The Ethylenation of Secondary and Tertiary Alkyllithiums. I. Conditions and Limits of the Reaction

Paul D. Bartlett, Stephen J. Tauber, and William P. Weber

Contribution from the Converse Memorial Laboratory, Harvard University, Cambridge, Massachusetts 02138. *Received March 21, 1969*

Abstract: The addition of ethylene to isopropyl- and *t*-butyllithium, previously reported,[3] occurs also with *sec*-butyl- and cyclohexyllithium, but not with cyclobutyl-, phenyl-, benzhydryl-, or triphenylmethyllithium. An ether or an amine is a necessary catalyst; both are attacked by alkyllithiums, but not at the low temperatures (below −10°) of these experiments, where the addition of ethylene is still rapid. No other acyclic, unconjugated olefin approaches ethylene in reactivity. The β-alkylethyllithium, which is formed quantitatively, has been characterized in each case both by carbonation to an acid–ketone mixture and by reaction with benzophenone to a tertiary alcohol whose methyl ether gives rise quantitatively in vapor chromatography to a 1,1-diphenylalkene. The ethylenation of secondary and tertiary alkyllithium is a reaction of potential synthetic utility.

The additions of alkyllithiums to conjugated unsaturated systems such as α,β-unsaturated ketones, dienes, fulvenes, and styrenes, and also to alkynes, are well-known reactions of synthetic, and in some cases economic, importance. *n*-Butyllithium also adds readily to the homoconjugated diene, norbornadiene.[1,2] On the other hand, the addition of alkyllithiums to unconjugated carbon–carbon double bonds in hydrocarbon molecules has been observed in comparatively few cases.

In 1953, Bartlett, Friedman, and Stiles[3] reported that isopropyllithium (**1**) in ethyl ether at low temperatures adds ethylene at atmospheric pressure, yielding isopentyllithium (**2**) as the sole reaction product. Similar results were reported for *t*-butyllithium (**3**), which formed neohexyllithium (**4**). In each case the secondary or tertiary alkyllithium added ethylene rapidly under conditons where the primary alkyllithium was inert to ethylene.

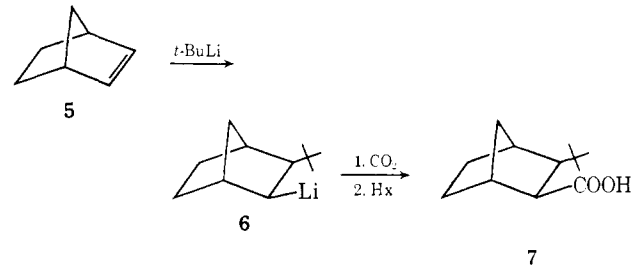
$$\underset{\mathbf{1}}{(CH_3)_2CHLi} + CH_2{=}CH_2 \longrightarrow \underset{\mathbf{2}}{(CH_3)_2CHCH_2CH_2Li}$$

$$\underset{\mathbf{3}}{(CH_3)_3CLi} + CH_2{=}CH_2 \longrightarrow \underset{\mathbf{4}}{(CH_3)_3CCH_2CH_2Li}$$

Primary alkyllithiums are ethylenated only under much more vigorous conditions. In 1950, Ziegler and Gellert[4] reported that *n*-butyllithium in a hydrocarbon solvent adds ethylene at high pressure in an autoclave. Further addition of ethylene to the product yielded a linear polyethylene of low molecular weight.

More recently it has been shown that *n*-butyllithium in the presence of a chelating tertiary amine, such as N,N,N′,N′-tetramethylethylenediamine, will polymerize ethylene at 50 atm pressure and 100° to yield a linear polyethylene[5,6] of high molecular weight.

Apart from ethylene, the only isolated double bonds reported to undergo addition of organolithiums have been somewhat activated by strain. Mulvaney and Gardlund have reported[7] that *t*-butyllithium adds to the unconjugated double bond of norbornene (**5**). This reaction was carried out either in ethyl ether solution below −40° or in the presence of triethylamine at room temperature. The product alkyllithium (**6**) was characterized by quenching the reaction with carbon dioxide to yield the corresponding carboxylic acid (**7**). The *t*-butyl group was shown by nmr to have the *exo* configuration.



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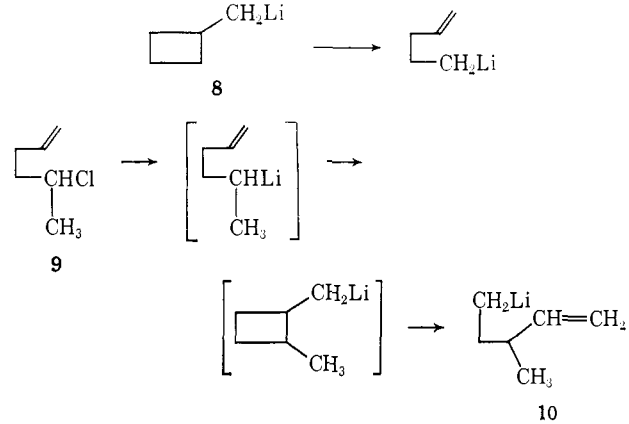
The double bond of cyclopropene is also active toward addition of phenyllithium at 0°.[8] Another interesting example has been reported by Hill, Richey, and Rees.[9,10] Although cyclobutylmethyllithium (**8**) undergoes a ring opening to pent-4-en-1-yllithium, the reversal of an addition to the double bond, yet the conversion of **9** to **10** indicates that the *secondary* hexenyllithium must



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undergo additive cyclization to a cyclobutylmethyllithium, which then cleaves to the final most stable product.

In our earlier communication[3] we reported the drop in reactivity and the low-polymeric character of the product mixture when propylene instead of ethylene was brought into reaction with branched organolithiums. In this paper we report observations made over a number of years on the scope of the ethylenation reaction with respect to variations in the organolithium reagent and in the ether or other complexing agent. In the following paper[11] of this series a detailed study of the kinetics and mechanism is reported.

Results

Attack on Ethers and Amines. In the accidental discovery of this reaction,[3] the ethylene came from decomposition of ether, a reaction previously observed.[12-15] Triethylamine is also attacked. When isopropyllithium in benzene–petroleum ether (bp 30–60°) was held at 15–19° with 2 mol equiv of triethylamine for 19 hr and then carbonated, 4-methylpentanoic and isobutyric acids were formed in yields of 25 and 5%, respectively. *t*-Butyllithium in pentane, heated at 46° overnight with a fourfold molar excess of triethylamine, yielded after carbonation 9.3% 4,4-dimethylpentanoic acid (identified by its amide and anilide) and 2.6% dineohexyl ketone (identified by its 2,4-dinitrophenylhydrazone). In all the low-temperature ethylenations attack of the lithium reagent on the ether or amine was undetectably small.

Stoichiometry. In the ethylenation with ether at −25°, the amount of ethylene taken up at atmospheric pressure agreed with the amount of starting secondary or tertiary alkyllithium, as determined by a modified Gilman double titration procedure.[16]

The original product identifications,[3] carried out by carbonation and characterization of the resulting ketones and acids, were confirmed by addition of benzophenone to the ethylenated alkyllithium solutions. This procedure had the advantage that it yielded a single derivative. The tertiary benzhydrol thus produced was converted under basic conditions to a relatively volatile methyl ether for vapor chromatography. Under the conditions of the vpc analysis methanol was quantitatively lost from the benzylic methyl ether, yielding the corresponding 1,1-diphenylalkene as the product isolated. The analytical conditions would have detected any additional products formed in a yield as high as 1%. In this manner the product mixtures from the reactions of *t*-butyl, *sec*-butyl, and isopropyllithium with ethylene were analyzed. The volatile derivatives used for the vpc analysis were isolated and characterized by uv, ir, and nmr spectra as well as by microanalysis.

Variations in Organolithium Reagent. Cyclopropyllithium, though secondary, has been observed not to add ethylene.[17] We find also that cyclobutyl-, benzhydryl-, triphenylmethyl-, and phenyllithium do not undergo the ethylenation reaction under the present conditions. Rapid ethylenation takes place with cyclohexyllithium, as well as with isopropyl-, *sec*-butyl-, and *t*-butyllithium.

Discussion

It is obvious that a mechanistic pathway exists in general for the addition of any organolithium reagent to any olefin, but that the rate of its occurrence is extremely sensitive to changes in the structures of the reactants. Since the enthalpy of insertion of ethylene into a hydrocarbon chain is about −20 kcal, the ethylenation of an organolithium compound at low temperatures may be expected in general to be favored thermodynamically. However, stability and strain factors affecting reactants and products differently may reverse the favored direction, as when cyclopropylmethyllithium rapidly undergoes ring opening to but-3-enyllithium,[18-20] or cyclobutylmethyllithium opens to pent-4-enyllithium.[9,10] In both these cases the equilibrium strongly favors the unsaturated alkenyllithium, and the primary isomer is favored thermodynamically over the secondary.

In the present study it seems likely that some of the cases of nonaddition of ethylene, such as that of triphenylmethyllithium, are due to unfavorable thermodynamic relations. We are chiefly concerned, however, with the very wide range of *kinetic* influences displayed by different olefins, organolithiums, and bases on the rate when addition *is* thermodynamically favored. For example, both *n*-butyllithium and *sec*-butyllithium react with ethylene in the forward direction, but their rates under comparable conditions must differ by a factor of at least a million.

Reactions of alkyllithiums have frequently been discussed in terms of the carbanions of which they are formally salts.[21] In reactions with acidic compounds the relation to carbanion behavior is quite direct. Also in additions to the carbonyl group the R group of RLi does just what the cyanide anion would do, and the carbanion analogy is close. It is credible in the RLi-initiated polymerization of styrene and of conjugated dienes. In the following paper[11] we shall consider in detail whether the addition of alkyllithiums to ethylene should be regarded as a carbanion reaction or not.

In the addition of alkyllithiums to ketones, every carbanion is inherently reactive enough to afford rapid reaction; there is no problem either of the capability of the carbanion or of its attaining sufficient freedom to react. If we carry the carbanionic view over to the mechanism of ethylenation, it is at once apparent that one or the other of these problems is very serious indeed. In the first place, no alkyllithium will react at low temperature with ethylene unless it is aided by a basic lig-

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and, such as ether or an amine. In carbanionic terms, the lithium cation must be appropriately solvated in order to make the carbanion available for reaction, although such special assistance is not necessary for reaction of the "carbanion" with a ketone.

In low-temperature ethylenation, unlike addition to a ketone, only certain alkyllithiums have the capability to react even under ether solvation of the lithium. The active alkyl groups are those *least* ready to appear as carbanions; indeed, there is an inverse correlation between activity of an alkyllithium and the kinetic acidity of the parent hydrocarbon,[22,23] as indicated in Table I. There also appears to be an inverse correlation between the rate of ethylenation and the rate of addition[24] of RLi to Michler's ketone, in which the order of reactivity phenyl > ethyl > isopropyl is directly that of the kinetic acidities of the hydrocarbons.

Table I. Ethylenation of Secondary and Tertiary Alkyllithiums

RLi	Relative kinetic acidity[a] of RH	Reaction with ethylene
t-Butyllithium		+
sec-Butyllithium		+
Isopropyllithium		+
Cyclohexyllithium	1.1×10^{-8}	+
Cyclobutyllithium	10^{-6}	−
Cyclopropyllithium[b]	10^{-3}	−
Phenyllithium	1	−
Benzhydryllithium	270	−
Triphenylmethyllithium	1100	−

[a] See ref 22 and 23. [b] See ref 15.

The inverse correlation between the ethylenation rate of RLi and the kinetic acidity of RH is also an inverse correlation with ionic dissociation of the alkyllithium. It is *covalent* character in the C–Li bond which favors reactivity, and *ionic* character which is unfavorable.

Propylene[3] having been observed to add more slowly than ethylene, other simple olefins were not investigated in the present work.[25] Among unstrained simple olefins ethylene may be regarded as unique in its ability to insert rapidly and quantitatively into a secondary or tertiary alkyllithium.

The role of ether in the ethylenation reaction will be discussed more fully in connection with the kinetic study.[11] The simplest hypothesis of its action proves inadequate: although as an electron donor to the metal atom ether might be regarded as increasing the polarity of the Li–C bond, such an effect would make a secondary alkyllithium more like a primary one, and primary alkyllithiums are unreactive in this reaction. Therefore the action of the ether is probably more subtle than a simple polarization of a bond.

Synthetic Utility. Finally it should be mentioned that, where appropriate, ethylenation represents an unusually clean and quantitative synthetic method. It will often be the most convenient way of beginning with a secondary or tertiary halide and adding an ethyl, β-haloethyl, or any other group beginning with $-CH_2-CH_2-$, since the new extended primary alkyllithium is ready for immediate use in any general reaction which an organolithium reagent can undergo.

Experimental Section

Analyses of compounds were performed at the Massachusetts Institute of Technology Microanalytical Laboratory by Dr. S. M. Nagy or by Dr. W. Manser at the Eidg. Technische Hochschule Zurich.

Infrared spectra were taken on a Perkin-Elmer Model 137 infrared spectrometer, and were calibrated against known absorption bands in polystyrene film. All nmr spectra were taken on a Varian A-60 spectrometer with tetramethylsilane as an internal standard. Ultraviolet spectra were obtained on a Perkin-Elmer Model 202 ultraviolet-visible spectrophotometer.

Reagents. Lithium Metal. The lithium metal used was of high sodium content (0.8% sodium)[26] obtained from the Lithium Corp. of America. The lithium metal rods were stored in a vacuum desiccator under argon prior to use.

***n*-Pentane.** Phillips 99 mol % *n*-pentane was purified by shaking with three or four portions of reagent grade sulfuric acid until it stopped discoloring the acid. The *n*-pentane was then washed twice with distilled water, dried over Mallinckrodt anhydrous magnesium sulfate, and finally distilled through a 50-cm vacuum-jacketed Vigreux column. A central fraction, bp 36° uncor, was collected (lit.[27] bp 36.2°) and stored over sodium wire.

Ethylene. The ethylene used in all experiments was a special ultrapure grade donated by the B. F. Goodrich Co. It was used without purification.

Mineral Oil. Kaydol mineral oil was used in the preparation of lithium sand. It was dried over sodium wire prior to use.

Oleic Acid. Baker White Label was used in the preparation of the lithium sand without further purification.

***sec*-Butyl chloride, isopropyl chloride, and cyclohexyl chloride,** all Eastman White Label materials, were dried over calcium chloride and distilled. The boiling ranges taken were, respectively, 66.5–67.5° ($n^{24}D$ 1.394), 35.5–36.5° ($n^{24}D$ 1.3748), and 141–142°.

***t*-Butyl chloride** was prepared from Eastman White Label *t*-butyl alcohol and Du Pont reagent hydrochloric acid by following the procedure of Norris and Olmsted,[28] and dried over anhydrous calcium chloride overnight. It was then distilled through a 3-cm Vigreux column. A central fraction, bp 50.5–52°, was collected, $n^{24}D$ 1.385 (lit. bp 50.4°, $n^{18}D$ 1.376).

Chlorotriphenylmethane, Eastman White Label, was used without further purification, mp 108–113°.

Chlorodiphenylmethane, Eastman White Label, was used without further purification, mp 15–18°.

Bromocyclobutane. Diethyl 1,1-cyclobutanedicarboxylate was prepared by the method of Mariella and Raube.[29] This was converted to 1,1-cyclobutanedicarboxylic acid and then to cyclobutanecarboxylic acid by the method of Heisig and Stodola.[30] Finally the conditions of Cason and Way were used to convert cyclobutanecarboxylic acid to bromocyclobutane. A central fraction, bp 107.1–107.5°, was collected, $n^{25}D$ 1.4777 (lit.[31] bp 108.2–108.3, $n^{20}D$ 1.4801).

Ethyl Ether. Mallinckrodt anhydrous ethyl ether was stored over sodium wire in an argon atmosphere.

1,2-Dimethoxyethane was treated with potassium hydroxide pellets overnight, then redistilled from lithium aluminum hydride under nitrogen, through a 30-cm Vigreux column. A central fraction, bp 82.5–83°, was used (lit.[32] bp 83°).

Procedure for the Preparation of Lithium Metal Dispersions. A 2-l. three-necked round-bottomed Morton flask equipped with a reflux condenser, Tru-bore stirrer with Teflon paddle, an argon gas inlet tube, and finally a large bore (no. 8) Teflon stopcock at the

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(23) See ref 21b, p 18.
(24) C. G. Swain and L. Kent, *J. Amer. Chem. Soc.*, **72**, 518 (1950).
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(32) F. K. Beilstein, "Handbuch der organischen Chemie," Vol. I, 4th ed, 1918, p 467.

bottom was used. A special heating mantle was fitted to the flask. The apparatus was cleaned and dried in an oven at 140° for 24 hr, then assembled and flamed with a bunsen burner and allowed to cool in a stream of argon.

In a typical preparation of lithium sand, 8 g-atoms of lithium metal rods (slightly more than 1 mol) were placed in the apparatus under an argon atmosphere. Dried Kaydol mineral oil (500 cc) and four drops of oleic acid, to prevent coagulation of the lithium melt, were added. The reaction vessel was heated to 186°. As the lithium melted a 3000-rpm stirring motor connected to the stirrer was turned on causing the lithium to form a fine dispersion. The flask was then cooled and the mineral oil below the floating lithium was drained through the bottom stopcock. The finely divided lithium sand was then washed three times with purified *n*-pentane.

An even more reactive lithium sand can be prepared by increasing the amount of sodium. Lithium sand containing at least 3% sodium is particularly useful in preparing *t*-butyllithium.

Demonstration of the Stability of Isopropyllithium in Ethyl Ether at −30°. A solution of isopropyllithium in ethyl ether was prepared from 6 g of lithium metal sand and 35 g of isopropyl chloride. The reaction was kept at −30° in a Dry Ice–acetone bath. After 2 hr the solution was carbonated by passing in an excess of dry carbon dioxide while maintaining the low temperature.

Distillation of the hydrolyzed product mixture yielded 12.7 g of diisopropyl ketone (55.5%) and 3.1 g of isobutyric acid as the only products isolated. The products were identified by comparison with authentic samples.

Reaction of Cyclohexyllithium with Ethylene. Lithium metal sand (4 g, 0.58 mol) was placed in the reaction flask with somewhat over 500 cc of ethyl ether under a stream of purified nitrogen. The flask was cooled in a methanol–Dry Ice bath. Chlorocyclohexane (30 g, 0.25 mol) was added to the vigorously stirred reaction mixture over a period of 3 hr. After completion of the addition, the reaction mixture was stirred for an additional 2 hr. Ethylene gas was then passed into the flask for 24 hr at atmospheric pressure while the temperature was maintained below −30°. After 24 hr dry carbon dioxide was passed into the flask for 1 hr. The product was separated by extraction into an acidic and a nonacidic fraction. The acid fraction consisted of 19.1 g of 3-cyclohexylpropanoic acid: ir 7.83, 8.97 μ (cyclohexanecarboxylic acid showed 7.75, 8.00, 8.29, 8.883 μ); nmr complex aliphatic region (13 H), triplet 2.32 ppm (2 H), protons α to the carboxyl group, a sharp singlet, 12.0 ppm (1 H), COOH. Anilide mp 93.2–94.4°.

The neutral fraction consisted of a single colorless liquid, di(2-cyclohexylethyl) ketone. The 2,4-dinitrophenylhydrazone was recrystallized from a mixture of ethanol and ethyl acetate, mp 81.3–82.2°.

Anal. Calcd for $C_{23}H_{34}N_4O_4$: C, 64.16; H, 7.96; N, 13.01. Found: C, 64.25; H, 7.75; N, 12.85.

The Attempted Reaction of Cyclobutyllithium with Ethylene. Cyclobutyllithium was prepared from 2.8 g (0.40 mol) of lithium metal sand and 11 g (0.08 mol) of bromocyclobutane in 60 ml of ether with cooling in a methanol–Dry Ice bath. Stirring was continued for an additional 2 hr at low temperature. Ethylene was then passed into the system below −30° for 20 hr, then dry carbon dioxide was bubbled through the reaction solution for 3 hr. The reaction mixture was hydrolyzed with distilled water and was acidfied with dilute hydrochloric acid. The product mixture, consisting of a carboxylic acid and a ketone, was separated by extraction.

There was isolated 1.6 g of crude acid and 6.6 g of crude neutral material. No attempt was made to characterize the carboxylic acid. The neutral material consisted entirely of dicyclobutyl ketone which was purified by preparative vpc on an F & M 300 thermal conductivity instrument with a Carbowax 20M 10 ft × 0.25 in. column operated at 125° with 80 cc of helium per minute. Under these conditions the pure ketone had a retention time of 8 min.

2,4-Dinitrophenyl hydrazone, recrystallized from ethanol–ethyl acetate, had mp 190.0–190.7°.

Anal. Calcd for $C_{15}H_{18}N_4O_4$: C, 56.60; H, 5.70; N, 17.60 Found: C, 56.63; H, 5.65; N, 17.53.

Ir analysis showed strong carbonyl absorption at 5.86 μ.

The nmr spectrum, in carbon tetrachloride, consisted of two sharp complex multiplets, one centered at 2.05 ppm (12 H) and another centered at 3.20 ppm (2 H), the latter assigned to the two protons α to the carbonyl group.

Attempted Reaction of Triphenylmethyllithium with Ethylene. The sand from 2.0 g (0.30 mol) of lithium metal and 100 ml of ethyl ether was stirred at room temperature with a small portion of an ethereal solution of 25.2 g (0.09 mol) of chlorotriphenylmethane in 300 ml of ethyl ether and a drop of mercury. After 15 min stirring an intense carmine color appeared. The rest of the chloride was added over 3 hr and formation of the reagent was completed under reflux. Ethylene was then passed into the solution for 48 hr at room temperature and atmospheric pressure. The reaction mixture was poured onto a large excess of Dry Ice. After work-up there was isolated 6.8 g of an oily orange neutral solid and 16.4 g of an acid.

The acid had a mp of 274–278° and was shown to be identical with an authentic sample of triphenylacetic acid.

The neutral material was separated into two fractions by trituration with isooctane. They were shown by comparison of their ir spectra with those of authentic samples to be triphenylmethane and triphenylcarbinol.

Attempted Reaction of Benzhydryllithium with Ethylene. A sixfold excess of *t*-butyllithium was prepared by reaction of *t*-butyl chloride with lithium sand in ether below −40°. To this solution was added chlorodiphenylmethane, 24.5 g (0.12 mol) in 90 ml of ethyl ether, over a period of 4 hr while the temperature of the reaction was maintained at −40°. The reaction mixture turned red. After an additional 2 hr of stirring, ethylene was passed into the system for 22 hr at atmospheric pressure, temperature being kept below −26°. Dry carbon dioxide gas was passed into the reaction mixture. After work-up the acid fraction was shown to be diphenylacetic acid, mp 143–146°, by comparison with an authentic sample, mp 144–147°.

The neutral fraction contained unreacted chlorodiphenylmethane and 2,2,8,8-tetramethyl-4-nonanone, the product from reaction of excess *t*-butyllithium with ethylene followed by carbonation.

Attempted Reaction of Phenyllithium with Ethylene. Phenyllithium was stirred similarly in a stream of ethylene for 50 hr at room temperature and atmospheric pressure.

After carbonation there was isolated a 65% yield of benzoic acid, mp 122–123°, identical with an authentic sample. The neutral fraction consisted of benzophenone and triphenylcarbinol as was shown by comparison with authentic samples.

Preparation of Secondary and Tertiary Alkyllithiums in *n*-Pentane Solution for Quantitative Study. All preparations of alkyllithiums for quantitative study were carried out in a Vacuum Atmospherics Corp. drybox having a continuously recirculated arbon atmosphere from which oxygen and water were removed catalytically. The atmosphere in the drybox was shown to contain less than 1 ppm water and 1 ppm oxygen by volume.

In a 2-l. three-necked round-bottomed flask, equipped with a Tru-Bore stirrer with Teflon paddle, an efficient reflux condenser, and a pressure-equalizing constant rate addition funnel, was placed 8 g of previously prepared lithium dispersion. Sufficient *n*-pentane was added to make the total volume in the flask between 500 and 750 cc. Stirring was begun and the alkyl chloride (0.5 mol) was slowly added over about 8 hr. A deep purple color marks the beginning of the reaction. The reaction was stirred for at least 2 hr. The crude reaction mixture after settling was filtered into a previously dried glass bottle, which was stoppered and removed from the drybox. Stock solutions of alkyllithiums thus prepared were stored in a freezer at −25°, under which conditions they were stable indefinitely. Typical yields of *sec*-alkyllithiums prepared in this way are about 75% based on the alkyl chloride added; for *t*-butyllithium yields were somewhat lower.

The double titration method of Gilman[16] was used to determine the purity of the alkyllithiums. Alkyllithium reagents in *n*-pentane solution of a purity better than 97% were routinely prepared.

Demonstration That the Reaction between Secondary or Tertiary Alkyllithiums and Ethylene Is Quantitative. All equipment was cleaned and dried overnight in an oven at 140°. The jacketed flask and the jacketed addition funnel were connected to a mercury gas buret and an open tube mercury manometer (Figure 1). A Teflon-covered magnetic stirring bar was placed in the bottom-jacketed flask and a special Teflon vacuum stirrer was suspended in the upper-jacketed addition funnel. The system was sealed and the whole apparatus was pumped out to a pressure of 0.02 mm and refilled with ethylene. This sequence was repeated several times. Dimethyl ether was then condensed into the outer jacket of the lower flask through a Dry Ice–acetone condenser.

Since solutions of secondary or tertiary alkyllithiums in *n*-pentane have no tendency to add ethylene in the absence of an ether, the alkyllithium solution can be saturated with ethylene prior to addition of ethyl ether from the upper addition funnel. From argon-flushed pipets, aliquots of alkyllithium solution and of dimethyl ether were added to the lower and upper flasks, respectively, against

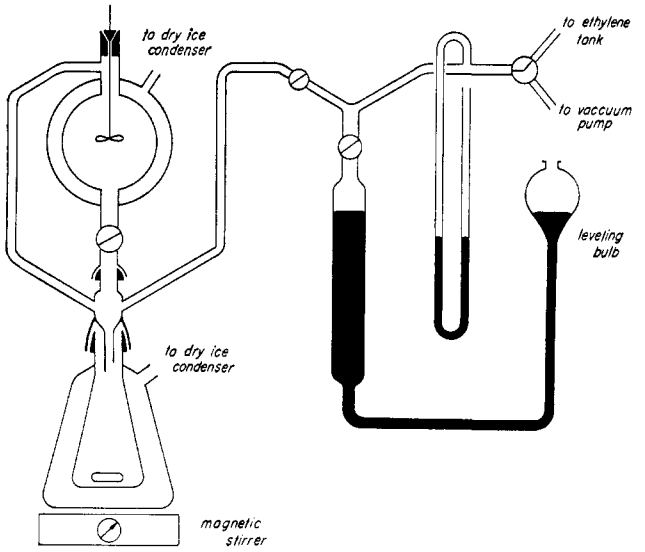


Figure 1. Apparatus used to measure ethylene uptake by a known amount of a secondary or tertiary alkyllithium. Reaction is started by mixing the upper solution (pentane and ether, saturated with ethylene) and the lower solution (pentane and RLi, saturated with ethylene).

an issuing stream of ethylene. Each solution was separately saturated with ethylene at exactly 1 atm pressure, and the gas volume over the saturated solutions was read with the gas buret.

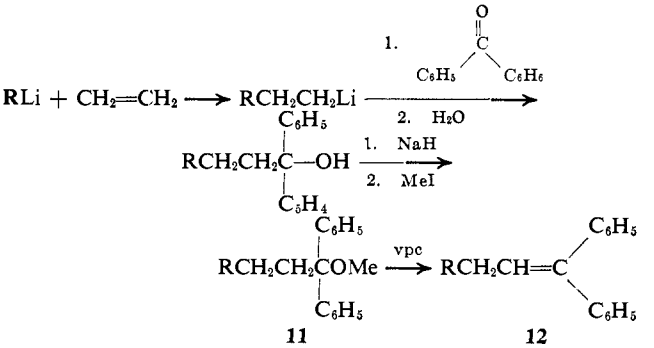
The addition reaction was begun by opening the stopcock permitting the ether catalyst to drain into the lower flask containing the alkyllithium solution. The leveling bulb was raised to maintain atmospheric pressure in the system. When the uptake of ethylene had ceased the final volume of ethylene in the gas buret was read. The ethylene uptake agreed with the amount of starting alkyllithium added as determined by the Gilman double titration within experimental error, *i.e.*, 2%. In this way it was shown that *t*-butyl, *sec*-butyl, and isopropyllithium react quantitatively with ethylene in the presence of ethyl ether at −25°.

Experimental Procedure for Product Studies with Benzophenone. After the uptake of ethylene had ceased, the primary alkyllithium produced was quenched by the addition of a threefold excess of benzophenone. The solution was stirred for 20 min under an inert atmosphere. The color of the solution during this procedure was at first green and then faded to yellow. A saturated solution of ammonium chloride (10 cc) was added, care being taken not to make the reaction mixture acidic to avoid dehydration of the tertiary alcohol. After washing, drying, and filtration, the organic layer was concentrated under reduced pressure. The product benzylic alcohol was converted to a methyl ether by sodium hydride in dimethoxyethane, heating to complete hydrogen evolution, then addition of methyl iodide. After extraction between pentane and water, drying, filtration, and evaporation of the pentane, the mixture of products was analyzed by vapor phase chromatography.

Analytical Conditions. An F & M Model 300 thermal conductivity vapor phase chromatograph was used for analytical separation and preparative isolation of authentic samples (0.25 in. × 10 ft column packed with 20% Carbowax 20M, 60/80 mesh Chromosorb P; column temperature 190°, flow rate 80 cc/min of helium).

A Varian Aerograph HyFi flame ionization vpc was used for analytical separation of the product mixtures ($^1/_8$ in. × 8 ft column packed with 20% SE-30 (silicone gum rubber) on 60/80 mesh Chromosorb P, column temperature 240°).

From each reaction mixture benzophenone (retention times, Carbowax 23.5 min, SE-30, 22 min) and benzhydryl methyl ether (retention times Carbowax 10.5 min, SE-30, 18.4 min; mp 67–68°; ir 1090 cm^{-1}; nmr 3.18 (s, 3 H); 5.08 (s, 1 H), 7.20 ppm (m, 10 H)) were identified in the product. The only other component in any product was the corresponding 1,1-diphenylalkene, where R =



isopropyl, *sec*-butyl, or *t*-butyl. Any other product present in even 1% yield would have been detected.

1,1-Diphenyl-4-methyl-1-pentene (**12**, R = isopropyl, from isopropyllithium) exhibited the following characteristics: retention time on Carbowax 20M 19.2 min; ir doublet centered at 1365 cm^{-1}; nmr 0.90 (d, J = 6 cps, 6 H), 1.50–2.00 (complex multiplet, 1 H); 1.95 (q, 2 H), 6.05 (t, J = 8 cps, 1 H), 7.20 ppm (m, 10 H); uv (ethanol) λ_{max} 251 mμ (ε 13,200).

Anal. Calcd for $C_{18}H_{20}$: C, 91.47; H, 8.53. Found: C, 91.31; H, 8.53.

1,1-Diphenyl-4-methyl-1-hexene (**12**, R = *sec*-butyl, from *sec*-butyllithium) exhibited the following characteristics: retention time on Carbowax 20M 19.6 min; nmr 0.90 (unsymmetrical doublet, 6 H), 1.10–1.70 (m, 3 H), 1.90–2.30 (complex multiplet, 2 H), 6.07 (t, J = 7 cps, 1 H), 7.20 ppm (m, 10 H); uv (ethanol) λ_{max} 250 mμ (ε 13,500).

Anal. Calcd for $C_{19}H_{22}$: C, 91.34; H, 8.82. Found: C, 91.14; H, 8.85

1,1-Diphenyl-4,4-dimethyl-1-pentene (**12**, R = *t*-butyl, from *t*-butyllithium) exhibited the following characteristics: retention time 19 min on the Carbowax 20M column; nmr 0.90 (s, 9 H), 2.00 (d, J = 7 cps, 2 H), 6.12 (t, 1 H), 7.14 ppm (m, 10 H); uv (ethanol) λ_{max} 249 mμ (ε 13,700).

Anal. Calcd for $C_{19}H_{22}$: C, 91.14; H, 8.85. Found C, 91.03; H, 9.05.

1-Methoxy-1,1-diphenyl-4,4-dimethylpentane (**11**, R = *t*-butyl) was isolated by recrystallization from ethyl ether. This ether was a white crystalline solid: mp 91–92°; ir a strong pair of bands at 1080 and 1090 cm^{-1}; nmr 0.82 (s, 9 H), 0.86–1.15 (complex multiplet, 2 H), 2.05–2.35 (complex multiplet, 2 H), 2.98 (s, 3 H), 7.20 ppm (m, 10 H).

Injection on the Carbowax 20M vpc column under conditions identical with those used previously yielded a single peak whose retention time was identical with that of 1,1-diphenyl-4,4-dimethyl-1-pentene (**12**, R = *t*-butyl).

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