TABLE IV

PROPERTIES OF DIALKYL SULFIDES AND SULFOXIDES

Sulfide	Bp, °C (mm) Lit.	Bp, °C (mm) Found	$n^{25}D$ Lit.	$n^{25}D$ Found	Yield, % mole	Purity[a]	Ref
Ethyl *n*-butyl	144–142 (?)	71.5 (97)	1.4491[b]	1.4472	55	99.2	*c, d*
Ethyl *sec*-butyl	133.6 (?)	63–64 (66)	1.4477[b]	1.4461	45	99.8	*d*
n-Propyl *n*-butyl	153–154 (?)	77.0 (38)		1.4480	47	99.9	*e*
n-Propyl *sec*-butyl	153–155 (?)	71.2 (41)		1.4472	82	99.9	*f*
Isopropyl *n*-butyl	154–156 (?) 78.5–79 (61)	70 (38)	1.4479	1.4440	49	99.9	*f, g*

Sulfoxide	Bp, °C (mm)	$n^{25}D$	Yield, % mole	Anal,[h] % C Calcd	C Found	H Calcd	H Found	S Calcd	S Found	Ref
Ethyl *n*-butyl	65 (0.6)	1.4662	68							*i*
Ethyl *sec*-butyl	45–48 (0.035–0.05)	1.4687	71	53.68	53.88	10.51	10.49	23.89	23.85	*i*
n-Propyl *n*-butyl	66–67 (0.025)	1.4647	78							*i*
n-Propyl *sec*-butyl	46–47 (0.02)	1.4679	81	56.70	56.69	10.88	10.73	21.62	21.68	
Isopropyl *n*-butyl	46.5–47.6 (0.02)	1.4652	75	56.70	56.59	10.88	10.84	21.62	21.70	*i*

[a] By gas–liquid partition chromatography. [b] At 20°. [c] T. C. Whitner, Jr., and E. E. Reid, *J. Am. Chem. Soc.*, **43,** 639 (1921). [d] D. T. McAllan, T. V. Cullum, R. A. Dean, and F. A. Fidler, *ibid.*, **73,** 3627 (1951). [e] J. von Braun and P. Engelbertz, *Ber.*, **56,** 1573 (1923). [f] M. Vecera, J. Gasparic, D. Snobl, and M. Jurecek, *Chem. Listy.*, **50,** 770 (1956). [g] F. Drahowzal and D. Klammann, *Monatsch.*, **82,** 594 (1951). [h] Performed by Spang Microanalytical Laboratories, Ann Arbor, Mich. [i] No physical properties of the compounds were given: V. Horak and J. Pecka, *J. Chromatog.*, **14,** 97 (1964).

ture of hydrocarbons obtained from the Phillips Petroleum Co. Two analyses were performed on the gas from each run, and the reported compositions are average values.

The rate constants were obtained from a plot of log ($V_\infty - V_t$) *vs.* time, where V_∞ is the total volume of gas produced in the run and V_t is the volume at time t. A good straight line could be drawn through the points obtained for the first 50–60% of reaction. There was usually a slight deviation toward a more rapid reaction by the second half-life and this became more pronounced as the run progressed. Two or more runs were made on each compound at each temperature. It was determined that the copper surface of the reactor was not significantly affecting the reaction by performing one run in which the surface area of copper was doubled by adding copper shot to the reactor.

Preparation of Sulfides.—The sulfides were prepared by adding the appropriate mercaptan to an equimolar solution of sodium ethoxide in absolute ethanol, then adding an equimolar quantity of the appropriate alkyl bromide. The reaction mixtures were allowed to stand for at least 16 hr at room temperature and diluted with water and the sulfides were extracted with 60–75° boiling petroleum ether which had been shaken with concentrated sulfuric acid, washed with sodium hydroxide, and distilled. The extracts were dried over calcium chloride and distilled in an 18-cm column packed with glass helices. The pertinent data are given in Table III.

Preparation of the Sulfoxides.—The sulfoxides were prepared by oxidation of the appropriate sulfides using an equimolar quantity of 30% hydrogen peroxide in *t*-butyl alcohol.[8] The reaction mixtures were concentrated by evaporating the solvent in a stream of air and distilling the resulting oil at reduced pressure. The distillates were stored over Linde 13 X Molecular Sieves. In all cases the distillates were water white liquids with a pleasant but almost imperceptible odor quite unlike the sulfides from which they were derived. The pertinent data are given in Table IV.

Acknowledgments.—We are indebted to Professor A. R. Emery for a computer program which aided in the processing of compositional data and to the Division of Literature, Science, and the Arts for funds to pay for the chemicals and the microanalyses.

Alkynyllithium Compounds from the Reaction of 1-Alkenes with Lithium

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Several 1-alkenes have been found to react with lithium dispersion under relatively mild conditions (20–120°) to give the corresponding 1-alkynyllithium compounds and lithium hydride as the major products. The yields of the alkynyllithium compounds varied markedly with variations in chain length of the 1-alkene, with the highest yield (65%) of organolithium compound obtained from the reactions of 1-hexene with lithium. Attempts to extend this novel reaction to include olefins other than 1-alkenes were unsuccessful.

The literature contains many reports describing reactions of alkali metals with olefins. For example, olefins containing double bonds in conjugation with centers of unsaturation, such as arylethylenes and 1,3-butadienes, readily form alkali metal addition compounds in ether solvents.[2] Under somewhat more vigorous conditions, nonactivated olefins are known to undergo metalations, dimerizations, and polymerizations with alkali metals.[3]

$$R_2C{=}CH_2 + M \longrightarrow [R_2CCH_2]^{-}M^{+}$$
$$R = \text{unsaturated group}$$

This paper describes the finding that some 1-alkenes react with lithium dispersion, under mild conditions, to give primarily the corresponding alkynyllithium compounds (up to 65%) and lithium hydride, according to the following equation.

$$RCH{=}CH_2 + 4Li \longrightarrow RC{\equiv}CLi + 3LiH$$
$$R = n\text{-}C_2H_5\text{-}n\text{-}C_{10}H_{21}$$

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(1) To whom inquiries concerning this paper should be sent.

(2) G. E. Coates, "Organo-Metallic Compounds," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1960, pp 27–42.

(3) See, for example, W. V. Bush, G. Holzman, and A. W. Shaw, *J. Org. Chem.*, **30,** 3290 (1965).

TABLE I

REACTIONS OF 1-ALKENES WITH LITHIUM DISPERSION

Expt	Olefin	Temp, °C	Time, hr	Promoter, mole %	Yield of alkynylsilane, %	Yield of alkenylsilane, %
1	1-Pentene	30	1.5		37	13
2	1-Hexene[a]	64	1.5		65.3	3.7
3	1-Heptene	82	1.5		41	
4	1-Octene[a]	100	2.25		0	
5	1-Octene[b]	100	1.5	[b]	21.8	
6	1-Octene	100	4	H_2O, 4	22.6	
7	1-Octene	100	1	H_2O, 8	45.7	
8	1-Octene	100	1.3	H_2O, 12	29	
9	1-Octene	100	2.15	CH_3OH, 8	35.4	
10	1-Octene	100	4	HCl, 5	34	
11	1-Octene	100	4	$(CH_3)_2NH$, 8	52.5	
12	1-Octene	100	4	$C_{12}H_{25}(CH_3)NH$, 4	35.2	
13	1-Octene	100	5	$C_4H_9C{\equiv}CH$, 8	36	
14	1-Decene	100	3.25	H_2O, 8	15	
15	1-Dodecene	100	2	$(CH_3)_2NH$, 5	9.4	

[a] Distilled from lithium aluminum hydride, under argon, immediately before use. [b] The 1-octene used in this experiment had been stored in a bottle for 3 years and contained a high concentration of "active" impurities.

As an example of this novel reaction, neat 1-hexene was converted into 1-hexynyllithium in 65% yield by lithium dispersion (particle size <100 μ) within 1 hr at the reflux temperature of the olefin (64°). The reaction was observed to begin almost immediately as evidenced by the formation of a white solid. No gas evolution was apparent during the course of the reaction. Subsequent to the 1-hr reaction time, there was no visual evidence for any unreacted lithium. Gas phase chromatographic and infrared spectral analyses showed that the excess olefin present in the reaction was essentially unchanged.

The 1-hexynyllithium was characterized by treatment with chlorotrimethylsilane to give 1-hexynyltrimethylsilane in 65% yield (based on lithium employed).

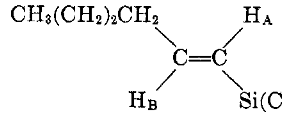
$$n\text{-}C_4H_9C{\equiv}CLi + ClSi(CH_3)_3 \xrightarrow[\text{excess olefin}]{\text{THF}} n\text{-}C_4H_9C{\equiv}CSi(CH_3)_3$$

The infrared and nmr spectra supported the structure assignment. Also, the compound was shown to be identical with a sample prepared by the metalation of 1-hexyne with *n*-butyllithium and subsequent coupling of the alkynyllithium compound with chlorotrimethylsilane.

The solid formed during the reaction of 1-hexene with lithium dispersion was identified as lithium hydride by X-ray powder diffraction analysis. Furthermore, the gas evolved during hydrolysis of the solid was shown to be hydrogen by mass spectral analysis.

The *approximate* quantity of lithium hydride formed during the reaction was determined by measuring the hydrogen evolution resulting from hydrolysis of the reaction mixture freed of the organolithium compound. Based on the reaction's proposed stoichiometry, three-fourths of the lithium should have been converted to lithium hydride, and, consequently, on hydrolysis, the quantity of hydrogen should approach 0.75 mole/g-atom of lithium used. Any unconsumed lithium would afford 0.5 mole hydrogen/g-atom of lithium. The quantity of hydrogen evolved from a typical run was *ca* 0.78 mole/g-atom of lithium, which supports the proposed stoichiometry.

In addition to isolating 1-hexynyltrimethylsilane from the reaction of 1-hexene with lithium dispersion and subsequent treatment with chlorotrimethylsilane, some (3.7%) 1-hexenyltrimethylsilane was obtained. It is of particular interest to note that this product was predominantly (*ca.* 96%) the *trans* isomer. The structure and geometric configuration of the unsaturated silane were established by spectral analysis; intense infrared absorption bands at 6.13 (C=C), 8.0 [$Si(CH_3)_3$], and 10.08 μ (C=C); H^1 nmr signals for



centered at τ 3.84 and 4.04 (H_B, two triplets, $J_{B\text{-}CH_2}$ = 5.8 cps), 4.4 (H_A, doublet, J_{AB} = 18 cps), 7.85 (α-methylene), 8.6 (β,γ-methylene), 9.04 (methyl), and 9.93 (silylmethyl) in the correct area ratios. These spectral data are in excellent agreement with the data reported by Seyferth and Vaughan for *trans*-propenyltrimethylsilane.[4] Also, the gc retention time of the compound was identical with that of the authentic *trans* isomer, prepared by an alternate procedure.[5]

Since it is expected that the alkenyllithium compounds would maintain their configurational integrity[6] under the conditions of the reaction, it is tentatively concluded that the 1-hexenyltrimethylsilane arises from the coupling of chlorotrimethylsilane with *trans*-1-hexenyllithium.[7]

A somewhat similar distribution of products was obtained from reactions of 1-butene and 1-pentene with lithium dispersion. However, from both experiments, the total yields of organolithium compounds were lower than that realized from the corresponding reaction of 1-hexene (see Table I). Thus, 1-pentene afforded 37% 1-pentynyltrimethylsilane and 13% *trans*-1-pentenyltrimethylsilane; 1-butene gave only *ca.* 3% 1-butynyltrimethylsilane and *ca.* 3% butenyltrimethylsilane.

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(4) D. Seyferth and L. Vaughan, *J. Organometal. Chem.*, **1**, 138 (1963).

(5) C. D. Boaddus, T. J. Logan, and T. J. Flautt, *J. Org. Chem.*, **28**, 1174 (1963).

(6) H. D. Kasez and F. G. A. Stone, "Organometallic Compounds," H. Zeiss, Ed., Reinhold Publishing Corp., New York, N. Y., 1960, p 101.

(7) However, the possibility that any *cis*-1-hexenyltrimethylsilane may have been converted into the *trans* isomer by lithium (in the presence of THF and excess olefin) must be considered; see D. Seyferth, R. Suzuki, and L. G. Vaughan, *J. Am. Chem. Soc.*, **88**, 286 (1966).

Similarly decreased yields were obtained with the higher homologs of 1-hexene. Thus, the reaction of 1-heptene with lithium dispersion was found to afford only 41% of the theoretical quantity of 1-heptynyltrimethylsilane upon derivatization. There was no evidence for the formation of 1-heptenyltrimethylsilane.

Surprisingly, pure 1-octene was found to be quite inert to lithium dispersion, even at 120° for prolonged periods of time.

However, the scope of the lithium–olefin reaction was extended to include 1-octene, 1-decene, and 1-dodecene by the use of chemical "promoters." Thus, the addition of small amounts (4–12 mole %) of various compounds such as ammonia, dimethylamine, methyldodecylamine, water, anhydrous hydrogen chloride, methanol, and 1-hexyne, to dispersions of lithium in these olefins at elevated temperatures (*ca.* 100°) resulted in the formation of the desired alkynyllithium compounds (see Table I). However, the yields of the alkynyllithium compounds again decreased with increasing chain length of the olefin; *i.e.*, 1-octene, 1 decene, and 1-dodecene afforded the organolithium compounds in yields of 53, 15, and 9%, respectively. None of the olefins above C_7 gave any evidence for the formation of alkenyllithium compounds.

Since the reactions of the higher 1-alkenes (C_8–C_{12}) with lithium dispersion were promoted with varying degrees of success by several compounds containing active hydrogen, it was of interest to determine whether a reactive olefin ($<C_7$), rigorously purged of all potential active hydrogen contaminants, would react with the metal. For this purpose, 1-hexene, as a model olefin for study, was freed of active hydrogen components by a distillation from lithium aluminum hydride under an atmosphere of oxygen-free argon immediately before use. The reactivity of the purified 1-hexene was found to be comparable to that observed with the 1-hexene containing impurities.[8] Therefore, this finding demonstrates that the promoter effect is only significant for the olefins above 1-heptene (compare expt 2, 4, and 6 of Table I).

The isolation of small quantities of 1-hexenyltrimethylsilane from reactions of 1-hexene with lithium dispersion suggested the possibility of 1-hexenyllithium as an intermediate in the reaction. Accordingly, it

$$RCH{=}CH_2 + 2Li \longrightarrow [RCH{=}CHLi] + LiH \xrightarrow{2Li} RC{\equiv}CLi + LiH$$

seemed appropriate to attempt to trap this alkenyllithium compound. For this purpose, chlorotrimethylsilane was chosen because it is known to be relatively inert to alkali metals and quite reactive toward organolithium compounds.[9]

In an initial experiment, employing 0.48 mole of 1-hexene, 0.25 g-atom of lithium, and 0.08 mole of chlorotrimethylsilane, 1-hexynyltrimethylsilane was obtained as the predominant product. However, in a repeat run, which utilized a small quantity of tetrahydrofuran to facilitate the coupling reactions of the chlorosilane with any organometallic compounds, 9.1% of *trans*-1-hexenyltrimethylsilane and 0.5% of 1-hexynyltrimethylsilane were obtained. An analogous experiment with 1-octene resulted in a similar product distribution.

Owing to the relatively low over-all yield of the latter two reactions, it is difficult to draw a conclusion as to the significance of alkenyllithium compounds as intermediates in the lithium–olefin reactions.

Attempts to extend the lithium–olefin reaction to olefins other than the 1-alkenes were unsuccessful. Thus, 1,3-pentadiene and 1,5-hexadiene failed to react with lithium dispersion at temperatures of 42 and 60°, respectively. Also, 2-heptene and cyclooctene were inert to the metal. The latter two olefins, of course, could not form alkynyllithium compounds, but the possibility existed for their conversion into 2-heptyne and cyclooctyne, respectively.

Experimental Section

Authentic 1-hexynyltrimethylsilane was prepared from the metalation of 1-hexyne by *n*-butyllithium and subsequent coupling of the hexynyllithium with chlorotrimethylsilane: bp 61–66° (*ca.* 20 mm), n^{25}D 1.4280 (lit.[10] bp 155°, n^{25}D 1.4318); H^1 nmr signals at τ 8.58 (β,γ-methylene), 9.14 (methyl), and 9.9 (silylmethyl) in the correct ratios. The H^1 nmr spectra of the homologs of 1-hexynyltrimethylsilane exhibited the expected similar signals.

All reactions and manipulations involving paraffin-free lithium dispersion, organolithium compounds, and purifications of tetrahydrofuran (THF) were performed under an atmosphere of oxygen-free argon. Nmr spectra were obtained on a Varian Associates HA-100 spectrometer, operating at 100 Mc.

In general, the most convenient apparatus for conducting the reactions of 1-alkenes with lithium dispersion consisted of a three-necked, round-bottom Grignard flask that had a sintered-glass filter incorporated into the taper of the flask immediately above the stopcock. This apparatus allowed the removal, under argon, of the protective paraffin coating from the air-sensitive lithium dispersion by successive washings with hexane and the olefin employed in the reaction. Also, the insoluble lithium hydride was readily removed by filtration under argon. Heating was effected by means of a lamp. Rapid, mechanical stirring was used in all experiments conducted in glassware.

The lithium dispersion, particle size less than 100 μ, and of claimed purity of 99.8% (0.02% Na, 0.07% K), was purchased from the Foote Mineral Co. The olefins, unless stated otherwise, were not purified before use.

The gaseous chemical promoters were added under the surface of the olefin at a constant rate by a power-driven syringe.

In all reactions of 1-alkenes with lithium dispersion, with the exception of 1-butene and propylene which were conducted in an autoclave, the following procedure was employed.

To the modified Grignard flask the desired weight of 50% paraffin-coated lithium (Foote's analysis) was added and the flask was thoroughly flushed with argon. The lithium dispersion was then washed successively with two 50-ml portions of hexane and 20 ml of the olefin to be employed in the reaction. Subsequently, the desired quantity of olefin was added and the mixture was heated to the reflux temperature of the olefin, or for the higher boiling 1-alkenes, to a maximum temperature of *ca* 100°. For the reactions of lithium dispersion with 1-octene and higher olefins, chemical promoters were then added at a uniform rate to the reaction mixture. After stirring for the desired length of time, the reaction mixture was allowed to cool, tetrahydrofuran was added to facilitate the derivatization reaction, and chlorotrimethylsilane was added dropwise, resulting in an exothermic reaction. After *ca.* 1 hr of additional stirring, the liquid portion of the reaction mixture was drained into chilled aqueous ammonium chloride. The organic phase was extracted with ether, dried over sodium sulfate, concentrated, and distilled under vacuum. The distillates were qualitatively analyzed by infrared and H^1 nmr spectroscopy, and quantitatively analyzed by gas phase chromatography.

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[8] Olefins are known to undergo facile autoxidations to form several products that could function as active hydrogen sources; see, for example, H. J. Dauben, Jr., and L. L. McCoy, *J. Am. Chem. Soc.*, **81**, 4863 (1959).

[9] Weyenberg has utilized alkylchlorosilanes in several interesting and somewhat related systems; see, for example, D. Weyenberg, L. H. Toporcer, and A. E. Bey, *J. Org. Chem.*, **30**, 4096 (1965), and references cited therein.

[10] K. C. Frisch and R. B. Young, *J. Am. Chem. Soc.*, **74**, 4853 (1952).

The experiments described below are representative reactions for each of the 1-alkenes that were reactive toward lithium dispersion.

Reactions of 1-Alkenes with Lithium Dispersion. Derivatization with Chlorotrimethylsilane. Hexene-1.—The products resulting from the reaction of 1.75 g (0.25 g-atom) of lithium dispersion and 70 ml (47 g, 0.56 mole) of purified 1-hexene (distilled from lithium aluminum hydride) after 1.5 hr at reflux were treated with 15 ml of tetrahydrofuran and 8.5 g (0.08 mole) of chlorotrimethylsilane. Distillation under vacuum gave the following fractions: (1) 0.25 g of material, bp 62–64° (18 mm), and (2) 6.6 g of material, bp 64–70° (18 mm). Fraction 2 was shown to consist of three compounds by gc; 2.7% of an unknown compound, 6.3% *trans*-1-hexenyltrimethylsilane, and 91% 1-hexynyltrimethylsilane.

The residue remaining in the Grignard flask was washed thoroughly with hexane, and dispersed in *ca.* 50 ml of octane. Water was then slowly and carefully introduced into the system resulting in the evolution of hydrogen. The volume of gas collected corresponded to 0.20 mole at STP [theory = (0.75) (0.25 g-atom of lithium used) = 0.19 mole].

Pentene-1.—The products resulting from the reaction of 1.4 g (0.2 g-atom) of lithium dispersion and 60 ml (38.4 g, 0.55 mole) of 1-pentene, refluxed for 1.5 hr, and subsequently treated with 5 ml of tetrahydrofuran and 8.5 g (0.08 mole) of chlorotrimethylsilane, were distilled to give 3.7 g of material, bp 62–64° (40 mm). A gas phase capillary chromatographic analysis demonstrated that the distillate consisted of 2% of an unknown compound, 26% *trans*-1-pentenyltrimethylsilane, and 72% 1-pentynyltrimethylsilane.

Heptene-1.—The products resulting from the reaction of 1.75 g (0.25 g-atom) of lithium dispersion and 53 ml (37 g, 0.38 mole) of 1-heptene, refluxed for a 1.25-hr period, and subsequently treated with 10 ml of THF and 8.5 g (0.08 mole) of chlorotrimethylsilane, were distilled to give 4.1 g (*ca.* 40%) of 1-heptynyltrimethylsilane, bp 72–82° (12 mm).

Octene-1 (Promoted with Water).—To a mixture of 1.75 g (0.25 g-atom) of lithium dispersion and 70 ml (50 g, 0.45 mole) of 1-octene at *ca.* 100°, 0.4 g (0.022 mole) of water was added over a 1-hr period. After an additional 1.5 hr of stirring, the reaction mixture was allowed to cool to room temperature and 15 ml of THF and 8.5 g (0.08 mole) of chlorotrimethylsilane (dropwise) were added successively. The products obtained on work-up were distilled to give 5.2 g (45.7%) of 1-octynyltrimethylsilane, bp 98–108° (26 mm).

Decene-1 (Promoted with Water).—To a mixture of 1.75 g (0.25 g-atom) of lithium dispersion and 50 ml (37 g, 0.26 mole) of 1-decene at *ca.* 100°, 0.35 g (0.02 mole) of water was added over a 1-hr period. After a 3.5-hr total reaction time, the mixture was allowed to cool, and 15 ml of THF and 8.5 g (0.08 mole) of chlorotrimethylsilane were then added successively. The usual work-up and distillation afforded the following fractions: (1) 0.55 g, bp 86–116° (15 mm), and (2) 2.0 g, bp 116–120° (15 mm). Fraction 1 was shown by gc to consist of a mixture of 81% 1-decene and 19% 1-decynyltrimethylsilane. Fraction 2 consisted of 10% 1-decene and 90% of the alkynyltrimethylsilane. The total yield of 1-decynyltrimethylsilane was 15%.

Butene-1.—A mixture of 3.5 g (0.5 g-atom) of lithium dispersion and an excess of 1-butene was heated at 50° for 16 hr in a rocking autoclave. After exhausting the excess 1-butene, the bomb liner was removed and cooled, and the contents were treated with 50 ml of THF and 17 g (0.16 mole) of chlorotrimethylsilane. After the usual work-up, distillation afforded the following fractions: (1) 0.3 g of a mixture, bp 49–59° (100 mm); (2) 0.21 g of a mixture, bp 55–60° (100 mm); and (3) 0.03 g, bp 61° (100 mm). Fraction 1 was shown to contain *ca.* 36% *trans*-1-butenyltrimethylsilane, 37% 1-butynyltrimethylsilane, and 23% of two unknown compounds by gc. An infrared spectrum of the distillation residue (0.77 g) revealed strong absorption bands at 4.61, 5.23, and 8.0 μ, characteristic of acetylenic, allenic, and trimethylsilyl groups, respectively.

Propene.—A mixture of 3.5 g (0.5 g-atom) of lithium dispersion and an excess of propene was agitated in a stirred autoclave at 60° for 24 hr without evidence of any reaction.

Reaction of 1-Hexene, Lithium, and Trimethylchlorosilane. In the Absence of THF.—A mixture of 40 g (0.48 mole) of 1-hexene, 3.5 g (0.25 g-atom) of lithium dispersion, and 8.5 g (0.08 mole) of trimethylchlorosilane was heated at reflux for 1 hr. Subsequently, the reaction mixture was cooled and 10 ml of THF was added to insure complete coupling of any organolithium compounds with the chlorosilane. Work-up in the usual manner afforded 4.04 g of a mixture comprised of 6% *trans*-1-hexenyltrimethylsilane and 94% 1-hexynyltrimethylsilane, as evidenced by gas phase chromatography.

In the Presence of THF.—A mixture of 67 g (0.8 mole) of 1-hexene, 2.8 g (0.4 g-atom) of lithium dispersion, 13.5 g (0.13 mole) of trimethylchlorosilane, and 20 ml of THF was heated at reflux for 12 hr. After standing overnight, the reaction mixture was filtered into chilled, aqueous ammonium chloride and worked up in the usual manner. Distillation afforded a 1.33-g fraction, bp 90–96° (90 mm), comprised of 5% of 1-hexynyltrimethylsilane and 93% 1-hexenyltrimethylsilane.

Acknowledgment.—The authors are grateful to Messrs. W. Dittmer and D. Bishop for technical assistance.

Metal Hydrides. Hydrogenation and Isomerization Catalysts

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Several metal hydrides are catalysts for the selective hydrogenation of 1,3-pentadiene and 2-pentyne to *n*-pentenes. The initial rates vary with the particular catalyst in the order: potassium hydride ≫ sodium hydride > magnesium hydride > lithium hydride > zirconium hydride > titanium hydride. The rates of hydrogenation are solvent dependent. In the presence of sodium hydride, 1,3-pentadiene is selectively hydrogenated to pentenes without affecting 1,5-hexadiene present in the same solution. On the other hand, potassium hydride promotes the hydrogenation of nonconjugated dienes to monoolefins. The hydrogenation of 1,3- or 1,5-cyclooctadiene and bicyclo[2.2.1]heptadiene produced, in addition to the expected monoolefins, *cis*-bicyclo[3.3.0]oct-2-ene and nortricyclene, respectively. Potassium hydride is a very effective catalyst in the absence of hydrogen for the isomerization of cyclooctadienes to *cis*-bicyclo[3.3.0]oct-2-ene. Stereochemical and deuterium tracer studies indicate that at least some of the alkali metal hydrides function as heterogeneous catalysts.

Lithium aluminum hydride ($LiAlH_4$) is a homogeneous catalyst for the selective hydrogenation of 2-pentyne and conjugated dienes to monoolefins.[1] The hydride promotes hydrogenation by adding to the unsaturated system to form an intermediate metal alkyl which subsequently undergoes hydrogenolysis (eq 1 and 2).

$$CH_2{=}CHCH{=}CHCH_3 + LiAlH_4 \longrightarrow Li(n\text{-}C_5H_9)AlH_3 \quad (1)$$

$$Li(n\text{-}C_5H_9)AlH_3 + H_2 \longrightarrow n\text{-}C_5H_{10} + LiAlH_4 \quad (2)$$

It has been claimed that group I and II metal hydrides also will add to double bonds to form metal

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[1] L. H. Slaugh, *Tetrahedron*, **22**, 1741 (1966).