ml of dioxane. Sodium (1.2 g-atoms) was added and the tube sealed. The tube and contents were heated to 130° in an oil bath for 12 hr. At the end of this period the tube was cooled and opened, and remaining concentrations of ketone were determined against an internal standard using the Carbowax 1500 column at 125° and 15 psi of helium. Several experiments at different relative concentrations of sodium to ketones indicated that the results were reproducible. Relative reactivities were calculated as before.

Acknowledgment. The senior author thanks Professor M. S. Newman for the gift of *cis*- and *trans*-2-phenylcyclopropyl phenyl ketone and for use of laboratory facilities through the tenure of a visiting professorship at Ohio State University, 1965. The authors also thank Professor Don C. De Jongh for obtaining the mass spectra reported. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

Nuclear Magnetic Resonance Investigation of α-C^{13}-Phenylmethyllithiums

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Contribution from the Dow Chemical Company, Eastern Research Laboratory, Wayland, Massachusetts. *Received October 8, 1965*

Abstract: The α-C^{13} nuclear magnetic resonance spectra of triphenylmethyllithium, diphenylmethyllithium, and benzyllithium indicate these species are substantially sp^2 hybridized in tetrahydrofuran solution. The chemical shift of the α-H of diphenylmethyllithium is downfield from that of diphenylmethane, whereas α-H of benzyllithium is upfield from toluene. The Li^7 resonances of these arylmethyllithiums are upfield from inorganic lithium, in contrast to those of alkyllithium compounds.

The long wavelength electronic absorption spectra[1] of the odd alternate "carbanions" triphenylmethyllithium, diphenylmethyllithium, and benzyllithium and the proton magnetic resonance spectra of these[2] and similar arylmethyllithiums[3] are indicative of extensive delocalization of the carbon–lithium bond electrons throughout the π system. Although for maximum overlap, it is supposed that the central carbon atom should be coplanar and sp^2 hybridized, the extent of sp^2 hybridization required for substantial electron delocalization is not known. Recently it was reported that in N-phenyl-substituted cyclic imines, which are isoelectronic with organolithium compounds, π–sp^3 conjugation is as effective as π–sp^2 conjugation.[4] Studies of rigid amines has also shown that "resonance is present to a remarkable degree even when N is pyrimidal," again illustrating the effectiveness of π–sp^3 conjugation.[5] The nuclear magnetic resonance of α-C^{13}-triphenylmethyl cation, in the highly polar sulfuric acid, has been interpreted as indicative of sp^2 hybridization of the central carbon atom.[6] Nevertheless sp^2 hybridization of organolithium compounds in a low dielectric medium, *e.g.*, tetrahydrofuran (THF), might be opposed by anion–cation coordination.

We wish to report evidence that the α-carbon atoms of triphenylmethyllithium, diphenylmethyllithium, and benzyllithium are substantially sp^2 hybridized, indicating that the electron pair is in an orbital having predominantly p character. The orbital occupied by the electron pair in benzyllithium may, however, have more s character than in the others. This conclusion is based on the α-C^{13} nuclear magnetic resonance spectra of these arylmethyllithium compounds in which the α-carbon atom is enriched with ~58% C^{13}. Also, as a result of C^{13}–H splittings in the proton spectra, it is possible to locate the α hydrogens on benzyllithium and diphenylmethyllithium which were not previously detected.

Experimental Section

The nuclear magnetic resonance spectra were observed on 0.9–1.2 *M* 100% THF solutions of the respective organolithium compound in sealed 0.25-in. o.d. thin wall tubes at ambient probe temperature. A modification of the high-resolution nmr spectrometer of Baker and Burd[7] was used for recording the spectra.

Benzyllithium was prepared from 2,2′-di-α-C^{13}-dibenzylmercury (obtained from Merck Sharp and Dohme Ltd. with ~58% C^{13} labeling) by reaction with lithium in THF.[1] After 3 hr of reaction at room temperature, a clear benzyllithium solution was obtained by centrifuging. In this and in the following preparations ultraviolet and visible spectral readings were used to determine complete reaction.

Diphenylmethyllithium was prepared from α-C^{13}-diphenylmethylchloride (obtained from Merck Sharp and Dohme Ltd. with ~58% C^{13}) by reaction with lithium in THF[1] at room temperature.

Triphenylmethyllithium was prepared from α-C^{13}-triphenylmethane by reaction with *n*-butyllithium in ~85:15 hexane–THF solution at room temperature. The precipitated triphenylmethyllithium was washed twice with hexane. The solid triphenylmethyllithium was pumped to dryness under high vacuum and made up to volume with THF. To prepare α-C^{13}-triphenylmethane 1.2 g of triphenyl-C^{13}-methanol (58% C^{13}, from Merck Sharp and Dohme Ltd.) was refluxed in 30 ml of 98–100% formic acid for 2 hr. The yellow solution (only partially dissolved when cold) first turned highly colored, then colorless on refluxing. On cooling, colorless

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

(2) V. R. Sandel and H. H. Freedman, *ibid.*, 85, 2328 (1963).

(3) R. Waack and M. A. Doran, *ibid.*, 85, 4042 (1963).

(4) A. T. Bottini and C. P. Nash, *ibid.*, 84, 734 (1962).

(5) "Progress in Stereochemistry," W. Klyne and P.B.D. de la Mare, Ed., Vol. 2, 1957, 122.

(6) G. A. Olah, E. B. Baker, and M. B. Comisarow, *J. Am. Chem. Soc.*, 86, 1265 (1964).

(7) E. B. Baker and L. W. Burd, *Rev. Sci. Instr.*, 28, 313 (1957); 34, 238 (1963).

Table I. C^{13} and Li^7 Nuclear Magnetic Resonance of Phenylmethyllithium Compounds

Compd	Solvent	$\delta_{C^{13}}$[a]	$J_{C^{13}-H}$, cps	δ_{Li^7}[b]	$\rho_{\alpha\text{-}C}$[c]
$(C_6H_5)_3CLi$	THF	+102 (singlet)	...	+1.07 (sharp)	0.32 (0.13)
$(C_6H_5)_3CH$	$CDCl_3$	+132[d]	107	...	...
$(C_6H_5)_2CHLi$	THF	+114 (doublet)	142	+1.16 (broad)	0.40 (0.08)
$(C_6H_5)_2CH_2$	$CDCl_3$	+157	126	...	...
$C_6H_5CH_2Li$	THF	+163 (triplet)	133	+0.12 (broad)	0.57 (0.38)
$C_6H_5CH_3$	Neat	+172[e]	126 (THF)	...	...

[a] In ppm relative to CS_2. [b] Relative to aqueous $LiNO_3$. [c] Hückel charge densities for anion calculated by standard LCAO MO methods. These values are given only to indicate relative magnitudes. The distribution of charge in these molecules no doubt differs considerably from that calculated according to Hückel theory owing to the influence of the negative charge on the effective electronegativity of the carbon cores and to anion–cation interaction. Values in parentheses are the sum of electron densities at the ring protons, as determined by the nmr method of ref 2, subtracted from unity. Charge densities calculated by a self-consistent molecular orbital treatment are reported by A. Brickstock and J. A. Pople, *Trans. Faraday Soc.*, **50**, 901 (1954). [d] It is interesting to compare these $\delta_{C^{13}}$ with the values calculated using the bond parameters of G. B. Savitsky and K. Namikawa, *J. Phys. Chem.*, **68**, 1956 (1964). The calculated values are 144 ($(C_6H_5)_3CH$), 160 ($(C_6H_5)_2CH_2$), and 176 ($C_6H_5CH_3$), and although uniformly high, are in reasonable agreement with the measured values. [e] P. C. Lauterbar, *Ann. N. Y. Acad. Sci.*, **70**, 841 (1958).

plates crystallized and were collected, washed with cold water, and dried. A second crop was obtained from the mother liquor. After recrystallization from alcohol the melting point was 93–94°, yield 90%. The sample showed no hydroxyl band in the infrared, and was identified as pure triphenylmethane by infrared, nmr, and glpc.

Results

The C^{13} chemical shifts, C^{13}–H coupling constants for the organolithium compounds and their precursors, and lithium resonances for the organolithium species are given in Table I. The proton chemical shifts of the α protons of diphenylmethyllithium and benzyllithium are compared with their neutral counterparts in Table II. Example spectra are shown in Figures 1–3.

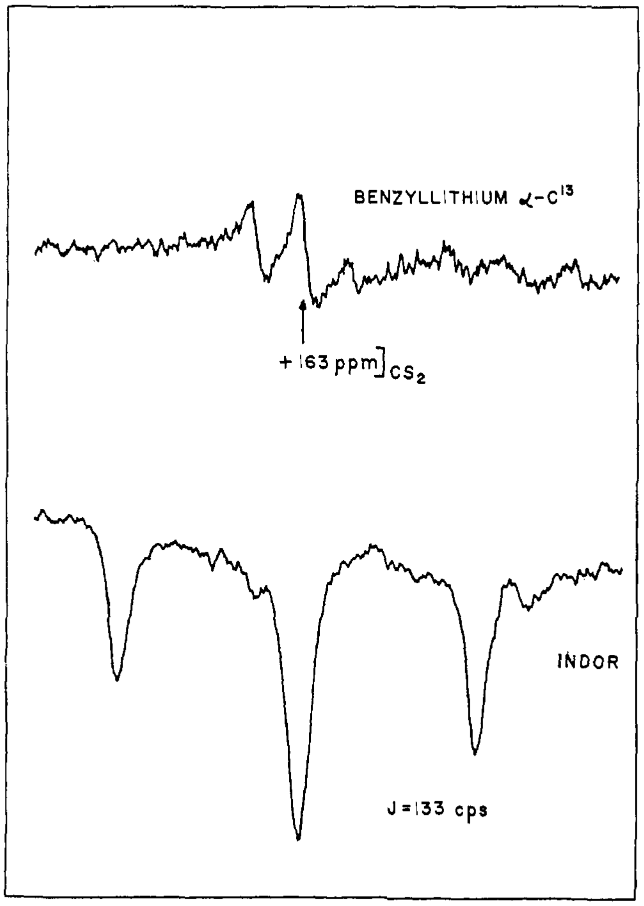

Figure 1. C^{13} nuclear magnetic resonance spectrum of α-C^{13}-benzyllithium. INDOR = internuclear double resonance (E. B. Baker, *J. Chem. Phys.*, **37**, 911 (1962)).

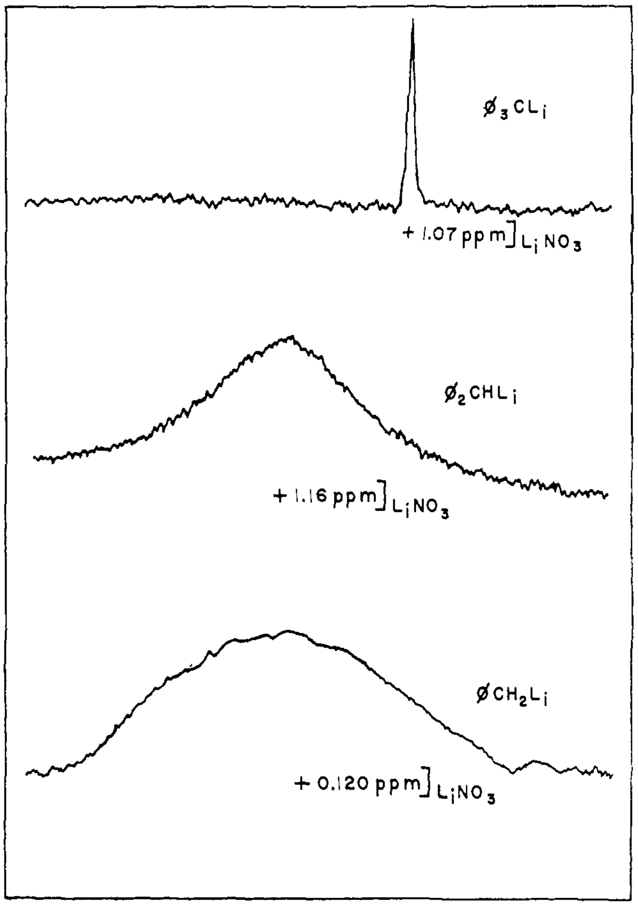

Figure 2. Li^7 nuclear magnetic resonance spectra of arylmethyllithium compounds.

Discussion

The α-C^{13} chemical shift found for each organolithium species is *downfield* from that of the sp^3 hybridized precursor. This is in contrast to the relationship demonstrated by Spiesecke and Schneider[8] that in the

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[8] H. Spiesecke and W. G. Schneider, *Tetrahedron Letters*, **14**, 468 (1961).

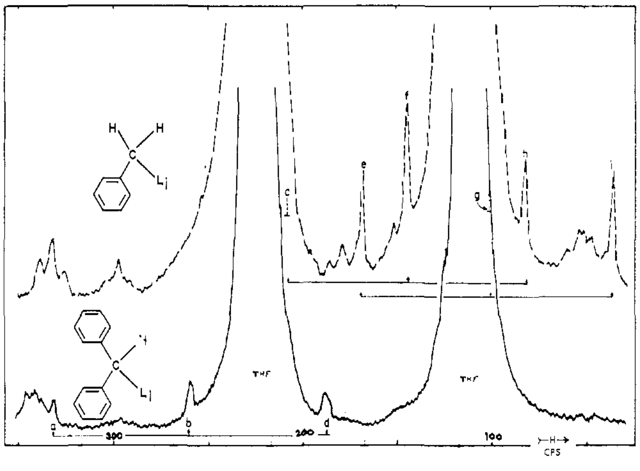

Figure 3. Proton magnetic resonance spectra of the α-H's in α-C^{13}-enriched diphenylmethyllithium and benzyllithium: a, b, and d designate the positions of the proton resonances for $C^{13}HLi$, $C^{12}HLi$, and $C^{13}HLi$ of $(C_6H_5)_2CHLi$; c, f, and h designate the $C^{13}H_3$, $C^{12}H_3$, and $C^{13}H_3$ resonances of toluene; e, g, and i designate the $C^{13}H_2Li$, $C^{12}H_2Li$, and $C^{13}H_2Li$ resonances of benzyllithium.

absence of rehybridization the C^{13} chemical shift in aromatic molecules is proportional to local charge density. For example, cyclopentadienyllithium is shifted upfield 30 ppm from cyclopentadiene.[8] Thus, on the basis of local charge density, the α-C^{13} chemical shift of the arylmethyllithium compounds would be expected to be *upfield* from that of the neutral counterparts.

Table II. α-Proton Resonance of Phenylmethyllithium Compounds[a] (ppm from TMS)

Compd	$\delta_{\alpha-H}$	Hydrocarbon in THF
$(C_6H_5)_2CHLi$	4.22[b]	3.89
$C_6H_5CH_2Li$	1.62	2.32

[a] It is possible to locate the α-H resonances with certainty because the compounds were ~58% C^{13} enriched. Thus, the spectra contain singlet resonances for α-$C^{12}H$ together with doublets arising *via* C^{13}–H splitting and having coupling constants identical with those obtained from the C^{13} spectra. [b] Using concentrated solutions of $(C_6H_5)_2CHLi$ (30–40%) in THF, Sandel has previously observed α-H as a sharp singlet at 4.08 ppm.

The literature[9] shows that the chemical shift of sp^3-hybridized C^{13} is typically in the range 160–170 ppm relative to CS_2, although both higher and lower values are known. On the other hand sp^2 C^{13} generally has chemical shift values of 60–70 ppm. Rehybridization from sp^3 to sp^2 would therefore be expected to result in a downfield shift of the C^{13} resonances.

Finding the arylmethyllithium α-C^{13} resonances downfield from their uncharged counterparts is direct evidence for sp^2 hybridization of the α-C atoms. Opposing the downfield shift arising *via* $sp^3 \rightarrow sp^2$ rehybridization of the "carbanions" will be an upfield shift in proportion to the negative charge on the α-C atoms. In agreement, the $\delta_{C^{13}}$ values of $(C_6H_5)_3CLi$ and $(C_6H_5)_2CHLi$, for which the predicted α-C charge densities are appreciably smaller than for $C_6H_5CH_2Li$, show a larger downfield shift from that of their neutral counterpart than does $C_6H_5CH_2Li$. Hückel and experimental[2] charge densities for the α-C of each "carbanion" are given in Table I.

The C^{13}–H spin–spin coupling constants ($J_{C^{13}-H}$) of these organolithium compounds are somewhat smaller than the 160–200 cps normally found for sp^2 carbon but are larger than normally found for sp^3 carbon. The few C^{13}–H coupling constants reported for ions suggest that $J_{C^{13}-H}$ is decreased by negative charge. For example the C^{13}–H couplings of MeMgBr[10] and MeLi,[11] which are presumably predominantly sp^3 hybridized, are 108 and 98 cps. $J_{C^{13}-H}$ values for the sp^2 hybridized anions $C_5H_5^-$, $C_8H_8^-$, and $C_9H_9^-$ are 157,[8] 145,[8] and 137[12] cps, respectively, all somewhat low for sp^2 C^{13}. Thus the α-C^{13}–H couplings found for $(C_6H_5)_2CHLi$ and $C_6H_5CH_2Li$ are in agreement with primarily sp^2 hybridization but with possible decreasing s character in the order given.

A nearly planar structure for diphenylmethyllithium is also suggested by the proton chemical shift of the α hydrogen of this species. In spite of being shielded by a partial negative charge, the α-proton resonance is downfield from those of neutral diphenylmethane. The probable explanation is that the α proton of the "carbanion" is being deshielded by ring currents induced in the π system, which now contains the α-carbon atom. An analogous relation was reported for H-9 of fluoroenyllithium and fluorene.[13] In contrast, the α protons of benzyllithium are upfield from toluene. They are presumably less subject to ring currents in addition to being adjacent to a larger charge density.

Li splitting of α-C–H in ethyllithium has been observed.[14] However, because the resonance of benzyllithium α proton is as sharp as that of toluene there is no indication of Li C–H splitting in this species.

The Li^7 resonances of alkyllithium compounds are typically found downfield 1–1.5 ppm from aqueous inorganic lithium salts.[15,16] In contrast, the lithium resonances of triphenylmethyllithium and diphenylmethyllithium are substantially upfield from inorganic lithium. Li^7 resonance for benzyllithium is only slightly upfield from that of the inorganic lithium salts. Li^7 resonance reported for lithium aluminum hydride in ether is also upfield (at 0.78 ppm from aqueous LiBr) and was suggested to be a consequence of $LiAlH_4$ being present as ion pairs.[11] Recently the lithium resonance of fluorenyllithium–THF complex was reported to be even more upfield from inorganic lithium (*i.e.*, 3.0 ppm), and was shown to be a consequence of the lithium being situated above the plane of the fluorenyl anion so as to be subject to the diamagnetic portion of the induced ring current.[13] These lithium resonances could, therefore, be indicative that $(C_6H_5)_3CLi$ and $(C_6H_5)_2CHLi$ exist as essentially planar ion pairs in which the lithium is located so as to be partially subject to the diamagnetic portion of the induced ring current, *i.e.*, somewhat

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(9) P. C. Lauterbur, "Determination of Organic Structures by Physical Methods," F. C. Nachod and W. D. Phillips, Ed., Academic Press Inc., New York, N. Y., 1962, pp 489, 490.

(10) G. Fraenkel, D. G. Adams, and J. Williams, *Tetrahedron Letters*, No. 12, 767 (1963).

(11) T. L. Brown, R. L. Gerteis, D. A. Bafus, and J. A. Ladd, *J. Am. Chem. Soc.*, **86**, 2135 (1964).

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(13) J. A. Dixon, P. A. Gwinner, and D. C. Lini, *ibid.*, **87**, 1379 (1965).

(14) T. L. Brown and J. A. Ladd, *J. Organometal. Chem.* (Amsterdam), **2**, 373 (1964).

(15) T. L. Brown, D. W. Dickerhoof, and D. A. Bafus, *J. Am. Chem. Soc.*, **84**, 1371 (1962).

(16) R. Waack, M. A. Doran, and E. B. Baker, unreported data.

above the plane of the conjugated system, and that the α-C atom is the central part of the π system. The lithium resonance of benzyllithium, being only slightly upfield from inorganic lithium, might then follow if the C–Li interaction is presumed to be stronger[17] and the average lithium position (as indicated by Hückel charge density) is near the perimeter of the aromatic moiety.

It is noteworthy that the lithium resonance of triphenylmethyllithium is sharp like that of inorganic lithium and ethyllithium.[15] On the other hand the lithium resonances of diphenylmethyllithium and benzyllithium are extremely broad. A broad resonance line could arise through quadrupole broadening which requires the Li to be in an unsymmetrical electric field gradient,[9] or *via* a slow lithium exchange process.[14] A sharp resonance line can be indicative of a spherically symmetrical environment[15] or a more rapid lithium exchange. A study of these and other lithium resonances is in progress.

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(17) R. Waack and M. A. Doran, *J. Phys. Chem.*, **69**, 148 (1963), and subsequent paper: R. Waack and M. A. Doran, *J. Am. Chem. Soc.*, in press.

Carbanions. VIII. Products and Mechanisms of Reaction of Allyl- and Cyclopropyltrimethylammonium Halides and of Ally Chloride, Alcohol, and *p*-Tolyl Sulfide with Sodium in Liquid Ammonia[1]

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Abstract: Allyltrimethylammonium chloride and cyclopropyltrimethylammonium iodide are readily cleaved by sodium in liquid ammonia to hydrocarbons and tertiary amines. Whereas the relative rate of cleavage of the cyclopropyl group *vs.* the methyl group in cyclopropyltrimethylammonium iodide was variable with the mode of mixing of the reactants and the concentration of sodium employed, the relative rate of cleavage of the allyl group *vs.* the methyl group in allyltrimethylammonium chloride was invariable under similar conditions. These results indicate that allyl and methyl groups cleave from quaternary nitrogen by two-electron addition as carbanions while cyclopropyl groups cleave by one-electron addition as free radicals. Allyl chloride, allyltrimethylammonium chloride, and allyl *p*-tolyl sulfide react with sodium in liquid ammonia to produce, besides propylene, biallyl and a mixture of isomeric hexenes. With allyl alcohol propylene, but no biallyl or hexenes, is formed. If ammonium chloride is present during these cleavages, the yield of biallyl relative to propylene is greatly reduced and formation of hexenes is prevented. Hexenes appear to be produced by isomerization of biallyl by strong bases to conjugated dienes which in turn are reduced by sodium to hexenes. Reductive cleavage of the corresponding allyl-1-C^{14} compounds and of allyl-1,3-C^{14}-trimethylammonium chloride in presence of excess of an acid such as ammonium chloride gave propylene having 6.4 ± 1.5% greater radioactivity at C-1 than at C-3. These results are most simply interpreted on the basis of formation of a symmetrically solvated, kinetically free allyl anion. The distribution of carbon-14 in biallyl formed from reaction of allyl-1-C^{14} chloride with sodium in liquid ammonia is in agreement with formation of biallyl primarily through attack of allyl anion upon allyl chloride by the normal mechanism of bimolecular nucleophilic substitution (S_N2).

In previous papers in this series[2] it was shown that quaternary ammonium halides of the type $R_n(CH_3)_{4-n}NX$ are rapidly cleaved by sodium in liquid ammonia at −33° to give hydrocarbons, RH and CH_4, and tertiary amines; in an accompanying reaction with sodamide, alkene and tertiary amine also are formed. The ratio of hydrocarbon (RH) to methane, after statistical correction for unequal numbers of groups, provides a convenient measure of the relative rates of cleavage of different groups from quaternary nitrogen. To account for the observed relative rates it was proposed that methyl and higher primary alkyl groups cleave from nitrogen as carbanions, by consecutive or simultaneous two-electron addition (eq 1), while secondary and tertiary alkyl groups predominantly cleave as free radicals, by one-electron addition (eq 2).

$$\mathrm{RZ} + 2e^- \longrightarrow \mathrm{R}:^- + :\mathrm{Z}^- \tag{1}$$

$$\mathrm{RZ} + e^- \longrightarrow \mathrm{R}\cdot + :\mathrm{Z}^- \tag{2}$$

The radicals then are reduced readily to carbanions and the latter, upon protonation by the solvent (or added acids), yield the observed hydrocarbons.

Although the contrary has sometimes been implied, it is not clear, *a priori*, that reductive cleavage of alcohols, ethers, sulfides, halides, quaternary ammonium salts, or like compounds (RZ) bearing identical alkyl or aryl groups (R) must proceed by similar mechanisms. In particular, cleavage by one-electron addi-

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(1) Abstracted in part from the following theses at the Georgia Institute of Technology: S. Chandra, Ph.D. Thesis, March 1961; C. E. Collum, M.S. Thesis, Sept 1964. These theses should be consulted for more complete experimental details.

(2) E. Grovenstein, Jr., and R. W. Stevenson, *J. Am. Chem. Soc.*, **81**, 4850 (1959); E. Grovenstein, Jr., and L. C. Rogers, *ibid.*, **86**, 854 (1964).