linearity to permit one to calculate approximate first-order constants, from which a value of α was calculated.

Activation energies were determined by obtaining rate constants at three different temperatures between 15° and 40°. Since the reaction with no catalyst is very slow at 15° (and also follows no simple rate law, even approximately) it was necessary to use initial rates to determine the activation energy in that case. The activation energies decrease with increasing catalyst concentration and then level off to a constant value. These limiting constant values of E_a are given in Table I for four different catalysts. It is probable that the lower effectiveness (smaller α) of the catalysts from diphenylamine and the dicyclohexylamine is not the result of higher activation energies, but rather of lower frequency factors.

TABLE I

CATALYTIC EFFECTS OF DIFFERENT CATALYSTS

Source of catalyst	α (× 10^2)[a]	E_a (kcal.)
Diethylamine	70 (±10%)	13 (±1)
Di-*n*-propylamine	60	..
Di-*n*-butylamine	55	12
Diisobutylamine	6.5	..
Di-*sec*-butylamine	4.0	..
Diphenylamine	1.0	10
Diisopropylamine	0.8	..
Dicyclohexylamine	0.6	12
No catalyst	..	17

[a] These values are for 36.5° and the units are l. × mole^{-1} sec.^{-1} The initial concentrations of lithium aluminum hydride and 1-hexyne ranged from 0.33 to 0.41 *M* and from 1.00 to 1.33 *M*, respectively.

Experimental

Materials.—1-Hexyne (Farchan) was found to contain traces of catalytic impurities after distillation. In order to remove these, most of the hexyne was treated with 2% hydrochloric acid solution, 2% sodium carbonate solution, washed with distilled water, dried with anhydrous calcium chloride, passed through an alumina column, and then distilled, b.p. 68° (745 mm.). Further treatment had no observable effect. In one case the hexyne was passed over alumina and distilled without the pretreatment with acid, and the results were not noticeably different from those obtained with the hexyne which had been washed with acid.

Phenylacetylene was passed over alumina and distilled, b.p. 140° (730 mm.).

The liquid amines were freshly distilled; diphenylamine was Fisher Certified. Dilute ether solutions were made and then stored under refrigeration.

The preparation of the lithium aluminum hydride solution has been described elsewhere.[3]

Apparatus.—The apparatus and method used to determine the reaction rates by following the hydrogen evolution previously has been described.[3] The reacting mixture was maintained under reflux and the temperature was varied by adding the appropriate amount of butane or hexane, or a mixture of these, to the ether solution. The total volume of hydrocarbon added never exceeded 21% of the total volume and no significant solvent effect other than the temperature effect was observed.

Error Estimates.—The estimated error of ±1 kcal. for the activation energies is based on the maximum scatter that was observed. Most points were within ±0.5 kcal. of the values given in Table I.

It was impossible to obtain a good estimate of the error in the values of α. The most rapid reactions were less reproducible than the slower ones. With some of the catalysts there was a definite decrease in the value of the rate constant with increasing initial lithium aluminum hydride concentration. This effect was not studied in detail and causes an increase in the uncertainty in the values of α. However, it is not likely that the error is great enough to cause the true relative order of the catalysts to be different from that shown in Table I.

A Convenient Preparation of Allyllithium[1]

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The recently reported preparation of allyllithium by the metal–metal exchange reaction between allyltin derivatives and organolithium compounds[3] has made accessible pure samples of this reactive organolithium compound. The chemical versatility of allyllithium has been exploited for the preparation of allyl derivatives of both metal and organic substrates in high yields.[3,4] However, the necessity of employing allyltin and organolithium starting materials detracts from the convenience of the method. On the other hand, alternate approaches to allyllithium, such as the interaction of allylsodium with lithium chloride,[5] the treatment of allyl Grignard reagents with metallic lithium,[6] and the cleavage of allyl halides by lithium,[3,7] are less advantageous and often low-yielding processes. Wurtz coupling, leading to biallyl, is a prominent side reaction when allyl halides are exposed to lithium metal.[3,7]

As a sequel to the observation that anisole could be cleaved by lithium–biphenyl adducts in refluxing tetrahydrofuran (THF) solution,[1c,8] the analogous cleavage reaction of allyl phenyl ether was investigated. Indeed, the cleavage of the allyl ether by the 2:1 lithium–biphenyl adduct proceeded rapidly even below 0°. Subsequently, it was found that lithium metal alone in tetrahydrofuran readily cleaved allyl phenyl ether at −15° to form allyllithium and lithium phenoxide[9] (equation 1).

$$CH_2{=}CH{-}CH_2{-}O{-}C_6H_5 + 2Li \xrightarrow[-15^\circ]{THF} CH_2{=}CH{-}CH_2Li + C_6H_5{-}O{-}Li \quad (1)$$

The yields of allyllithium, as determined by the double titration method of Gilman and Haubein,[10] ranged from 45%, in runs using stoichiometric quantities of lithium metal, up to 65%, when a sixfold excess of lithium was employed. Yet in instances where the yields of allyllithium also were determined by formation of chemical derivatives and subsequent isolation of the pure product (*cf. infra*), the resultant figures were ap-

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(1) Paper IV in the series, Chemistry of Alkali Metal–Unsaturated Hydrocarbon Adducts. Previous papers are (a) J. J. Eisch and W. C. Kaska, *J. Org. Chem.*, **27**, 3745 (1962); (b) J. J. Eisch and R. M. Thompson, *ibid.*, **27**, 4171 (1962); and (c) J. J. Eisch, *ibid.*, **28**, 707 (1963).

(2) Undergraduate Research Participant, National Science Foundation, 1962.

(3) D. Seyferth and M. A. Weiner, *J. Org. Chem.*, **24**, 1395 (1959); **26**, 4797 (1961).

(4) D. Seyferth and M. A. Weiner, *Org. Syn.*, **41**, 30 (1961).

(5) E. J. Lanpher, *J. Am. Chem. Soc.*, **79**, 5578 (1957).

(6) T. E. Londergan, U. S. Patent 2,734,091 (February 7, 1956).

(7) W. Kawai and S. Tsutsumi, *J. Chem. Soc. Japan, Pure Chem. Sect.* **81**, 109 (1960), report the preparation of allyllithium from allyl halides and lithium metal in ethyl ether solution. However, subsequent workers (ref. 3) were unable to achieve satisfactory results with this approach.

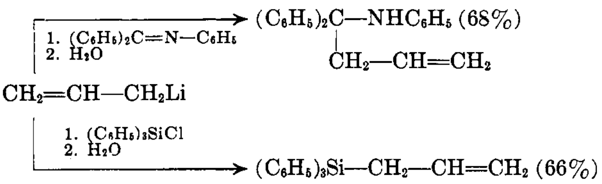
(8) J. J. Eisch and W. C. Kaska, *Chem. Ind.* (London), 470 (1961).

(9) Although the presence of biphenyl had little discernible effect upon the yields of allyllithium obtained from allyl phenyl ether and lithium metal, small amounts of biphenyl served as an excellent initiator for the cleavage. (*Cf.* Paper III of this series, *J. Org. Chem.*, **28**, 707 (1963), for the role of lithium–biphenyl adducts in such cleavage reactions).

(10) H. Gilman and A. H. Haubein, *J. Am. Chem. Soc.*, **66**, 1515 (1944).

proximately 5% higher. This suggests that the yields based upon the titration data are to be viewed as minimum values.

The methods employed for the formation of chemical derivatives of allyllithium illustrate the high reactivity of this organometallic reagent in two types of reactions. The first involved the facile addition of allyllithium to the azomethine linkage of benzophenone anil[11] (equation 2), while the second was the substitutional allylation of chlorotriphenylsilane[12] (equation 3).

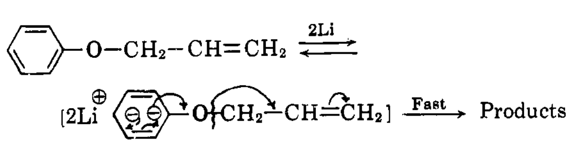


$$CH_2{=}CH{-}CH_2Li \xrightarrow[2.\ H_2O]{1.\ (C_6H_5)_2C{=}N{-}C_6H_5} (C_6H_5)_2C(CH_2{-}CH{=}CH_2){-}NHC_6H_5\ (68\%) \qquad (2)$$

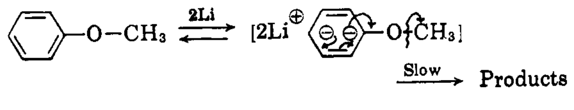
$$CH_2{=}CH{-}CH_2Li \xrightarrow[2.\ H_2O]{1.\ (C_6H_5)_3SiCl} (C_6H_5)_3Si{-}CH_2{-}CH{=}CH_2\ (66\%) \qquad (3)$$

If it is assumed that the preceding reactions (equations 2 and 3) occur quantitatively, the yield of allyllithium (equation 1) must be at least about 70%. The cleavage of allyl phenyl ether by lithium metal, therefore, constitutes a convenient method for the preparation of allyllithium from readily accessible and stable starting materials. Moreover, its preparation in tetrahydrofuran furnishes directly an excellent solvent medium for subsequent chemical reactions.[13] It should be noted that the by-product, phenol, can be separated easily from the hydrolyzed reaction products simply by extraction of the lithium phenoxide with water.

The striking ease with which allyl phenyl ether undergoes lithium metal cleavage contrasts sharply with the inertness of anisole toward lithium metal alone in refluxing tetrahydrofuran.[1c,8] Rather it is with other allylic ether types, such as alkyl cumyl ethers[14] and alkyl benzyl ethers,[15] that a similar facility toward metal cleavage must be sought. In a previous study[1c] the ease with which related unsaturated substrates were cleaved by lithium metal was correlated with the tendency of such substrates to form transitory lithium adducts. In this view the marked facility with which allyl phenyl ether is cleaved, compared with methyl phenyl ether, can be related to the resonance stabilization of *both* the incipient anionic fragments in the transition state of the cleavage reaction (equation 4).



(4)



(5)

Amplification of these principles for the preparation of other useful organometallic compounds is being actively investigated.

Experimental[16]

Cleavage of Allyl Phenyl Ether.—To a 500-ml., three-necked, round-bottomed flask, equipped with a sealed paddle stirrer, a Friedrichs condenser surmounted by a nitrogen inlet tube and a pressure-equalized addition funnel, were added 50 ml. of anhydrous tetrahydrofuran and 4.2 g. (0.60 g.-atom) of freshly cut lithium pieces (2 × 12 mm.). The system was cooled to $-15 \pm 5°$ (external temperature) by an ice–salt bath while a solution of 6.7 g. (0.050 mole) of allyl phenyl ether[17] in 25 ml. of anhydrous ethyl ether was added dropwise to the rapidly stirred lithium suspension. (If a pale green or blue color signaling the start of the cleavage was not noticed after a portion of the allyl phenyl ether was added, a pinch of biphenyl was introduced.[1c]) At the close of the 45-min. addition period the cooling bath was removed and the reaction mixture was stirred for an additional 15 min. The dark red solution was decanted through glass wool from the lithium metal and aliquots were analyzed by the usual double titration technique.[10] Yields obtained in this manner ranged from 62 to 66%.

The titrated yields of allyllithium ranged from 40 to 50% in runs in which 0.10 mole of the allyl phenyl ether in 25 ml. of ethyl ether were added to 0.22 g.-atom of lithium pieces in 50 ml. of tetrahydrofuran over a 60-min. period at 0°.

Derivatives of Allyllithium. (a) With Benzophenone Anil.—A solution of 12.85 g. (0.050 mole) of benzophenone anil in 50 ml. of dry benzene was added to the allyllithium solution obtained from the treatment of 0.050 mole of allyl phenyl ether with 0.60 g.-atom of lithium, according to the first procedure described in the preceding section. The system was allowed to stir for 12 hr. and then was treated with water. The organic components were extracted with ether and the ether layer then dried with anhydrous calcium sulfate. The organic solvents were evaporated and the residue was taken up in a minimum of petroleum ether (b.p. 30–60°). This solution was chromatographed on an alumina column and the 1-allyl-1,1-diphenylmethylaniline was eluted from the column selectively by additional portions of petroleum ether. The total yield of 1-allyl-1,1-diphenylmethylaniline thereby obtained was 10.2 g. (68%), m.p. 75–77° (lit.[11] m.p. 78.5–80°). Recrystallization of this product from 95% ethanol raised the melting point to 77.5–79.5°. Admixture with an authentic sample caused no melting point depression.

(b) With Chlorotriphenylsilane.—A solution of 13.28 g. (0.045 mole) of chlorotriphenylsilane in 50 ml. of anhydrous ethyl ether was added to a solution of allyllithium which was prepared in the aforementioned manner and was estimated to contain 0.031 mole by the double titration method.[10] The resulting solution was stirred at the reflux temperature for 12 hr. and thereupon hydrolyzed. The separated ether layer was dried with anhydrous calcium sulfate and then evaporated. The residual colorless solid was recrystallized from 95% ethanol to yield 9.90 g. (66%) of allyltriphenylsilane, m.p. 88–89° (lit.[12] m.p. 91°).

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[11] *Cf.* H. Gilman and J. J. Eisch, *J. Am. Chem. Soc.*, **79**, 2150 (1957), for the reaction of benzophenone anil with allyl and alkyl Grignard reagents.

[12] R. H. Meen and H. Gilman, *J. Org. Chem.*, **22**, 684 (1957).

[13] For the enhanced rates of organolithium reactions in tetrahydrofuran, *cf.* H. Gilman and B. J. Gaj, *ibid.*, **22**, 447, 1165 (1957), and H. Gilman and S. Gray, *ibid.*, **23**, 1476 (1958).

[14] K. Ziegler, F. Crössman, K. Kleiner, and O. Schäfer, *Ann.*, **473**, 1 (1929); K. Ziegler and H. Dislich, *Chem. Ber.*, **90**, 1107 (1957).

[15] *Cf.* H. Gilman and G. L. Schwebke, *J. Org. Chem.*, **27**, 4259 (1962), for the preparation of benzyllithium from such ether cleavages.

[16] All organometallic reactions were conducted under an atmosphere of dry, oxygen-free nitrogen. The tetrahydrofuran was purified by successive treatments with sodium hydroxide pellets, sodium slices, and lithium aluminum hydride. The tetrahydrofuran was distilled from the lithium aluminum hydride directly into the reaction vessel. All glassware was dried at 120° for at least 4 hr. All melting points are uncorrected.

[17] L. Claisen, *Ann.*, **418**, 78 (1919).

Cleavage of Silicon–Silicon Bonds on an Alumina Column

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In a recent publication from these laboratories,[1] it was proposed that dilute hydrochloric acid promoted the hydrolytic cleavage of the silicon–silicon bonds in 1,4-dihydroxyoctaphenyltetrasilane (II) which were

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[1] A. W. P. Jarvie and H. Gilman, *Chem. Ind.* (London), 1271 (1960).