ganometallic compound. Since trimethyllead halides and dimethyllead dihalides have been shown to be monomeric in solution[51] we assume that most of the organometallic compounds studied are monomeric also in the benzene solutions used. A more serious consideration is the possibility that the organometallic compound forms a complex or addition product with the nitrone. This could either tie up an appreciable frac-
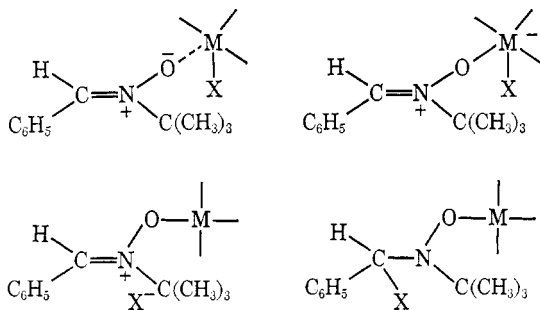
(51) R. J. H. Clark, A. G. Davies, and R. J. Puddephatt, *J. Am. Chem. Soc.*, **90**, 6923 (1968).

tion of the substrate and/or the nitrone or in fact be the precursor to the spin adduct. The interaction could range from a weak attraction as in a complex to an actual bond formation as in an addition product of salt-like structure.

Perhaps the latter occurred in the reaction between phenyltin trichloride where a precipitate formed upon mixing and no spin adduct was detected in the photolysis. If complexes such as I photolyzed more readily than the uncomplexed molecules, trapping of the produced radical would be more efficient since it could take place as a cage reaction. The somewhat surprising successful trapping of acetoxy radicals in the thermal decomposition of lead tetraacetate, and in the photolysis of trimethyl- and triethyllead acetate and mercuric acetate might be rationalized in this way. However since the acetoxy spin adduct has been obtained from a number of other sources it appears that acetoxy radical can be trapped by PBN. Further investigations into this question are in progress.

Organometallic Photochemistry. I. The Photolysis of Ethyllithium

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Abstract: The photolysis of ethyllithium with mercury resonance radiation apparently proceeds by two competing photolytic mechanisms: a lithium hydride elimination reaction which yields ethylene, and a homolytic process which yields lithium metal, ethane, and ethylene. The absence of butane and deuterated ethane (when the photolysis is carried out in C_6D_6 or C_6D_{12}) indicates that the homolytic process occurs *via* an intraaggregate disproportionation mechanism. Photolysis in the solid state yields ethane, ethylene, and butane as well as a polymeric material. Solution photolysis in the presence of a mercury pool yields only ethane (and no LiH).

The thermolysis of alkyllithium compounds has been the subject of several investigations[1-7] and is generally conceded to proceed *via* a concerted β elimination of lithium hydride, unless no β-hydrogens are available.[7] The possibility of radical participation has been rejected by most workers,[2,3] except possibly in the thermolysis of potassium and sodium alkyls.[8] The *photolysis* of alkyllithium compounds has not been reported, and one purpose of the work reported here was to compare the mechanism of photolytic decomposition with that of the

corresponding thermal process. van Tamelen and co-workers[9] have reported that phenyllithium photolyzes by an interesting intradimer process which yields principally biphenyl. A further purpose of this work was to examine the generality of this mechanism among aliphatic lithium compounds.

Absorption Spectrum of Ethyllithium. Notwithstanding a report to the contrary,[10,11] the ultraviolet spectrum

(1) K. Ziegler and H. G. Gellert, *Ann. Chem.*, **567**, 179 (1950).
(2) D. Bryce-Smith, *J. Chem. Soc.*, 1712 (1955).
(3) R. H. Finnegan and H. W. Kutta, *J. Org. Chem.*, **30**, 4139 (1965).
(4) W. H. Glaze, J. Lin, and E. G. Felton, *ibid.*, **30**, 1258 (1965); **31**, 2643 (1966).
(5) W. H. Glaze and G. M. Adams, *J. Amer. Chem. Soc.*, **88**, 4653 (1966).
(6) R. L. Eppley and J. A. Dixon, *J. Organometal. Chem.*, **11**, 174 (1968).
(7) W. H. Glaze, T. L. Brewer, R. Hatch, and J. Nathan, "Decomposition of Organometallic Compounds to Refractory Ceramics, Metals, and Metal Alloys," K. S. Mazdiyasni, Ed., University of Dayton Press, Dayton, Ohio, 1968, pp 187–194.
(8) A. A. Morton and E. J. Lanpher, *J. Org. Chem.*, **20**, 839 (1955); **21**, 93 (1956).

(9) E. E. van Tamelen, J. I. Brauman, and L. E. Ellis, *J. Amer. Chem. Soc.*, **87**, 4964 (1965).
(10) T. L. Brown, *Advan. Organometal. Chem.*, 365 (1965).
(11) A referee has suggested that the absorption shown in Figure 1 is due to an allyllithium compound formed by α metalation of olefin impurities in the solvent, and that alkyllithiums show only end-type absorption.[12] In view of the high intensity of the absorption shown in Figure 1, however, the allyllithium so formed must have an extinction coefficient of a remarkable magnitude; we estimate *ca.* 10^5 l./(mol cm). Moreover, we have observed no time dependency of the spectrum which would parallel the rather slow metalation process referred to above. Finally, Professor Oliver indicates in a private communication that he has found the same extinction coefficient for alkyllithium as we report in this work, a most fortuitous circumstance if one assumes that a metalated product is responsible for the absorption. (Note also the Beers law dependence of the absorption of butyllithium in benzene.[13])
(12) R. Waack and M. A. Doran, *J. Amer. Chem. Soc.*, **85**, 1651 (1963).

Table I. Summary of Photolysis Products of Ethyllithium[a]

Run no.	Solvent	Photolysis time, hr	RLi reacted, mmol	Gaseous hydrocarbon products				LiH, mmol	Liquid products,[b] mmol
				Total, mmol	% C_2H_6	% C_2H_4	% C_4H_{10}		
1	Isooctane	7.0	1.19	1.00	29	71	0	0.25	Trace
2	n-Decane	7.0	1.65	1.33	31	69	0	d	0.2
3	n-Decane[c]	10.0	d	d	55	45	0	d	0.2
4	Benzene	7.0	d	d	42	58	0	d	Trace
5	Isooctane[e]	4.0	3.40	2.40	100	0	0	Trace	0.7
6	Benzene[e]	5.0	d	d	86	14	0	d	d
7	None (solid phase)	7.0	d	7.0	51	18	31	0.8	(Polymer)

[a] Data refer to an average of at least three runs in each case. Relative yields of hydrocarbon products are ±2%. [b] Liquid products refer to C_{10} and C_{12} branched-chain hydrocarbons presumably due to ethyl radical coupling with decane and isooctane solvents, respectively. [c] Solvents used in these early runs contained impurities which caused absorbance at 253.7 mμ in excess of 0.3. [d] No mass balance attempted for these runs. [e] Mercury pool present.

of ethyllithium in isooctane (Figure 1) consists of a broad absorption beginning around 300 mμ with a maximum near 210 mμ. A similar spectrum for n-butyllithium was reported by Oliver, et al.[14] The extinction coefficient of ethyllithium at the maximum is 2.0 × 10³ l./(mol cm), and 3.8 × 10² l./ (mol cm) at 253.7 mμ. This absorption is predicted by a simple MO treatment of the tetramer by Weiss and Lucken,[15] although more elaborate SCF calculations[16] predict the transition to occur at 100 mμ. The band reportedly broadens in but-3-enyllithium[14] or upon the addition of a Lewis base such as tetrahydrofuran.[12,17] Urwin and Reed[13] have reported that the maximum absorption of n-butyllithium in benzene shifts from 278 mμ at 6 × 10⁻³ M to 282 mμ at 3 × 10⁻² M. The extinction coefficient at 285 mμ was reported to be 91.1 l./(mol cm).[13] The effects of alkoxide, which are inevitably present in alkyllithium solutions, have not been investigated previously and the possibility exists that the tail of the absorption shown in Figure 1 extending beyond 300 mμ is due to some type of alkoxide complex. However, the absorption of ethyllithium at 254 mμ, the wavelength utilized in the photolysis studies, does not appear to depend on the quantity of alkoxide in the solution. Furthermore, as noted in the Experimental Section, the concentration of "other soluble bases," as measured by the Gilman titration[18] does not change during a photolysis run. Until further data is available, therefore, we shall assume that the alkyllithium aggregate is the principal absorbing species.

Photolysis of Ethyllithium. The results of this work are summarized in Table I. Since ethyllithium is only moderately soluble in aliphatic hydrocarbons, saturated solutions (ca. 0.1 M) were employed. The percentage of carbon-bound lithium, as determined by the modified Gilman titration,[18] varied from 95 to 85%, but was usually greater than 90%.

As shown in Table I, ethylene is the predominate gaseous product when photolysis is carried out in "optically pure" aliphatic hydrocarbon solution (entries 1 and 2). In the presence of large quantities of optical

(13) J. R. Urwin and P. J. Reed, J. Organometal. Chem., 15, 1 (1968).
(14) J. P. Oliver, J. B. Smart, and M. T. Emerson, J. Amer. Chem. Soc., 88, 4101 (1966).
(15) E. Weiss and E. A. C. Lucken, J. Organometal. Chem., 2, 1967 (1964).
(16) A. H. Cowley and W. D. White, J. Amer. Chem. Soc., 91, 34 (1969).
(17) C. G. Screttas and J. F. Eastham, ibid., 88, 5668 (1966).
(18) H. Gilman and F. K. Cartledge, J. Organometal. Chem., 2, 447 (1964).

impurities, somewhat larger quantities of ethane are produced (entry 3). In each case, butane is produced in quantities of less than 1 mol %. These results contrast with those of van Tamelen, et al., who report that phenyllithium yields 80% biphenyl when photolyzed in
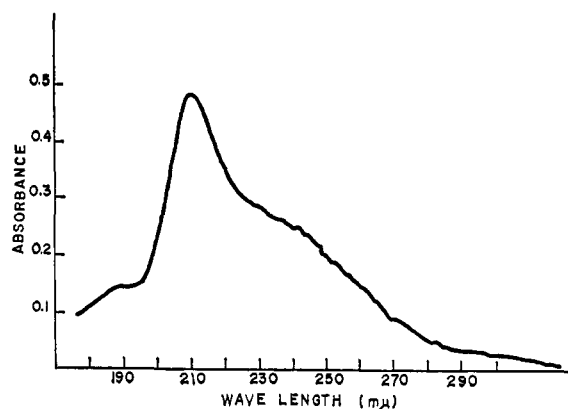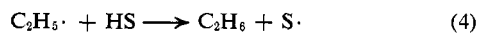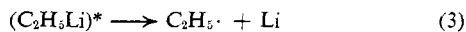

Figure 1. Ultraviolet spectrum of ethyllithium solution in isooctane, $[C_2H_5Li] = 3.5 \times 10^{-4} M$.

ether solution.[9] The absence of butane is also evidence that ethylene does not result from the disproportionation of two "free" ethyl radicals. Another possible source of the ethylene is lithium hydride elimination, although the control experiments require a nonthermal elimination mechanism (eq 1). Since a portion of the

$$(C_2H_5Li) \xrightarrow{h\nu} (C_2H_5Li)^* \longrightarrow LiH + C_2H_4 \qquad (1)$$
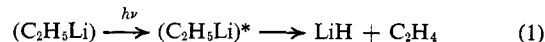
lithium hydride produced would be expected to survive the exposure to the ultraviolet radiation,[19] the residue obtained from solution runs was analyzed for hydride by the method of Frazer, et al.[20] (eq 2). The results

$$2LiH + Hg \xrightarrow{300°} Li_2Hg + H_2 \qquad (2)$$
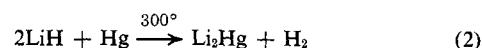
shown in Table I indicate that abundant quantities of hydride were found. Approximately one-third of the quantity of hydrogen to be expected from the ethylene yields was obtained in one analysis shown in Table I. This can only be regarded as an approximate figure in view of the possible photolysis of lithium hydride and

(19) D. J. E. Ingram, M. J. A. Smith, and W. T. Doyle, Phys. Rev. Lett., 2, 497 (1950).
(20) J. W. Frazer, C. W. Schoenfelder, and R. L. Tromp, U. S. Atomic Energy Comm., UCRL-4944 (1957).

the effect of impurities such as LiOH on the analytical method.[20] The remainder of the solid residue apparently is lithium metal,[21] a portion of which may result from the photolysis of lithium hydride. However, the presence of ethane among the gaseous products suggests that a competing mechanism may occur, and the most reasonable choice seemed to us to involve homolytic bond cleavage of excited ethyllithium to yield lithiu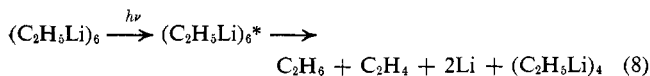m metal and an ethyl radical (eq 3). Under the conditions employed, the ethyl radical would be expected to abstract a hydrogen atom from solvent (eq 4).
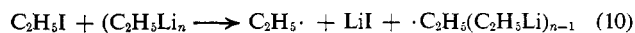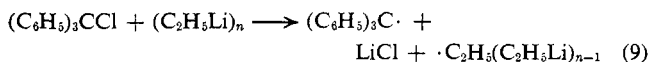
$$(C_2H_5Li)^* \longrightarrow C_2H_5\cdot + Li \qquad (3)$$

$$C_2H_5\cdot + HS \longrightarrow C_2H_6 + S\cdot \qquad (4)$$

The mechanism proposed in eq 3-4 was tested by photolyzing ethyllithium in C_6D_{12} with the surprising result that very small quantities of C_2H_5D were observed in the mass spectrum of the gaseous product.[22] The result cannot be explained by any reasonable isotope effect since the solvent contained 99.5% deuterium. Apparently, some mechanism exists by which normal isotopic ethane is formed by the abstraction of a hydrogen atom from ethyllithium. The following reaction scheme is proposed to account for these results.

$$(C_2H_5Li)_n^* \longrightarrow \cdot C_2H_5(C_2H_5Li)_{n-1} + Li \qquad (5)$$

$$\cdot C_2H_5(C_2H_5Li)_{n-1} \longrightarrow C_2H_6 + \cdot C_2H_4Li(C_2H_5Li)_{n-2} \qquad (6)$$

$$\cdot C_2H_4Li(C_2H_5Li)_{n-2} \longrightarrow (C_2H_5Li)_{n-2} + C_2H_4 + Li \qquad (7)$$
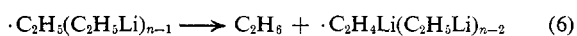
The over-all homolytic process summarized in eq 8 corresponds to an intraaggregate disproportionation process.

$$(C_2H_5Li)_6 \xrightarrow{h\nu} (C_2H_5Li)_6^* \longrightarrow$$
$$C_2H_6 + C_2H_4 + 2Li + (C_2H_5Li)_4 \qquad (8)$$

responds to an intraaggregate disproportionation process. With the present data, it is not possible to distinguish between the concerted reaction (eq 8) and a mechanism involving intermediate caged (or complexed) radicals (eq 5-7). It is interesting to note, however, that reactions 6 and 7 have been proposed by D'yachkovskii and coworkers[23] on the basis of their studies of alkyllithium coupling reactions. They also found only small percentages of deuterated ethane (C_2H_5D) when reactions 9 and 10 were carried out in perdeuteriobenzene, -cyclohexane, and -toluene.

$$(C_6H_5)_3CCl + (C_2H_5Li)_n \longrightarrow (C_6H_5)_3C\cdot +$$
$$LiCl + \cdot C_2H_5(C_2H_5Li)_{n-1} \qquad (9)$$

$$C_2H_5I + (C_2H_5Li)_n \longrightarrow C_2H_5\cdot + LiI + \cdot C_2H_5(C_2H_5Li)_{n-1} \qquad (10)$$

zene, -cyclohexane, and -toluene. The presence of radicals was indicated by the detection of the triphenylmethyl radical by esr, and by the formation of large quantities of ethane and ethylene. In the case of reaction 9, however, no butane was found, indicating that the ethyl radical reacted within its cage, presumably by a disproportionation step as shown in eq 7. The similarity between this case and the photolysis reaction is striking, and suggests that radicals formed from alkyllithium reagents will not behave as "free" radicals.[23]

Photolysis of crystalline ethyllithium is apparently a more complex process as indicated by the results shown

in Table I. In this case we find significant quantities of butane for the first time, and also rather sizeable amounts of an oily polymeric material. Mass spectral measurements indicate that this material contains hydrocarbon species in the $C_{16}-C_{26}$ range. These results, and the observation that the ethylene:ethane ratio is less than unity, suggest that ethylene may be polymerized by some process. D'yachkovskii and Shilov[23] have suggested that ethylene may add to alkyllithium-radical intermediates (eq 11) to form a butyllithium-ethyllithium mixed aggregate. A continuation of

$$\cdot C_2H_5(C_2H_5Li)_n + C_2H_4 \longrightarrow \cdot C_4H_9(C_2H_5Li)_n \qquad (11)$$
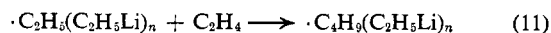
this process and subsequent steps such as eq 1 and 8 would account for the results summarized above.

The lithium hydride elimination process which competes with the homolytic process is apparently retarded by the presence of optical impurities in hydrocarbon solvents. The nature of these impurities is unknown to us, but it is conceivable that they behave either as photosensitizing agents or, alternatively, as quenching agents. In view of the very high extinction coefficient of ethyllithium, and its high concentration relative to the impurities, we prefer to consider the latter to be quenching agents. The apparent decrease in the ethylene yield may then be attributed to a process such as 12 which competes with reaction 1 but not with reaction 8. For this reason, it is tempting to attribute the hydride elimination process to a triplet excited ethyllithium species, and to assume that homolytic processes such as 8 proceed through a singlet state. However, there is little evidence to confirm this speculation.
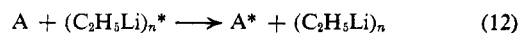
$$A + (C_2H_5Li)_n^* \longrightarrow A^* + (C_2H_5Li)_n \qquad (12)$$
$$A = \text{impurity}$$

Finally, we note that the presence of a mercury pool during the photolysis results only in the formation of ethane and lithium amalgam. Moreover, where this reaction is carried out in deuterated cyclohexane, the ethane again is found to contain only ca. 10-15% C_2H_5D. This system is presently under further study, and we prefer to reserve further comment at this writing.

Experimental Section

Preparation of Ethyllithium Solutions. Ethyllithium was prepared by the usual procedure from ethyl bromide and lithium sand in n-pentane. The compound was purified by crystallization in a drybox. Solutions were prepared as needed and analyzed by the modified Gilman procedure.[18]

Isooctane (Eastman spectro grade) and benzene (Phillips pure grade) were distilled from lithium aluminum hydride and stored over sodium metal prior to use. Absorbance of isooctane at 250 mμ was less than 0.05 (1-cm path length). n-Decane (Phillips pure grade) was washed with hot sulfuric acid, then with water, and distilled from lithium aluminum hydride. The distillate was passed through activated silica gel three times before using. Significant absorbance at 250-260 mμ could not be eliminated reproducibly, however, and isooctane became the solvent of choice in the latter phases of the work.

Absorption Spectra. Spectra were obtained in 0.1-cm cylindrical quartz cells with a Cary 14 spectrophotometer. The strong absorption of ethyllithium in decane or isooctane solution (Figure 1) beginning at approximately 300 mμ is completely annihilated by the addition of ethanol to the cell.

Photolysis of Ethyllithium Solutions. Most of the photolysis experiments were carried out in quartz round-bottomed flasks (125 or 250 ml) with 19/38 $\bar{\text{\textsf{T}}}$ connections, or in 28 mm o.d. quartz tubes with rubber stoppers. In either case, the vessel was loaded with analyzed ethyllithium solution in a drybox, sealed, removed from the box, and connected to a small vacuum line which was

(21) No evidence for any organic product was obtained in the solid residues with the exception of the residue obtained from the photolysis of solid ethyllithium (vide infra).

(22) The ratio of the peaks at m/e 30 and 31 was approximately 15:1 indicating the possible presence of approximately 6-7% C_2H_5D.

(23) F. S. D'yachkovskii and A. E. Shilov, Usp. Khim., **35**, 699 (1966); Russ. Chem. Rev., **36**, 300 (1966), and references cited therein.

constructed such that the vessel containing the solution was centered in a Rayonet RP-100 reactor. Approximately 90% of the lamp output consists of 253.7-mμ mercury resonance radiation.

The ethyllithium solution, which was under an atmosphere of helium, was opened to the evacuated line and the total pressure of the closed system was adjusted to approximately 300 mm with helium gas. The pressure was measured with a mercury manometer before photolysis. The hydrocarbon gases produced by the photolysis were collected at liquid nitrogen temperature in a trap which was connected to the vacuum line at a point outside the photoreactor. A small quantity of solvent distilled over during the photolysis, but its quantity was never significant compared to the total amount remaining in the reaction vessel. A black, sometimes mirror-like, solid was also formed during the photolysis and usually coated the walls. For this reason, few photolysis runs were carried beyond 12% decomposition of the original ethyllithium.

The final pressure was measured manometrically, and the composition of the residual gas was determined by gas chromatography. Hydrogen gas was detected with a 10 ft × 0.25 in. Linde 5A Molecular Sieve column (40°, nitrogen carrier gas). Hydrocarbons were determined with a 6 ft × 0.25 in. silica gel column, a 6 ft × 0.25 in. Poropak Q (40°) and a 6 ft × 0.25 in. Poropak S column (40°). Infrared spectra of the gases confirmed the analyses. Retention times were compared with standard mixtures. Thermal conductivity corrections were made using literature values. The number of moles of each component in the product gas was calculated from the relative composition, as determined chromatographically, and the total number of moles of gas, as determined from the *PVT* data. The volumes of the vacuum line parts were determined in separate experiments by conventional methods.

The condensed gases remaining in the trap were allowed to vaporize into the vacuum line in a subsequent step. The relative composition and total number of moles of trapped gases were determined by the same methods as described above.

The photolyzed ethyllithium solution, which had been isolated from the rest of the vacuum line after the lamps were turned off, was removed to the drybox. The solution was allowed to settle in the box for several hours and two aliquots for Gilman analysis were removed, being careful not to carry any black solid in the pipet. In every run, except one which was discarded, the concentration of basic materials other than ethyllithium remained constant during a photolysis run. The total number of moles of ethyllithium which decomposed was determined by this titration.

The remainder of the ethyllithium solution was filtered through a Milipore filter and hydrolyzed with dilute hydrochloric acid. The hydrocarbon layer was analyzed by glpc.

The black solid which remained on the walls of the quartz vessel was analyzed by the method of Frazer, *et al.*[20] Mercury metal was added and the vessel removed from the drybox to the vacuum line and heated with a mantle until the evolution of gas was complete. The gas was determined to be nearly pure hydrogen, presumably resulting from the decomposition of lithium hydride.[20] The hydrogen pressure was determined quantitatively and the number of moles of lithium hydride present in the black solid was deduced. Quantitative reaction of the black solid product could never be achieved, however, since some of it was inevitably lost when the residual ethyllithium solution was filtered or decanted away. Photolysis of ethyllithium solutions with benzene or mercury added were carried in a similar fashion to that described above. Mercury was stirred with the isooctane (or decane) solution for several minutes with a pool of mercury allowed to remain in the reaction vessel during photolysis.

A control run was carried out in a similar fashion except that the flask was carefully wrapped with black electrical tape. Only a trace of ethane and ethylene resulted, *i.e.*, less than 1% of the amount produced in an equivalent time when the flask was not wrapped. Apparently, thermal decomposition is not a competitive reaction of any consequence under the conditions used.

As mentioned above, each of the photolyses were carried out on a vacuum line containing a mercury manometer. However, a control photolysis of an ethyllithium solution utilizing a new vacuum line with no mercury manometer gave identical results.

Photolysis of Ethyllithium in Perdeuterated Solvents. Cyclohexane-d_{12} and benzene-d_6 (99.5% deuterium) were obtained from Stohler Isotope Chemicals and Merck Sharp and Dohme of Canada, Ltd., respectively. They were used as received. Saturated ethyllithium solutions in these solvents were prepared in the drybox in 60- or 10-mm diameter tubes, the lower 60 mm of which were of quartz construction. The tubes were connected to greaseless high-vacuum stopcock adapters for connecting to the vacuum line. The entire apparatus was placed in the reactor. After photolysis, all volatile components in the tube were transferred to a trap on the vacuum line at liquid nitrogen temperature. The ethylene–ethane mixture was purified by diffusion of the mixture from this trap through a second trap at −78°, or in later experiments, at −95°, and finally condensed at −170°. The ethane–ethylene mixture, now essentially free of solvent vapor, was analyzed by mass spectroscopy at 70 eV.

Photolysis of Crystalline Ethyllithium. Crystalline ethyllithium was coated on the inner walls of a round-bottomed quartz vessel by evaporating a pentane solution while rotating the flask. After photolysis, the vessel was removed to the drybox and the contents extracted with dry pentane. The solid residue was analyzed for hydride by the method described above.[20] The pentane extract was filtered, hydrolyzed, and acidified. The hydrocarbon layer yielded an oily polymeric material the mass spectrum and gas chromatograms of which indicated a mixture of hydrocarbons in the C_{16}–C_{26} range.