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complications than techniques using discharge sources of fluorine atoms. The $CH_3F\cdots HF$ product forms upon photolysis of a F_2 molecule adjacent to methane in the matrix, and the $H_3C\cdots HF$ product forms after diffusion and reaction of methane with free fluorine atoms. This two-step process conclusively shows that two different species are produced. The reactions of fluorine atoms with methane in solid argon at 25 K show that this reaction requires virtually no activation energy.

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Determination of the Basicities of Benzyl, Allyl, and *tert*-Butylpropargyl Anions by Anodic Oxidation of Organolithium Compounds

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Abstract: Electrochemical oxidation potentials have been determined by using cyclic voltammetry and second-harmonic ac voltammetry for benzyllithium, allyllithium, *tert*-butylpropargyllithium, and triphenylmethyllithium in tetrahydrofuran/hexamethylphosphoramide. The use of these potentials along with bond dissociation energies and the known pK_a of triphenylmethane permit the estimation of ion-pair acidities of the corresponding hydrocarbons, expressed as pK_a's. These are compared with other estimates for the pK_a of toluene and with estimates of the pK_a's of isobutane and methane. Electrochemical studies are also reported for diphenylmethyllithium, cyclopentadienyllithium, vinyllithium, phenyllithium, methyllithium, and *n*-butyllithium. The first two were well-behaved and permit us to calculate the pK_a of cyclopentadiene and a bond dissociation energy for diphenylmethane. The others give electrochemistry so poor that it is useful only to estimate lower limits to the corresponding pK_a's.

Introduction

We have described the use of electrochemical data to provide thermodynamic estimates of the basicities of a variety of carbanions.[1-7] The general validity of the approach was demonstrated by its ability to reproduce a number of directly determined equilibrium constants reflecting stabilities not only of carbanions but also of carbonium ions[8] and of radicals.[5] For hydrocarbon acidities the method[6] is simple: the sequence of eq 1 is examined

$$R\text{–}H \xrightarrow{\text{BDE}} H\cdot + R\cdot \xrightarrow{+e^-} R^- \ (H\cdot \xrightarrow{-e^-} H^+) \qquad (1)$$

for the unknown and for a known model compound. Using the bond dissociation energy (BDE) for each and the electrochemical reduction potential for each radical, it is straightforward to calculate the pK_a of R–H from the known pK_a of the model compound, assuming that it mirrors the other changes (e.g., from gas-phase BDE to solution electrochemistry) involved in the sequence. With this method we have determined[6] the pK_a of isobutane (forming a *tert*-butyl anion) to be 71.

It was shown[7] that the result for isobutane is not very sensitive to the medium used for the electrochemistry, and in the same publication it was reported that in the electrochemical reduction of benzyl iodide, of allyl iodide, and of propargyl iodide there were two reduction waves, the second of which was assigned to reduction of the corresponding radicals to anions. Unfortunately, the "first wave" was actually a prewave due to adsorption of iodide on the metal electrodes and is not seen at vitreous carbon electrodes. This has been shown by Bard[9] for allyl iodide, and we[10] and Bartak[11] have shown it for benzyl iodide. Thus the "second wave" for benzyl, allyl, and propargyl was not for the one-electron reduction of carbon radicals to anions, and the pK_a's derived from it are invalid. The pK_a's of 54, 53, and 63 which were reported[7] for the formation of benzyl, allyl, and propargyl anions are simply upper limits if the true reduction potential of the radicals is anodic of the potentials required to reduce the covalent iodides to carbanions. Our results described below will show that this is indeed the case. By contrast, we find that *tert*-butyl iodide shows the same two reduction waves at a vitreous carbon electrode as those we have described earlier[6] at metal. Thus the complication in the previously reported electrochemistry of benzyl iodide, allyl iodide, and propargyl iodide is not present for *tert*-butyl iodide.

In principle the reduction potential for conversion of a radical to an anion is obtainable from the reverse process, oxidation of the anion.[8,9] The experimental problem is to produce stable solutions of the appropriate carbanions for study. This can be approached by the use of organolithium species.[8] Extensive studies have shown that compounds such as benzyllithium[12] and allyllithium,[13] with delocalized carbanion components, do not have covalent carbon–lithium bonds but exist as carbanion–lithium ion pairs in solvents such as tetrahydrofuran (THF) or hexamethylphosphoramide (HMPA). The situation is less clear for lithio derivatives of less stable anions, as in methyllithium. Such species often exist as clusters,[14] and the extent to which they can be thought of as containing methyl anion is problematical.

In order to obtain better electrochemical and pK_a data, we have thus examined the anodic oxidation of benzyllithium (**1**) and of allyllithium (**2**). As an approximation to propargyllithium we have prepared and examined 1-lithio-4,4-dimethylpent-2-yne (*tert*-

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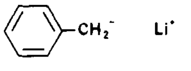
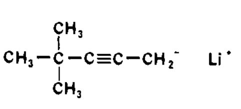
butylpropargyllithium) (**3**), in which the acidic acetylenic hydrogen is missing. We have also examined the electrochemical oxidation of triphenylmethyllithium (**4**) in our media as the model system with known pK_a and the related diphenylmethyllithium (**5**). Since



1

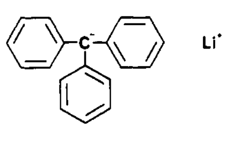
$CH_2{=}CH{-}CH_2^-\ \ Li^+$

2

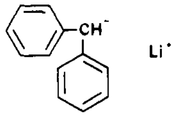


$(CH_3)_3C{-}C{\equiv}C{-}CH_2^-\ \ Li^+$

3



4



5

the electrochemistry of carbanions proved to be particularly well-behaved in some of our solvent systems, we have reinvestigated cyclopentadienyllithium, which in earlier work[8] had given poorly behaved anodic waves. We also tried to examine the oxidation potentials for phenyllithium, vinyllithium, *n*-butyllithium, and methyllithium in our systems, but with less success. They were stable in our media but gave poor electrochemistry (vide infra). *tert*-Butyllithium reacted rapidly with our solvents, so it could not be examined.

The choice of solvent and temperature can affect the state of the organolithium compound.[15] Solvent can break up clusters, solvate contact ion pairs, and produce solvent-separated ion pairs or dissociated ions. For this reason we have examined all our compounds in THF at several temperatures with and without added HMPA. Preliminary experiments showed that tetramethylethylenediamine (TMEDA) was not as useful as HMPA electrochemically as an additive of THF and useless (very large resistances) as a pure solvent in its own right for electrochemistry. Our results show some remarkable effects of added HMPA.

Of course electrochemistry in a particular medium only lets us deduce a pK_a in that same medium, and relative p*K*s can show strong solvent dependences.[16] Furthermore, while hydrocarbon "pK_a" would seem to refer to the ionization to a carbanion, one must consider the interaction of that carbanion with cations in the medium, not just with the solvent. If the anion is stabilized by ion pairing, then the p*K* we determine is for what is called[17] an "ion-pair acidity". Such stabilization, or even more so covalent bonding, will lead to a p*K* lower than that for formation of a free (solvated) carbanion. The p*K*s obtained by our measurements are those for conversion of a hydrocarbon into whatever carbanion–lithium associated or dissociated pair is actually present in our electrochemical system.

As is described in the Experimental Section, pure solid samples of benzyl-, allyl-, vinyl-, phenyl-, and cyclopentadienyllithium were prepared by known procedures. Triphenylmethyl-, diphenylmethyl-, and *tert*-butylpropargyllithium were prepared in solution by reaction of the parent hydrocarbons with *n*-butyllithium. The survival of the most reactive organolithiums in our electrochemical media was confirmed by treatment of the solution with trimethylsilyl chloride. This led to disappearance of the electrochemical waves assigned to the carbanion and formation of the appropriate organosilanes which were identical with authentic samples. This test was successfully applied to benzyl-, allyl-, *tert*-butylpropargyl-, vinyl-, and *n*-butyllithium. The survival of *n*-butyllithium in THF/HMPA at −62 °C was also established by quenching with benzaldehyde and isolation of the adduct in 60% yield; *tert*-butyllithium reacted with solvent and failed this test, producing immediate gas evolution and giving none of the benzaldehyde adduct on quenching after standing in THF/30% HMPA at −63 °C for a brief time.

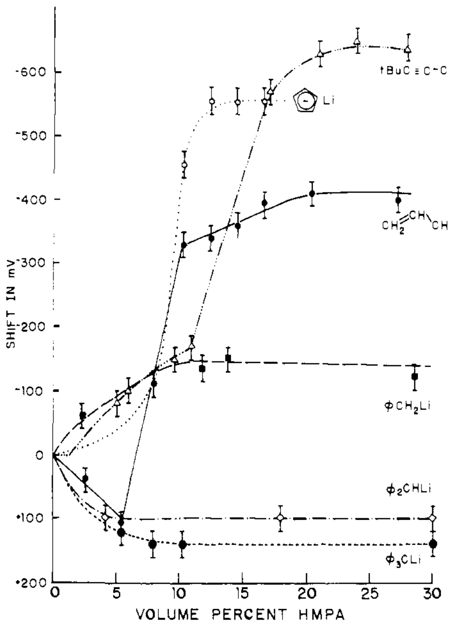


Figure 1. The shift in peak potential E_p in the cyclic voltammograms of organolithium compounds at a sweep rate of 200 mV/s and a temperature of −25 °C except for cyclopentadienyllithium and *tert*-butylpropargyllithium which are at −60 °C. In the steep portion of the cuves for allyllithium and *tert*-butylpropargyllithium two species are seen (cf. Results and Discussion).

Solutions of the organolithium compounds were made up in THF and THF/HMPA with lithium perchlorate as electrolyte and examined electrochemically with a polished vitreous carbon anode. The principal technique used was cyclic voltammetry, but second-harmonic ac voltammetry was also studied in the cases of interest. Studies were performed at −62, −25, 0, and +25 °C and occassionally at other temperatures; at the highest temperature HMPA was not added, since in some cases it caused chemical decomposition. A silver/silver chloride quasi-reference electrode was used, and the potentials were calibrated against ferrocene.

Results and Discussion

The data from cyclic voltammetry and second harmonic ac voltammetry on the well-behaved compounds examined are listed in Table I. The results of using THF with various amounts of HMPA added are shown in Figure 1. In all cases there was some shift in the observed potentials on adding HMPA, but this normally leveled off after a moderate amount had been added.

The observed potentials can be shifted from the true reversible potentials by two general effects. First of all, any kinetic barrier to rapid electron transfer can require an overpotential to achieve significant reaction rates, and this leads to an anodic shift relative to the true reversible potential. Such charge-transfer problems will in general also lead to the broadening of the cyclic voltammetric wave,[18] and this can be detected by examining $E_p - E_{p/2}$, the difference in potential between the peak and half-the-peak current.[18] We have examined this for all of our cases and have displayed it in Table I. In addition, we have calibrated our systems with ferrocene, a well-behaved system[19] which does not normally

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Table I. Electrochemical Data on Organolithium Compounds

			cyclic voltammetry, V			second-harmonic ac voltammetry	
lithium derivative[a]	temp, (°C)	% vol[b] of HMPA in THF	$E_p{}^c$	$E_p - E_{p/2}{}^d$	rel $E_p - E_{p/2}{}^e$	freq, Hz	$E_{cp}{}^{c,f}$
triphenylmethyl	+25	0	−1.33	0.08	1.0		
	0	0	−1.30	0.08	1.0		
	−25	0	−1.27	0.06	1.0		
	−25	8-30 (10)	−1.13	0.06	1.0	50	−1.12 ± 0.01
	−62	8-30 (10)	−1.09	0.04	1.0		
	+25	8-30 (10)	−1.18	0.06	1.0	50	−1.15 ± 0.01
diphenylmethyl	+25	0	−1.37	0.07	0.52		
	0	0	−1.30	0.05	0.56		
	−25	0	−1.26	0.05	0.64		
	−25	4-30 (18)	−1.17	0.05	0.69		
	−62	4-30 (18)	−1.16	0.05	0.64	45	−1.16 ± 0.01
	+25	4-30 (18)	−1.21	0.05			
benzyl	+25	0	−1.45	0.09	1.0		
	0	0	−1.46	0.10	1.1		
	−25	0	−1.38	0.14	1.2		
	−25	10-30 (20)	−1.47	0.06	1.0		
	−62	10-30 (20)	−1.39	0.07	1.0	205	−1.43 ± 0.03
allyl	+25	0	−1.40	0.15	1.25		
	0	0	−1.30	0.14	1.35		
	−25	0	−1.24	0.14	1.75		
	−25	17-27 (17)	−1.62	0.13	1.45		
	−62	17-27 (17)	−1.61	0.06	1.0	230	−1.63 ± 0.04
tert-butylpropargyl	+25	2.5	−0.79 ± 0.04	0.12	1.3		
	−25	2.5	−0.54 ± 0.04	0.14	1.6		
	−62	20-28 (28)	−1.12 ± 0.05	0.16	2.0		
cyclopentadienyl	+25	0	−0.18 ± 0.03	0.21	2.1		
	−25	0	+0.03 ± 0.03	0.20	2.0		
	−62	17	−0.37	0.05	0.60		

[a] Organolithium concentrations ca. 5 mM. [b] The peak potentials are constant within the range of HMPA concentration indicated. The numbers in parentheses give the HMPA concentration at which the data in this table were measured. [c] Potentials in volts vs. SCE (see section on Data Treatment). Errors are ±0.02 V unless otherwise indicated. [d] Separation between potential at the peak and the point where the current rises to half that value. [e] $E_p - E_{p/2}$ relative to that for ferrocene under the same conditions. Ferrocene, as an internal standard, corrects for any line broadening due to uncompensated *iR* drop. [f] The potential at the crossing point of the in-phase voltammogram.

show electron-transfer problems. Thus in Table I we also compare the behavior of our organolithium compound with that of ferrocene under the same conditions.[20]

The second source of errors is cathodic shifts from fast, following reactions such as dimerization of the product radicals. As one approach to this question, we have examined the use of second-harmonic ac voltammetry.[21] Since the time scale of this technique is much faster than that of cyclic voltammetry, shifts due to fast following reactions are known to be much less with the second harmonic method. Good agreement between these techniques thus indicates that the effect is not large in either case. Alternatively, one can calculate the possible shifts from a detailed theoretical treatment of such processes. This will be addressed in a later section, after we have discussed the electrochemical behavior of the compounds examined.

Triphenylmethyllithium. The cyclic voltammogram of triphenylmethyllithium in THF at room temperature exhibited two consecutive one-electron oxidations.[8] When the system was swept over the entire potential range, both waves were poorly reversible, but reversing the potential sweep between the two waves led to a totally reversible first oxidation. The ratio of anodic to cathodic peak currents of 1.06 indicates this, as do the ΔE_p values. No complications due to adsorption arose ($i_p/v^{1/2}$ was constant) and the half-wave potential measured was independent of the scan rate after correction for residual *iR* drop. A small anodic shift occurred

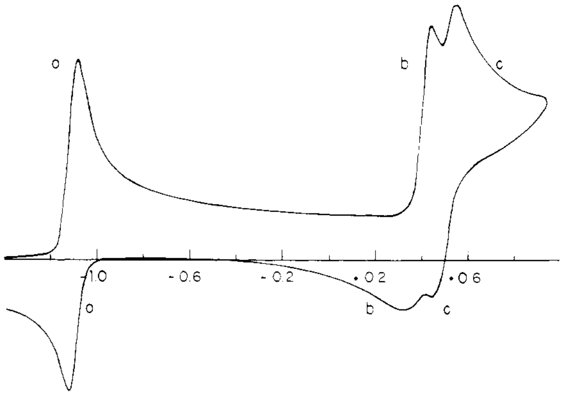

Figure 2. Cyclic voltammogram of triphenylmethyllithium and ferrocene in 10% v/v HMPA in THF at −62 °C and 200 mV/s, showing the first (a) and second (b) waves for triphenylmethyllithium and the waves (c) for ferrocene.

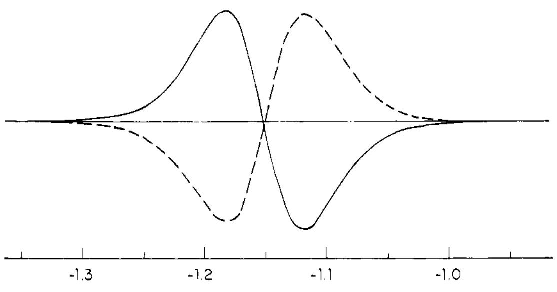

Figure 3. Second-harmonic ac voltammogram of triphenylmethyllithium in 10% v/v HMPA in THF at −30 °C with a dc sweep rate of 20 mV/s and an ac modulation with 10-mV amplitude and 50-Hz fundamental frequency. The solid line shows the in-phase response and the dotted line the quadrature response.

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(20) For experimental reasons all cyclic voltammetry waves were somewhat broadened by residual *iR* drop (see ref 43). Studies with ferrocene alone could be done with almost complete electronic *iR* compensation in our media. They showed the $E_p - E_{p/2}$ values expected for reversible waves down to −65 °C and in second-harmonic ac voltammetry up to 200 Hz. Below this temperature and at higher frequency some contribution of irreversible charge transfer to the form of the wave was observed.

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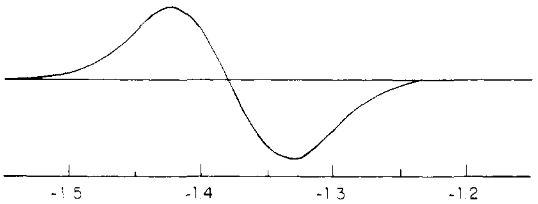

Figure 4. Second-harmonic ac voltammogram of benzyllithium in 10% v/v HMPA in THF at -35 °C with a dc sweep rate of 20 mV/s and an ac modulation with 10-mV amplitude and 230-Hz fundamental frequency. The in-phase response is shown; the quadrature response showed only one lobe.

on lowering the temperature to -25 °C, and there was also an initial anodic shift observed upon addition of HMPA to the solution. The temperature dependence of $E_{1/2}$ was unaffected by the addition of HMPA, and the oxidation was still fully reversible. Because in the mixed solvents we can perform measurements at temperatures as low as -75 °C, we were able to observe completely reversible behavior for both oxidation waves at -62 °C and lower (Figure 2).

Second-harmonic ac voltammograms confirm the reversible potential and clearly demonstrate that there is no limitation due to heterogeneous charge-transfer problems. This voltammogram (Figure 3) complies with all the standard criteria for reversibility.

Diphenylmethyllithium. In THF at room temperature the cyclic voltammogram of this case gave a single oxidation wave. No rereduction of the product radical could be detected at sweep rates up to 0.5 V/s. No electrode fouling was observed, and the voltammograms were highly reproducible in consecutive sweeps. The effects of temperature changes and addition of HMPA parallel very closely those observed with triphenylmethyllithium. Second-harmonic ac voltammetry gave good reversible behavior in THF/HMPA at -62 °C with frequencies from 45 to 160 Hz. Thus there is no problem with heterogeneous charge transfer. Furthermore, the $E_{1/2}$ value obtained from second-harmonic ac voltammetry was within 20 mV of the value calculated from cyclic voltammetry under the same conditions. This compound does not show the ideal behavior of triphenylmethyllithium, but there is no difficulty obtaining a good value for the reversible potential.

Benzyllithium. The cyclic voltammogram in THF at room temperature consisted of one irreversible wave. This was considerably broader than the previous cases, but this broadening is largely due to the uncompensated *iR* drop, and under the same sweep conditions the ferrocene wave was also broad. The peak/half-peak width for benzyllithium was only slightly greater than that for ferrocene, indicating that there is only a small effect of irreversible charge transfer. No electrode fouling could be detected in consecutive scans. Second-harmonic ac voltammetry with THF/HMPA as solvent substantiated our conclusion that the principal cause of the irreversibility of the wave was the very fast subsequent chemical reaction of benzyl radical. Between 160 and 230 Hz a kinetic window could be found in which the in-phase voltammogram approaches a reversible response. The voltammogram (Figure 4) has two lobes, but the quadrature voltammogram is not symmetrical to the in-phase wave, in contrast to the situation for triphenylmethyllithium or diphenylmethyllithium. Furthermore there is a small dependence of the crossing-point potential on the DC potential scan rate (less than 50 mV for a 10-fold increase in the scan rate). Thus some caution must be applied in assigning the crossing potential as equal to the true half-wave potential for oxidation of benzyllithium. Lowering the temperature from 25 to -25 °C gave a shift of the cyclic voltammetric wave similar to the ones observed previously in direction and magnitude. However, in contrast to the previous cases addition of HMPA to the solvent led to a cathodic shift which leveled off (Figure 1) after addition of ca. 10% v/v HMPA. A low-temperature voltammogram is shown in Figure 5.

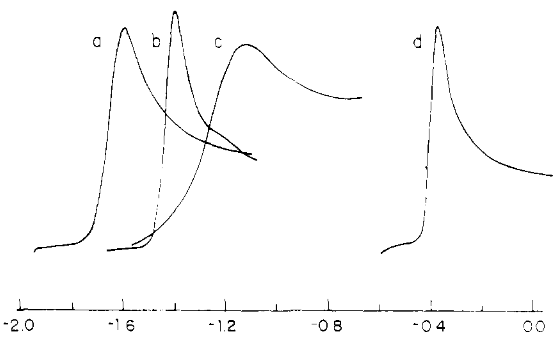

Figure 5. Cyclic voltammograms of allyl- (a), benzyl- (b), *tert*-butylpropargyl- (c), and cyclopentadienyllithium (d) at -62 °C in HMPA/THF with a sweep rate of 200 mV/s. The solvent composition is 20 (a), 30 (b), 30 (c), and 17% v/v (d).

Allyllithium. Cyclic voltammetry in THF at room temperature gave a single irreversible wave with a peak/half-peak width 25% larger than that for ferrocene under the same conditions. No adsorption effects could be detected, and consecutive scans showed no electrode fouling. Lowering the temperature to -25 °C led to an anodic shift, but the most striking effects were observed on the gradual addition of HMPA at -25 °C. From 0 to 5% v/v HMPA the initial wave became significantly broader, and above this concentration the wave separated into two distinct peaks. Then at 10% and above of HMPA a single rather sharp wave was seen (Figure 5) with a half-peak width identical with that of ferrocene. The effect leveled off at 15% HMPA with a total cathodic shift of 425 mV. At -62 °C the same curious behavior was observed, and the peak potentials with 25% HMPA were the same at -25 and -62 °C.

The observed changes clearly indicate the transformation of one state of the organolithium species into another state[22] (chemical quenching indicates that the compound is still allyllithium). The change reflects better solvation by HMPA. Interestingly, equilibration between these two states of allyllithium is apparently slow on the time scale of the electrochemical experiment. With 25% HMPA at -62 °C second-harmonic ac voltammetry gave an in-phase response between 160 and 230 Hz but the anodic lobe was far smaller than the cathodic one. As with benzyllithium, the quadrature response was not symmetrical with respect to the in-phase response, in contrast to the situation with the two earliest compounds. Consequently, the crossing point may be shifted with respect to the true half-wave potential,[21] but in fact it is within 30 mV of the formal half-wave potential calculated from the cyclic voltammograms.

***tert*-Butylpropargyllithium.** Cyclic voltammetry in THF with 1.5% HMPA at room temperature gave a single irreversible wave. This was 25% broader than the ferrocene wave under these conditions; in successive scans a slow degradation of electrode performance was observed. The peak potential showed a strong temperature dependence in this medium, shifting by 500 mV anodically on going from 25 to -62 °C. The behavior on addition of further HMPA was similar to that for allyllithium, with the separation into two peaks[22] and the eventual observation of a single wave with a very large 650-mV cathodic shift on changing from 1.5% to 30% HMPA at -62 °C. Even when additional HMPA caused no further shift the resulting new peak (Figure 5) was 1.8 times as broad as the ferrocene wave under those conditons. Thus in this case we cannot exclude the possibility of some barrier to heterogeneous charge transfer. This is the most poorly behaved case for which we feel that the data can be used to estimate a p*K*.

Cyclopentadienyllithium. Oxidation of this compound at a platinum anode is very poorly behaved and accompanied by repeated electrode fouling.[8] At a vitreous carbon electrode in THF at room temperature such fouling also occurred to some extent, although reproducible cyclic voltammograms could be taken for several consecutive scans with a freshly polished electrode. The

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[22] The most likely effect is to break up clusters in THF, producing solvated ion pairs with HMPA present. However, we cannot exclude the possibility that contact ion pairs may be present in THF and solvent-separated or -dissocated ion pairs with HMPA may be present. With this latter interpretation the presence of two distinct populations, which do not equilibrate rapidly so as to produce an average electrochemical response, is particularly remarkable.

observed wave was almost twice as broad as that for the ferrocene standard. Lowering the temperature to −25 °C shifted the peak but did not sharpen the wave, but a dramatic change was observed upon addition of HMPA at −62 °C. At HMPA concentrations larger than 12% the wave became very sharp (Figure 5), no electrode fouling was observed, and the peak was shifted cathodically. Thus there is apparently some lithium-anion association[22] in THF alone, leading to broadening of the wave and an anodic shift of the potential, which is removed when HMPA is added.

Phenyllithium, Vinyllithium, Methyllithium, and *n*-Butyllithium. With all of these compounds electrode-fouling effects were observed even at −62 °C with 30% HMPA present. In the case of *n*-butyllithium an additional problem was chemical degradation by reaction with the solvent even at −65 °C. Phenyllithium was oxidized under these conditions in a single broad cyclic voltammetric wave with a peak potential of ca. −0.340 V and $E_p - E_{p/2}$ of 180 mV. Even during the scan the shape of the wave indicated some changes in the electrode surface, and consecutive scans yielded rapidly diminishing peak currents which could be restored only by polishing the electrode. Vinyllithium behaved in a similar manner, and in 30% HMPA at −62 °C showed a peak potential of ca. −0.57 V with an $E_p - E_{p/2}$ of 160 mV.

Under these conditions methyllithium gave a broad wave with E_p of −0.72 V and $E_p - E_{p/2}$ of 140 mV. Electrode fouling was less of a problem, but solvent attack led to the increasing development of a new broad wave near −0.2 V ascribed to degradation products. *n*-Butyllithium had a peak potential of −1.41 V, with a surprisingly sharp $E_p - E_{p/2}$ of 50 mV. Some electrode fouling was observed, and in a few minutes the butyllithium wave began to disappear in favor of a new wave from solvent degradation near −0.2 V. These data are not included in Table I, since they are the result of poorly behaved electrochemistry.

Data Treatment. Since for experimental reasons it was not feasible to use the SCE directly, our potentials were measured relative to an internal ferrocene standard, which was assigned a half-wave potential of 510 mV vs. SCE. It is widely believed[19] that the half-wave potential of ferrocene is relatively insensitive to changes in medium or temperature. Thus we assume that any shift in the measured potential of ferrocene upon changing the medium or the temperature is due to changes in the potential of the silver/silver chloride reference electrode rather than to variations of the potential of ferrocene itself. This assumption might introduce some systematic errors in the absolute potentials given in Table I, particularly in the potential shift with temperature or with varying concentrations of HMPA. However, for the use of these data to calculate hydrocarbon p*K*s (vide infra) it is necessary only to compare the potentials of various compounds under a given set of identical conditions. Since the ferrocene half-wave potential proved to be highly reproducible at a fixed temperature and HMPA concentration, this comparison is probably excellent.

More difficulties are introduced by the experimentally observed irreversibility of most of the electrochemical oxidations. Triphenylmethyllithium gave classical reversible behavior both in cyclic voltammetry and in second-harmonic ac voltammetry, and $E_{1/2}$ can thus be directly obtained from the observed waves. However, for the other cases we must be concerned about errors which could be introduced because of slow heterogeneous charge transfer or because of rapid chemical reaction of the products of anodic oxidation.

We believe that irreversible charge transfer has been eliminated as a problem for all of the compounds in Table I, under at least some experimental conditions, with the exception of *tert*-butylpropargyllithium. Irreversible charge transfer normally leads to a considerable broadening of the wave, as reflected in the $E_p - E_{p/2}$ value. However, in almost all of our cases $E_p - E_{p/2}$ is comparable to or smaller than that for ferrocene under the same conditions, particularly when HMPA is added to the medium. This is true even for cyclopentadienyllithium with HMPA but not for *tert*-butylpropargyllithium. In some cases our waves are even narrower than those for ferrocene, as expected since a fast following reaction such as dimerization of the product radicals will narrow the wave.[18]

In the case of diphenylmethyl, benzyl, and allyl, we can also exclude the contribution of an appreciable charge-transfer problem, at −62 °C with HMPA present, from the fact that we obtain second-harmonic ac in-phase voltammograms with a window in the frequency scale. The higher frequency limit of such a window usually results from the onset of rate-limiting charge transfer, whereas the lower limit is due to fast coupled chemical reactions.[21] Since the higher limits are near 200 Hz in the second-harmonic experiments, heterogeneous charge transfer cannot be contributing to the rate in our cyclic voltammetry experiments, whose time scale is several orders of magnitude slower. The smooth systematic trends observed for triphenylmethyl and diphenylmethyl with changing temperature and changing solvent composition are mirrored in part for benzyl but poorly for allyl, *tert*-butylpropargyl, and cyclopentadienyl. Thus in these last three cases we cannot exclude some charge-transfer contribution even for allyl and for cyclopentadienyl in the high temperature cases without HMPA. For this reason we calculate our best esimates of the potentials from the data in THF/HMPA at either −25 or −62 °C. In all cases examined there is only a very small difference in the data at these two temperatures (cf. Table I) so we assume that the data can also be extrapolated to room temperature. Unfortunately, the chemical instability of some of the systems makes it impossible to perform the measurements directly at room temperature with HMPA present in the medium.

The magnitudes of the effects which can be contributed by rapid chemical reactions of the oxidation products are well understood and can be calculated. The most probable pathway for destruction of the oxidation products is irreversible dimerization of the radicals. The result of such dimerization with second-order rate constant k_2 has been treated theoretically by Nicholson et al.[23] and leads to eq 2. This equation is valid when ψ is greater than 10, which

$$E_{pa} - E_{1/2} = \frac{RT}{3nF}(3.12 - \ln \psi) \quad [\mathrm{mV}] \tag{2}$$

$$\psi = k_2 C_0 RT/nFv$$

$$v = \text{sweep rate} \quad [\mathrm{V/s}]$$

$$C_0 = \text{bulk concentration}$$

under our conditions (−62 °C, v = 0.2 V/s, C_0 = 5 mM) is equivalent to k_2 being greater than 2×10^3 M^{-1} s^{-1}. At −62 °C it predicts a shift of 14 mV for E_p in the anodic direction for each 10-fold increase in scan rate or 10-fold decrease in k_2 or concentration. (If the product were destroyed in a first-order reaction with the solvent, the shift at −62 °C would be 21 mV/decade.) An estimate can be made of the lower limit for the rate constant k_2 from the fact that no rereduction wave can be observed in all the cases except triphenylmethyllithium even with sweep rates as high as 10 V/s for 0.01 M benzyllithium or allyllithium. This means[24] that ψ is certainly greater than 5, and thus the rate constant k_2 for benzyl or allyl must be greater than 3×10^5 M^{-1} s^{-1} at −62 °C. Since k_2 cannot exceed ca. 10^9 M^{-1} s^{-1}, the diffusion-controlled rate limit in our viscous solvent at −62 °C, we can substitute these two limits into eq 2 and obtain a range for $E_{1/2}$ of benzyllithium or allyllithium:

$$E_{1/2} = E_p + 0.024 \text{ V } (k_2 = 3 \times 10^5 \text{ M}^{-1}\text{s}^{-1}) \text{ to } E_p + 0.074 \text{ V } (k_2 = 10^9 \text{ M}^{-1} \text{ s}^{-1})$$

This means that for allyl, for instance, we first take the E_p of −1.61 V at −62 °C in THF/HMPA and correct it to an $E_{1/2}$ of −1.54 to −1.59 V at this temperature. We then note that E_p is essentially constant on going from −62 °C (211 K) to −25 °C (248 K), with the slight anodic shift being expected because of the fact that temperature appears in the correction term of eq 2. We thus assume that there is also no significant change when this number is extrapolated to 25 °C (298 K), a 20% increase in temperature

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[23] Olmstead, M. L; Hamilton, R. G.; Nicholson, R. S. *Anal. Chem.* **1969**, *41*, 260–7.

[24] This estimate was obtained by inspection of Figures 1 and 4 in ref 23.

Table II. Reversible Potentials, Bond Dissociation Energies, and pK_a's

amino R⁻	E_p[a]	$E_{1/2}$[b]	BDE for R-H[c]	pK_a of R-H[d]
triphenylmethyl		−1.12	75[e]	31.5[f]
diphenylmethyl	−1.16	−1.09 to −1.16	76.7–78.3[g]	33.4[f]
benzyl	−1.39	−1.32 to −1.37	88[h]	44.4–45.2[g]
allyl	−1.61	−1.54 to −1.59	86.6[h]	47.1–48.0[g]
tert-butylpropargyl	−1.12	−1.05 to −1.12	94[i]	44.2–45.4[g]
cyclopentadienyl	−0.37	−0.30 to −0.37	81.2[j]	22.2–23.4[g]

[a] The peak potentials at −62 °C in THF with 30% v/v HMPA, in volts vs. SCE. [b] The derived $E_{1/2}$'s at 25 °C in the same medium, in volts vs. SCE. [c] Bond dissociation energies in kcal/mol. [d] In the THF/HMPA medium at 25 °C, to form a solvated Li^+R^- species. [e] Reference 25. [f] Reference 28. [g] Calculated from our data, as described in the text. [h] Reference 26. [i] Reference 29. [j] Reference 30.

compared with the previous 18% temperature increase which lead to little observed change. On this basis we derive the values of $E_{1/2}$ listed in Table II, which we believe can be intercompared at room temperature.

The electrochemical reduction of allyl iodide goes in a single irreversible wave[9] which is presumably a two-electron reduction process. Thus the reduction potential of the allyl radical must be anodic to the observed wave for reduction of allyl iodide. We find that allyl iodide in THF/HMPA (20% v/v at −55 °C) is reduced in a single irreversible wave with $E_p - E_{p/2}$ of 0.11 V, 2.0 times the width for ferrocene under these conditions, and E_p of −1.70 V vs. SCE. As expected, this value is cathodic of our estimate for the allyl radical reduction potential obtained from oxidation of allyllithium, but the difference is not large. Thus the oxidation potential for allyllithium cannot be much more negative than the values we list in Table II, supporting our assumption that in the oxidation there is no significant overpotential from irreversible charge-transfer problems.

Diphenylmethyl-, *tert*-butylpropargyl-, and cyclopentadienyllithium also showed no rereduction waves, but the cyclic voltammetry was not taken to high velocities so our limit for these cases is that k_2 must be 10^4 M^{-1} s^{-1} or greater. This leads, from eq 2, to a slightly larger range for $E_{1/2}$ of $E_p + 0.004$ V to $E_p + 0.074$ V.

pK_a's of the Corresponding Hydrocarbons. As we have described previously,[6] it is a straightforward calculation to combine these estimates for the reduction potential of the radicals with known bond dissociation energies for the production of the radicals from hydrocarbons. For example, the bond dissociation energy of triphenylmethane is reported[25] to be 75 kcal/mol while that for toluene is reported[26] to be 88 kcal/mol. This difference of 13 kcal/mol, if it reflects the same difference in free energies, corresponds to 9.5 pK units.[27] Similarly, the difference in $E_{1/2}$ of 200–250 mV would correspond, at room temperature, to a pK difference of 3.4–4.2 units. Thus the total difference in pK_a between triphenylmethane and toluene should be 12.9–13.7 units, and taking the known pK_a of triphenylmethane at 31.5 leads to an estimate for toluene of 44.4–45.2.

In all cases the estimates of $E_{1/2}$ obtained from cyclic voltammetry are in good agreement with the values of E_{cp}, the electrochemical crossing point from second-harmonic ac voltammetry. Since 1 pK_a unit corresponds to 59 mV at room temperature, the uncertainties in the pK value introduced by the error ranges for our experimental determinations are quite small. Of course, there are also errors in the pK_a's which may be introduced by our assumption that bond dissociation energies may be translated from the gas phase into relative free energies in solution.[27] Furthermore, there are certainly also errors in the experimentally determined bond dissociation energies themselves. Perhaps most worrisome is the value for triphenylmethane,[25] which is a rather old number and which has not been checked by modern methods.

Despite these reservations, our estimates of pK_a's seem reasonable. Thus Streitwieser[31] has estimated a pK_a for toluene of 41 by a short extrapolation of other measurements, and Bordwell[32] has estimated the value of 42 by another extrapolation involving additivity of substituent effects. Our value of 44–45 is in good agreement. Our finding that allyl anion is somewhat more basic than benzyl anion also seems sensible. The propargyl number is probably the least reliable of the set.[33] For one thing, we have used the BDE for propargyl itself[29] but measured the electrochemistry on *tert*-butylpropargyl. The *tert*-butyl perturbation may be significant. Also, the electrochemistry was poorest for this compound, suggesting some residual overpotential. This could reflect simple charge-transfer problems or more likely stabilization of the lithio compound by clustering which has not been completely broken up by HMPA. Our estimate of 22–23 for the pK_a of cyclopentadiene is higher than the value of 16 determined in water[34] but may not be unreasonable for an organic solvent.[34]

We were not able to use the bond dissociation energy of diphenylmethane in order to calculate a pK_a of the hydrocarbon since that bond dissociation energy has apparently not yet been determined experimentally. For this reason we have reversed the process and have used the known pK_a of the hydrocarbon to calculate a probable range for the bond dissociation energy. Because the electrochemistry of triphenylmethyllithium and diphenylmethyllithium is essentially identical with respect to $E_{1/2}$, the estimated difference in bond dissociation energies corresponds to the known difference in pK_a's. The fact that both of these differences are rather small presumably reflects the crowding in the triphenylmethyl species, which permits three phenyls to stabilize anions or radicals only a little better than the two phenyls do in the diphenylmethyl series.

The electrochemistry of methyllithium, *n*-butyllithium, vinyllithium, and phenyllithium gave broad waves, and we cannot use them to assign $E_{1/2}$'s or pK_a's. However, if we assume that the overpotentials involved exceed the shifts due to fast following reactions, then the $E_{1/2}$'s for the corresponding anions must be cathodic of the observed E_p's. The E_p's can then be used to calculate lower limits to the pK_a's. From the observed E_p's, the pK_a of ethylene must be higher than 46, for benzene higher than 34.2, for butane higher than 53.2, and for methane higher than 46. The ethylene value is probably not far from the correct pK_a, but certainly methane, for instance, must be much less acidic than this limit suggests. Stabilization of the methyl "anion" by organolithium clustering[14] probably accounts for much of the discrepancy.

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(25) Swarc, M. *Proc. R. Soc. London, Ser. A*, **1951**, *207*, 5.

(26) Rossi, M.; Golden, D. M. *J. Am. Chem. Soc.* **1979**, *101*, 1230–5.

(27) In a few of our cases small entropy correlations could have been made. The major extrapolation is that solvation effects will cancel, since solvation of the radical center should be minor and the rest of the solvation is present in both hydrocarbon and radical. Thus we assume that *differences* in BDE's will be the same in solution as in the gas phase.

(28) Streitwieser, Jr., A.; Murdoch, J. R.; Häfelinger, G.; Chang, C. J. *J. Am. Chem. Soc.* **1973**, *95*, 4248–61.

(29) O'Neal, H.; Benson, S. W. In "Free Radicals"; Kochi, J., Ed.; Wiley-Interscience: New York, 1973; Vol. I, pp 275–85.

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(32) Bordwell, F. G.; Algrim, D.; Vanier, N. R. *J. Org. Chem.* **1977**, *42*, 1817–9.

(33) Our finding that propargylic hydrogens are more acidic than allylic hydrogens is, however, well precedented. Cf.: Krantz, A.; Lipkowitz, G. S. *J. Am. Chem. Soc.* **1977**, *99*, 4156–9 and ref 31–36 therein.

(34) (a) Streitwieser, A.; Nebenzahl, L. L. *J. Am. Chem. Soc.* **1976**, *98*, 2188–90. (b) Breslow, R.; Washburn, W. *Ibid.* **1970**, *92*, 427. They report a pK_a of 18.2 at 35 °C in THF. This was based on an aqueous pK_a of 19.0 for *tert*-butyl alcohol, but in a solvent like THF *tert*-butyl alcohol will have a much higher[16] pK_a. Since the actual experimental finding was that cyclopentadiene has a pK_a 0.8 unit lower than that of *tert*-butyl alcohol in THF, the result is consistent with our present estimate of the pK_a.

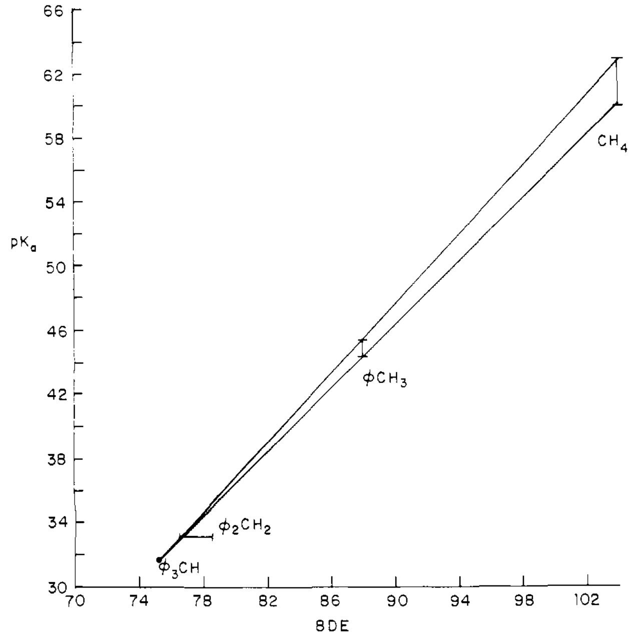

Figure 6. Bond dissociation energies (in kcal/mol) of phenylated methanes vs. pK_a's. The pK_a range for methane is by extrapolation (cf. Results and Discussion).

We have tried to estimate what the pK_a would be for methane ionizing to form the sorts of solvated ions or ion pairs which are present with benzyllithium in THF/HMPA, for instance. One approach is to extrapolate our data for phenyl-substituted methanes. Successive phenylations will stabilize the methyl anion to different extents because (a) substituent effects tend to saturate and (b) steric crowding causes phenyl twisting with loss of the full conjugation effect when the second and third phenyl are added. Thus one needs a nonlinear extrapolation. We suggest that this can be calibrated from the successive phenyl substitution effects on the bond dissociation energies of methane and phenyl-substituted methanes. That is, the substituent effects of phenyls in stabilizing methyl *anions* are larger than the effects in stabilizing methyl *radicals*, but the same trends with respect to saturation of the effect and with respect to steric crowding should be seen.

Considering only the previously known data, the BDE's change by 16 kcal/mol for the first phenyl (i.e., methane[29] vs. toluene) and 13 kcal/mol for the next two (toluene vs. triphenylmethane). From our results for the BDE of diphenylmethane, that 13 kcal/mol is 10–11 kcal/mol for the second phenyl and 2–3 kcal/mol for the third. The pK_a change on adding the second and third phenyl to toluene is 13.5 units, corresponding to 18.4 kcal/mol, a 40% larger energy relative to the BDE effect. Again this is divided into a large 15.8 kcal/mol for the second phenyl and a small 2.6 kcal/mol for the third.

This relationship is shown in Figure 6, in which we plot pK_a's vs. BDE's. We also have extrapolated the lines to a BDE of 104 kcal/mol for methane itself.[29] With our data for toluene the extrapolation gives a pK_a for methane of 60.3–62, while if toluene had[31] a pK_a of only 41 but the other data were correct, the methane pK_a would be 52.7. Thus this large extrapolation is rather sensitive to errors in the "known" points.

A second estimate for the pK_a of methane can be obtained from the value obtained by Schiffrin[35] for the reduction potential of methyl radical in aqueous solution at a mercury electrode by the use of photoelectrochemistry. Putting his value of −1.47 vs. SCE into our thermodynamic treatment gives a pK_a of 58.7 for methane. On the basis of both of these estimates, it seems likely that the pK_a of methane is 58 ± 5, with the uncertainty perhaps less than this.

The pK_a scale derived by our method seems reasonable, and the estimates for methane are consistent with our previous value[6] of 71 for the less-acidic isobutane. Thus we suggest that this electrochemical–thermodynamic method, when it is applicable, is probably the most reliable way to estimate the pK_a's of very weak acids.

Experimental Section

Materials. Benzyllithium,[36] allyllithium,[37] vinyllithium,[38] phenyllithium,[39] and cyclopentadienyllithium[40] were prepared as solids by literature procedures with the use of a Schlenck-type apparatus. The solid products were carefully washed to remove traces of *n*-butyllithium and organotin compounds, used in some of these preparations. Benzyl-, allyl-, and phenyllithium were dissolved in ether, and vinyl- and cyclopentadienyllithium were dissolved in tetrahydrofuran to give stock solutions approximately 0.5 M in organolithium compound. The stock solutions were doubly titrated for total base and residual hydroxide and contained less than 5 mol % of hydroxide. All stock solutions were stored at −30 °C or lower to prevent solvent attack. Triphenylmethyllithium, diphenylmethyllithium, and 4,4-dimethylpent-2-ynyllithium were prepared from the parent hydrocarbons by in situ deprotonation of 0.5 M solutions in tetrahydrofuran with 0.95 equiv of *n*-butyllithium at −30 °C or lower. In the case of 4,4-dimethylpent-2-yne[41] the addition of 17% of hexamethylphosphoramide (HMPA) was necessary to achieve rapid complete deprotonation with 1 equiv of *n*-butyllithium. *n*-Butyllithium in hexane and methyllithium in ether were commercially available solutions.

The approximate lifetime of *n*-butyllithium (the most reactive of the investigated compounds) in mixtures of THF and HMPA was determined by injecting 0.2 mL of a 1.5 M solution of *n*-butyllithium in hexane into 30 mL of 1:2 HMPA/THF, 0.2 M lithium perchlorate and 0.01 M dodecane as a standard at −62 °C, and after 10-min of quenching by the addition of a fivefold excess of benzaldehyde. The mixture was warmed to room temperature, diluted with saturated NH_4Cl, and extracted with ether, and the content of 1-phenylpentanol was assayed by vapor-phase chromatography relative to the dodecane peak. Under these circumstances 60% of the theoretical yield of 1-phenylpentanol was formed.

The survival of vinyllithium, allyllithium, and benzyllithium in the electrochemical system was confirmed by adding an excess of trimethylsilyl chloride to the cell at the end of the electrochemical measurements. This led to the disappearance of the oxidation waves assigned to these lithium compounds; after extraction with water and ether, vapor-phase chromatography of the organic phase showed the formation of the expected trimethylsilylethylene etc. identical with authentic samples.

Tetrahydrofuran (THF, gold label, Aldrich) was distilled twice from potassium/benzophenone over a bubble-bell column (reflux ratio 10:1) discarding the first 10% each time. Hexamethylphosphoramide (HMPA, 99+%, Aldrich) was distilled at 0.5 mm through a 1.2-m vacuum-jacketed column filled with glass helices (reflux ratio 10:1), and 30% of the distillate was discarded. It was then refluxed under vacuum over calcium hydride for 2 days and again distilled under the conditions described above. Lithium perchlorate (Alfa, anhydrous) was predried for several days at 130 °C (0.1 mm), weighted into the electrolyte storage flask, and dried for another 12 h under the same conditions. The flask was then flushed with argon, and distilled solvent was transferred onto the electrolyte with a cannula to give a 0.2 M solution.

Cell and Apparatus. Electroanalytical measurements were performed in a three-electrode cell with two compartments separated by a fine fritted-glass disk. Each compartment had an inlet stoppered with a serum cap, a connection to argon or to a vacuum manifold, and a pressure equalizer between the two compartments. The working electrode compartment had a small magnetic stirrer. The vitreous carbon-working electrode consisted of a disk with an area of 0.06 cm^2 made from a rod (VC 2500, Atomergic Chemetals) sealed vacuum tight into a glass tube, along with a nonexposed platinum wire to establish contact. The vitreous carbon electrode was polished with a micropolish alumina before each series of measurements and with some of the less well-behaved compounds between measurements as well. The counterelectrode was a platinum coil. A silver wire was coated with silver chloride by anodic

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(41) Bourguel, M. *Ann. Chim. (Paris)* **1925**, [10] *3*, 325–38. *tert*-Butylmethylacetylene was made by a slightly modified procedure from *tert*-butylacetylenyl magnesium bromide and dimethylsulfate in ether/HMPA.

oxidation in 0.1 M HCl and used as a quasi-reference electrode. It was isolated from the solution by a glass tube ending in a luggin capillary 0.5 mm from the surface of the working electrode. Before use the cell was cleaned with chromerge, bicarbonate solution, deionized water, and pure methanol and dried in the oven. It was assembled hot and then evacuated at a vacuum line for 2 h and flushed with argon.

Cyclic voltammograms were recorded with a PAR 173/176 Potentiostat driven by a PAR 175 Universal Programmer. Voltammograms were recorded with a normal X-Y recorder up to a sweep rate of 200 mV/s and beyond that speed on a storage oscilloscope. The temperature of the cell was controlled with a conventional low-temperature bath within ±2 °C. Second-harmonic ac voltammograms were measured with a PAR 174A polarographic analyzer with PAR 174/50 ac interface, a Hewlett-Packard 3300 A function generator, and a PAR 122 lock-in amplifier. The applied modulation amplitude was 10-mV peak to peak, the dc sweep rate was 20 mV/s unless otherwise noted. The 0 °C phase was measured at the output of the voltage follower connected to the reference electrode. Very little contribution of capacitance current was detectable, the maximum of the current being almost exactly at a phase angle of −45° from the applied potential in the reversible cases. Both in-phase and quadrature voltammograms were recorded for all sets of conditions.

Typically the residual current of THF and 0.2 M $LiClO_4$ at 200 mV/s and room temperature was ca. 5 μA. The anodic and cathodic limits of the electrochemical range were +1.2 and −3.1 V vs. SCE before the current exceeds 20 μA. Considerable electronic *iR* drop correction was necessary in pure THF, especially at lower temperatures.[20] The lowest useful temperature was −30 °C, since in THF below that temperature electrolyte slowly crystallized. Addition of HMPA extended the useful temperature range dramatically, since THF with 4.3% HMPA and 0.2 M $LiClO_4$ stayed homogeneous at −78 °C whereas THF with 30% HMPA, 0.2 M $LiClO_4$, separated crystalline HMPA at temperatures below −65 °C. With HMPA present the cathodic limit was −2.5 V[42] while the anodic limit was +1.0 V. Even small amounts of HMPA strongly increased the conductivity of the solution (5000-Ω resistance in pure THF dropped to 300 Ω with 20% HMPA at room temperature and 550 Ω at −72 °C with our normal 0.2 M $LiClO_4$).

General Procedure for Electroanalytical Measurements of Benzyllithium, Allyllithium, *tert*-Butylpropargyllithium, Diphenylmethyllithium, Cyclopentadienyllithium, and Triphenylmethyllithium. Both compartments of the cell were filled with THF, 0.2 M in $LiClO_4$ with a gastight syringe, and the background was checked at room temperature. Ferrocene was weighed in a small tube, dissolved under argon in 1–2 mL of electrolyte solution, and transferred out of the anodic compartment with a cannula, and the resulting ferrocene solution was then transferred back through the cannula to give a 1.5 mM solution in the cell. The cyclic voltammogram of ferrocene was taken at room temperature. The cell was then cooled to −25 °C, and enough organolithium stock solution (60–100 μL) was added with a gastight syringe to give a ca. 5 mM solution in the anodic compartment. The earliest part of this solution, typically 35–50 μmol, was destroyed by residual moisture, but no change in the electrochemical background was detectable from this. Monitoring by cyclic voltammetry was used to establish the excess amount of organolithium compound required to produce a clear signal, which in the case of triphenylmethyllithium, diphenylmethyllithium, cyclopentadienyllithium, and benzyllithium could also be followed from the appearance of a red or yellow color in the cell.

Cyclic voltammograms were recorded by switching the cell in at potentials on the cathodic side of the wave (normally at −2.0 V), adjusting the *iR* drop compensation,[43] and sweeping to a potential anodic of the ferrocene oxidation wave and back. Voltammograms at 200, 100, 50, and 20 mV/s and again at 200 mV/s were recorded, the last sweep being a control for electrode fouling during the slow sweeps. For the best behaved compounds reproducible results were obtained and the electrode did not need to be repolished. Titrations with HMPA were done by adding small aliquots (400 mL) of HMPA, 0.2 M in $LiClO_4$, to the cell and following the change of the cyclic voltammograms. Studies of the sweep rate on the wave were done at several points during the titration in order to safeguard against artifacts due to electrode fouling. In all cases in which HMPA addition was studied, the waves became steeper and electrode fouling was much less pronounced on addition of ca. 20% v/v of HMPA. Because of some residual water and oxygen in the HMPA added, we also occassionally had to add small additional amounts of organolithium solution to the cell during these studies.

n-Butyllithium, methyllithium, vinyllithium, and phenyllithium were investigated in THF, 30% in HMPA with 0.2 N $LiClO_4$ at −62 °C only, and no temperature studies were done. Rapid electrode fouling was observed in these cases, and reproducible results were obtained only by repolishing the electrode before each sweep.

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(42) At this potential, the formation of solvated electrons begins. Cf.: Kanzaki, Y.; Aoyagui, S. *J. Electroanal. Chem.* **1972**, *36*, 297–310.

(43) Full electronic *iR* drop compensation was very difficult to obtain in these highly resistive solutions. If full feedback was used, the summing amplifier drifted into large amplitude oscillations during the sweep, which caused immediate fouling of the electrode. Voltammograms of compounds which are oxidized at potentials cathodic to −1.2 V were therefore taken with deliberately incomplete *iR* compensation.