_{\text{obsd}} = (n\text{-PrI})(\text{EtLi}) / (n\text{-PrLi})(\text{EtI}).$$

ethylolithium and *n*-propyl iodide were taken to be equal, from the stoichiometry. The average value of *K*_{obsd} is 2.53, with an average deviation of 0.17. Note that in this run even the first determination was made after equilibrium had been essentially reached. In other cases, the first few values of *K*_{obsd} were discarded because equilibrium had not been reached.

Results

Equilibrium data are summarized in Table II for the reaction



$$K_{\text{obsd}} = (\text{RI})(\text{R}'\text{Li}) / (\text{RLi})(\text{R}'\text{I})$$

In each case, the R and R' are so chosen that *K*_{obsd} > 1. Some qualitative observations which do not appear in the table or which may be deduced from the table should be noted: Reactions in ether at -70° were generally complete after 30 min., but in 40% ether at the same temperature, 200–500 min. was typically required. Reactions were again fast in 40% ether at -25°, but in pentane at this temperature, 30,000 min. was a typical time for completion. Despite these large solvent effects on rate, the equilibrium constants are remarkably insensitive to solvent (compare the *n*-propyl-isobutyl constants, for example). Furthermore, the temperature effect is so small in the case where it was measured (*n*-propyl-isobutyl in 40% ether) that we can probably ignore errors due to poor temperature control.

To determine whether the measured equilibria are sensitive to the total concentration of lithium reagent or to the equilibrium ratios of lithium reagents (see discussion below), several special runs in one system were performed (Table III). These showed *K*_{obsd} to be invariant with total lithium concentration over a 13.7-fold range, and invariant with the ratio of ethyllithium to propyllithium over a 9.5-fold range. The lack of dependence of the apparent equilibrium constant upon total lithium concentration suggests that the activities of lithium reagents should be nearly proportional to concentration from the concentrations used through infinite dilution (neglecting dissociation), and activity coefficient corrections are therefore ignored throughout this work. One further check on the validity of the equilibrium constants was to analyze the reaction mixture of *n*-propyllithium with both ethyl iodide and isobutyl iodide at the same time in 40% ether at -70°. The relative amounts of the three iodides at equilibrium gave *K*_{obsd} values for the ethyl-*n*-propyl system (2.24 ± 0.06) and the *n*-propyl-isobutyl system (5.20 ± 0.40) in satisfactory agreement with the values determined in binary systems (Table II).

(27) (a) C. W. Kamienski and D. L. Esmay, *J. Org. Chem.*, **25**, 115 (1960); (b) K. C. Eberly, *ibid.*, **26**, 1309 (1961); (c) P. F. Collins, C. W. Kamienski, D. L. Esmay and R. B. Ellestad, *Anal. Chem.*, **33**, 468 (1961).

TABLE II^a
 EQUILIBRIUM CONSTANTS FOR $R\text{Li} + R'\text{I} \rightleftharpoons \text{RI} + R'\text{Li}$

R'	R	K_{obsd}^b			
		Ether, -70°	40% Ether-60% pentane, -70°	40% Ether-60% pentane, -23°	Pentane, -23°
Vinyl	Phenyl	258 ± 11			
Phenyl	Cyclopropyl	9.55 ± 0.46			
Cyclopropyl	Ethyl		333 ± 23		
Ethyl	<i>n</i> -Propyl	2.38 ± 0.20 ^c	2.56 ± 0.10		
<i>n</i> -Propyl	Isobutyl	5.11 ± .28	5.45 ± .22	7.96 ± 0.33	7.77 ± 0.22
Isobutyl	Neopentyl	7.49 ± .28	(6.92 ± .70) ^e		21.59 ± 1.47
Isobutyl	Cyclobutyl		35.3 ± 3.5		
Neopentyl	Cyclobutyl		5.10 ± 0.11 ^d		
Cyclobutyl	Cyclopentyl		5.82 ± 1.22		

^a Except where otherwise indicated, data for each reaction were collected in two runs, one from each direction. ^b Errors shown are average deviations of all points after equilibrium had been reached. ^c There were four runs, two in each direction. ^d There was only one run, a reaction of neopentyllithium with cyclobutyl iodide. ^e Calculated from the isobutyl-cyclobutyl and neopentyl-cyclobutyl K_{obsd} 's.

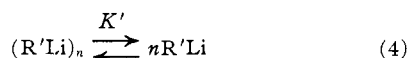
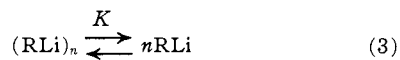
 TABLE III
 CONCENTRATION EFFECTS IN ETHER AT -70°

Run	Equilibrium concentrations, <i>M</i>				K_{obsd}
	$\text{C}_2\text{H}_5\text{I}$	<i>n</i> - $\text{C}_3\text{H}_7\text{Li}$	$\text{C}_2\text{H}_5\text{Li}$	<i>n</i> - $\text{C}_4\text{H}_9\text{I}$	
1	0.0442	0.0614	0.0827	0.0827	2.53 ± 0.17
2	.0174	.00602	.0170	.0170	2.59 ± .15
3	.0229	.0229	.293	.0045	2.54 ± .11

Discussion

The most important question to be answered in the interpretation of the exchange equilibrium data is whether they indeed reflect the relative stabilities of carbanions in a quantitative way, or whether they are strongly influenced by other factors, of which the most obvious possibility is the stability of the polymeric aggregate of each lithium reagent with respect to monomer. It is known from freezing-point data that ethyllithium is approximately hexameric in benzene,²⁸ and from mass spectral evidence that it is a tetramer and/or a hexamer in the gas phase.²⁹ Evidence from n.m.r. and infrared spectra in hydrocarbon media has provided support for highly symmetrical structures for the polymers.³⁰ In ether media, the structure is apparently broken down by coordination with ether, but less is known about the structures in ether. Wittig, Meyer and Lange³¹ have measured the apparent degrees of association of four lithium reagents in ether by boiling-point elevation, and found them to be two-to fivefold aggregates.

The relationship of the observed equilibrium constants (which we designate K_{obsd}) to the true K_{eq} for the exchange of monomeric reactants (reaction 2) may be considered in terms of the dissociation equilibria for the two lithium reagents, reactions 3 and 4. The mathematics relating the true K_{eq} to K_{obsd} is most easily handled for two extreme cases in both of which



n is assumed for simplicity to be a single constant. In the first case, the bonding in the aggregates is assumed to be of such a specific nature that no mixed complexes occur; *i.e.*, all RLi is in the form of $(\text{RLi})_n$ and all R'Li is in the form of $(\text{R}'\text{Li})_n$. If we define $[\text{RLi}]_{\text{obsd}}$ to be the total concentration of RLi determined by the above analytical procedure, then it follows immediately from

(28) T. L. Brown and M. T. Rogers, *J. Am. Chem. Soc.*, **79**, 1859 (1957).

(29) J. Berkowitz, D. A. Bafus and T. L. Brown, *J. Phys. Chem.*, **65**, 1380 (1961).

(30) (a) T. L. Brown, D. W. Dickerhoof and D. A. Bafus, *J. Am. Chem. Soc.*, **84**, 1371 (1962); (b) R. West and W. H. Glaze, *ibid.*, **83**, 3580 (1961).

(31) G. Wittig, F. J. Meyer and G. Lange, *Ann.*, **571**, 167 (1951).

$$(\text{RLi}) = [K((\text{RLi})_n)]^{1/n} \quad (5)$$

and

$$[\text{R}'\text{Li}]_{\text{obsd}} = n((\text{R}'\text{Li})_n) \quad (6)$$

that

$$K_{\text{obsd}} = K_{\text{eq}} \left(\frac{K}{K'}\right)^{1/n} \left(\frac{[\text{RLi}]_{\text{obsd}}}{[\text{R}'\text{Li}]_{\text{obsd}}}\right)^{1-n/n} \quad (7)$$

Thus, for this extreme case, the K_{obsd} would be a function of the relative concentrations of the two lithium reagents, the magnitude of the dependence being a function of *n*. The 9.5-fold variation in the ratio which was tested (runs 1 and 3, Table III) would have produced about a 3-fold change in K_{obsd} if *n* were 2 and about a 1.5-fold change in K_{obsd} if *n* were 6. Since no variation in K_{obsd} even approaching such magnitudes was observed (Table III), the extreme case of specific aggregate formation is clearly ruled out. This result is hardly surprising, since it would be difficult to imagine the bonding forces which could lead to such specifically homogeneous aggregates.

The second extreme, and a more reasonable one from a chemical point of view, is that in which the bonding energy associated with a particular RLi molecule in an aggregate is independent of the identities of the other alkyls in the aggregate. This implies zero enthalpy changes in all exchanges of monomeric alkylolithiums between aggregates, and leads therefore to a random array of aggregates in which $(\text{RLi})_n$ and $(\text{R}'\text{Li})_n$ would be minor constituents if $[\text{RLi}]_{\text{obsd}}$ and $[\text{R}'\text{Li}]_{\text{obsd}}$ were of comparable magnitude. It is easily shown³² that under these conditions, K_{obsd} would obey eq. 8.

$$K_{\text{obsd}} = K_{\text{eq}} \left(\frac{K}{K'}\right)^{1/n} \quad (8)$$

Thus in this extreme situation, the observed equilibrium constants would be independent of the ratio of lithium compounds and of total lithium concentration, but might still to some degree reflect changes in K/K' rather than, as desired, changes in K_{eq} . To the extent that some intermediate situation prevails, in which the composition of aggregates is nearly random but with some preference for homogeneous or for particular

(32) The relative concentrations of the various complexes are given by the coefficients from the binomial expansion

$$\left[(\text{RLi}) + \frac{[\text{R}'\text{Li}]_{\text{obsd}}}{[\text{RLi}]_{\text{obsd}}} (\text{R}'\text{Li}) \right]^n$$

where the exponents of each term represent the composition of the complex whose concentration is given by the coefficient of that term. Hence

$$\frac{((\text{RLi})_n)}{((\text{R}'\text{Li})_n)} = \left(\frac{[\text{RLi}]_{\text{obsd}}}{[\text{R}'\text{Li}]_{\text{obsd}}}\right)^n$$

Since

$$(\text{RLi}) = [K((\text{RLi})_n)]^{1/n}$$

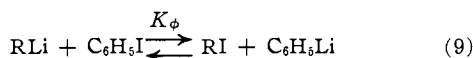
then

$$\frac{(\text{RLi})}{(\text{R}'\text{Li})} = \left(\frac{K}{K'}\right)^{1/n} \frac{[\text{RLi}]_{\text{obsd}}}{[\text{R}'\text{Li}]_{\text{obsd}}}$$

Equation 8 follows directly from this relation.

heterogeneous aggregates, we would expect the K_{obsd} values to exhibit some dependence upon the ratio $[\text{RLi}]_{\text{obsd}}/[\text{R}'\text{Li}]_{\text{obsd}}$. Such a dependence may exist for some cases, but the evidence of Table III is strongly indicative of a random array of aggregates in the ethyl-*n*-propyl system, and we shall assume that this result may be extrapolated to all of the systems considered in this work.

Further consideration of the data of Table II is facilitated by conversion of all equilibrium constants to constants (K_{ϕ}) for reactions (9) of the various lithium reagents with a single standard iodide which we will arbitrarily select to be iodobenzene. The calculated constants are shown as their logarithms in Table IV.



Data from ether or 40% ether at -70° are combined since the solvent effects are small. Where data from both solvents are available, those from pure ether are shown. This choice is entirely arbitrary, and the insensitivity of the calculated long-range constants to solvent effects is shown by the calculated ethyl-neopentyl constant, which is 91.0 in ether and 96.5 in 40% ether-60% pentane (from the data in Table II).

There are two principal arguments that the equilibrium constants in Tables II and IV are controlled primarily by the relative stabilities of monomeric lithium reagents (K_{ea}) rather than the K/K' ratio which appears in eq. 8. The first argument is that the insensitivity of the equilibrium constants to solvent changes which cause extremely large changes in rate of reaction and state of aggregation^{30,31} would be most surprising if K/K' is a number very different from 1.

TABLE IV

EQUILIBRIUM CONSTANTS FOR $\text{RLi} + \text{C}_6\text{H}_5\text{I} \rightleftharpoons \text{RI} + \text{C}_6\text{H}_5\text{Li}$			
R	$\log K_{\phi}$	R	$\log K_{\phi}$
Vinyl	-2.41 ± 0.02	Isobutyl	4.59 ± 0.06
Phenyl	(0.00)	Neopentyl	$5.46 \pm .06$
Cyclopropyl	0.98 ± 0.02	Cyclobutyl	$6.14 \pm .07$
Ethyl	$3.50 \pm .04$	Cyclopentyl	$6.90 \pm .10$
<i>n</i> -Propyl	$3.88 \pm .05$		

The second argument is that the order of stability of lithium reagents in Table IV is qualitatively that expected from the current embryonic notions of carbanion stability. Thus the most stable lithium compounds are those with sp^2 -hybridized carbons bearing lithium and one (cyclopropyl) whose hybridization must approach sp^2 .³² Of the sp^3 compounds, the primary lithiums are more stable than the secondary ones, and the qualitative order can be explained by the electron-donating destabilization of β -alkyl groups and by the assumption of somewhat more *s*-character in the cyclobutyl-lithium bond than in the cyclopentyl-lithium bond.

A quantitative accounting for the constants in Table IV is more difficult. One interesting comparison is with the orbital electronegativities (Mulliken scale) of Hinze and Jaffe.³⁴ If one takes 17.58 and 15.95 to be the electronegativities of vinyl and cyclopentyl (sp^2 and sp^3 , respectively) and calculates³⁴ 17.12 to be the electronegativity of cyclopropyl on the basis of an assumed $\text{sp}^{2.28}$ hybridization,³³ then a nearly linear correlation of $\log K_{\phi}$ with electronegativity for these three cases is obtained. It would be imprudent to attach great significance to this result, but it is certainly

(33) C. A. Coulson and W. E. Moffitt, *J. Chem. Phys.*, **15**, 151 (1947).

(34) J. Hinze and H. H. Jaffe, *J. Am. Chem. Soc.*, **84**, 540 (1962).

in agreement with the postulate that K_{ϕ} is determined by carbanion stability.

The primary alkylolithiums show an effect which cannot easily be accounted for in terms of simple electronic effects of alkyl substituents on monomeric lithium reagents, namely, that each successive β -methyl group added to ethyllithium produces a somewhat larger destabilizing effect than the one before. A steric explanation is suggested, and the phenomenon is probably the only indication in this work that a variation in the ratio K/K' (eq. 8) affects K_{obsd} . The fact that the last methyl group (isobutyl to neopentyl) has nearly a 3-fold larger effect in pentane than in ether (Table II) is in support of the steric interpretation if one assumes that in pentane, alkyl-alkyl repulsions in the unsolvated aggregates are most important, whereas in ether, alkyl-solvent repulsions prevail.

One possible effect which could make K_{ϕ} values less valid than K_{a} values as measures of anion stability would be ionic character in the carbon-iodine bond, so that structural changes would affect K_{ϕ} at least in part in such a way as to favor the iodide whose alkyl or aryl group could best support a positive charge. A theoretical argument against this possibility is that the electronegativities of carbon and iodine on the Pauling scale are equal (corresponding to zero ionic character in the bond), whereas the carbon and lithium electronegativities differ by 1.5 (corresponding to over 40% ionic character).³⁵ Such thermochemical data as there are suggest that C-I bond strengths parallel the corresponding C-H bond strengths. Thus the heat of formation of iodobenzene³⁶ exceeds that of benzene²⁵ by 13.96 kcal., and the heat of formation of isopropyl iodide³⁷ exceeds that of propane²⁵ by 13.37 kcal. A similar parallel may be found in reported bond dissociation energies.³⁸

Conclusion

The halogen-lithium interchange equilibrium constants in Tables II and IV, in view of the foregoing arguments, certainly represent an approximate measure of relative carbanion stability, and may be good enough for application in linear free energy correlations with other reactions in which a buildup of negative charge on carbon is suspected. The extent to which the constants here presented are sensitive to steric effects in the alkylolithium aggregates may best be determined by examination of such attempted correlations with other reactions, and some efforts in this direction will be made in this Laboratory. It would be desirable, of course, to combine the scale of K_{ϕ} values with the K_{a} scale which has been used for the more acidic hydrocarbons, but the necessary overlapping data are not yet available.

Acknowledgment.—This research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of said fund. We wish also to thank the National Science Foundation for support during the later stages of the work.

(35) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, pp. 93, 98.

(36) W. S. Graham, R. J. Nichol and A. R. Ubbelohde, *J. Chem. Soc.*, 115 (1955).

(37) C. T. Mortimer, H. O. Pritchard and H. A. Skinner, *Trans. Faraday Soc.*, **48**, 220 (1952).

(38) (a) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 50; (b) E. T. Butler and M. Polanyi, *Trans. Faraday Soc.*, **39**, 19 (1943).