stant was determined as 0.978 ± 0.002 for 0.470 and 0.990 *M* lithium nitrate in liquid ammonia at −33°. The constant was calculated from the standard values given by Gmelin.[11]

The cell was placed in 850 ml of a liquid ammonia suspension of dilithium acetylide[12] at −33° in a 1-l. flask. Acetylene was admitted to the suspension by means of a fritted-glass disperser at a rate of 146 ml/min. Aliquots of 5 ml each were withdrawn at 8.8-min intervals by means of a pipet whose only entrance was a medium-fritted-glass filter, so that only dissolved material was withdrawn. At the same time, the resistance of the solution was determined. Each aliquot was hydrolyzed at once in water and the pipet thoroughly washed with water. The solution was boiled until evolution of ammonia ceased, cooled, and titrated with 0.1071 *N* HCl to the phenolphthalein end point. The results are plotted in Figure 1. This is the standard curve used in the rate studies. The concentration of the saturated solution was determined as 1.04 *M*.

Rate of Solution of Dilithium Acetylide.—A slight excess of dilithium acetylide was suspended in 850 ml of liquid ammonia at −33° and acetylene was admitted at a rate of 146 ml/min. The resistance of the solution was determined at periods varying from 10 sec at the beginning to 120 sec at the end of the experiment. The concentration of the solution at each reading was determined from the standard curve (Figure 1) and the data were plotted as concentration *vs.* time (Figure 2).

Example of a Saturated Ethynylation Reaction (3-Methyl-1-penten-4-yn-3-ol).—To a 240-ml, nitrogen-swept flask, equipped with a magnetic stirrer, Dry Ice condenser, dropping funnel, and inlet tube, was added 3.8 g (0.10 mole) of dilithium acetylide, and 100 ml of ammonia was condensed over it. Acetylene was bubbled through the suspension at a rate of 146 ml/min until a nearly clear solution was obtained (12–15 min). The solution was then cooled to −55° by means of a Dry Ice–acetone bath, and neat methyl vinyl ketone (6.3 g, 0.90 mole) was added dropwise over a 10-min period. The reaction mixture was held at −55° with continuous acetylene passage for 2 hr and then gradually allowed to warm to −5° over a 1-hr period while 100 ml of ether was added dropwise. Then the reaction mixture was hydrolyzed over a mixture of ice and excess glacial acetic acid. Solid sodium chloride was added, and the mixture was neutralized with a saturated sodium bicarbonate solution. The mixture was extracted twice with ether; the combined extracts were dried over anhydrous sodium sulfate and weighed. An aliquot (0.5–0.7 g) was taken and titrated with $AgNO_3$. The yield was calculated by the method of Siggia.[13] The average yield obtained (three runs) was 6.7 g (77.5%) of 3-methyl-1-penten-4-yn-3-ol.

Example of a "Crowding" Reaction (3-Methyl-1-penten-4-yn-3-ol).—To a 250-ml, nitrogen-swept flask, equipped with a magnetic stirrer, Dry Ice condenser, dropping funnel, and inlet tube, was added 7.9 g (0.208 mole) of dilithium acetylide, and 100 ml of ammonia was condensed over it. Acetylene was bubbled through the suspension at a rate of 146 ml/min until a 50% excess had been added (about 15 min). The reaction mixture still appeared to be a gray suspension. The reaction mixture was cooled to −55° and, with acetylene passage continuing, neat methyl vinyl ketone (12.8 g, 1.82 mole) was added dropwise over a 25-min period. At the end of this period a slightly hazy yellow solution formed, indicating that all of the dilithium acetylide had been consumed. The reaction mixture was held at −55° for 2 hr with continuous acetylene passage, then gradually allowed to warm to −5° over a 1-hr period while 100 ml of ether was added dropwise. The mixture was then hydrolyzed, extracted, and analyzed as in the previous example. The yield of alkynol was 72%.

Registry No.—Delithium acetylide, 1070-75-3; benzalacetone, 122-57-6; β-ionone, 79-77-6; diisopropyl ketone, 123-19-3; ethyl β-chlorovinyl ketone, 105-32-8; methyl vinyl ketone, 78-94-4; mesityl oxide, 141-79-7; cyclopentanone, 120-92-3; 2 (R,R′ = $-(CH_2)_4-$), 5325-62-2.

Acknowledgments.—We wish to thank Abbott Laboratories for samples of ethyl β-chlorovinyl ketone and its alkynol, Placidyl®, and Chas. Pfizer & Co. for samples of methyl vinyl ketone. We also thank Mr. R. C. Morrison for the gas chromatographic studies and Mr. L. C. Mitchem for synthesis of the dilithium acetylide.

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[11] Gmelins Handbuch der Anorgischen Chemie, System No. 20 (Lithium), p 105.

[12] Available from Lithium Corp. of America, Bessemer City N. C.

[13] S. Siggia, "Quantitative Organic Analysis *via* Functional Groups," 3rd ed, John Wiley and Sons, Inc., New York, N. Y., 1963, p 381.

A Carbonyl Olefination Reaction Using Silyl-Substituted Organometallic Compounds

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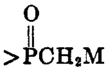
Trimethylsilyl-substituted organometallic compounds, $(CH_3)_3SiCHMR$, have been demonstrated to be effective intermediates in the conversion of carbonyl compounds to the corresponding olefins, $>C{=}CHR$. These conversions, which involve the formation and decomposition of $\gtrdot SiCHRC(OM)<$ compounds, appear to be closely related to the classical methods of preparing olefins from reactions of phosphorus-substituted carbanions with aldehydes and ketones.

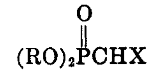
During the past few years, several methods have been developed for the conversion of carbonyl compounds to the corresponding methylene derivatives. The most frequently used methods for this conversion have the common feature of employing phosphorus-substituted carbanions, *i.e.*, the well-known "Wittig" reagents,[1] which are phosphorus ylides (1), as the reactive intermediates. The phosphinylalkyl metal compounds (2) resulting principally from the work of Horner and coworkers[2] and the phosphonate carbanions (3) of Wadsworth and Emmons[3] have been similarly employed. Corey and Kwiatkowski have extended this series of phosphorus-substituted carb-


$\gtrdot\overset{+}{P}\overset{-}{C}H_2$

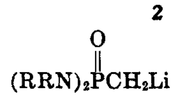
1


$>\overset{O}{\overset{\|}{P}}CH_2M$

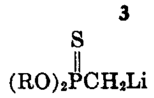
2


$(RO)_2\overset{O}{\overset{\|}{P}}CHXM$

3


$(RRN)_2\overset{O}{\overset{\|}{P}}CH_2Li$

4a


$(RO)_2\overset{S}{\overset{\|}{P}}CH_2Li$

4b

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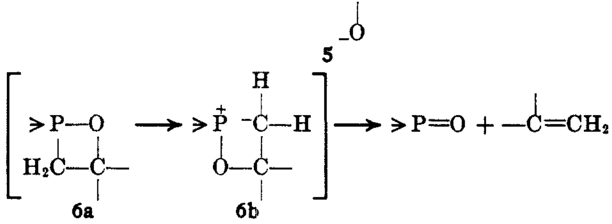
[1] For a review of the Wittig reagent, see A. W. Johnson, "Ylid Chemistry," Academic Press Inc., New York, N. Y., 1966.

[2] L. Horner, H. Hoffmann, H. G. Wippel, and G. Klahre, *Chem. Ber.*, **92**, 2499 (1959).

[3] W. S. Wadsworth, Jr., and W. D. Emmons, *J. Am. Chem. Soc.*, **83**, 1733 (1961).

anions to include α-lithiophosphonic acid bisamides[4] (**4a**) and O,O′-dialkyl α-lithiophosphonothioate esters[5] (**4b**). These latter reagents appear to offer some advantage over the classical synthetic intermediates. However, olefination reactions of this type are not unique to organophosphorus compounds. This has been exemplified by two recent reports which describe the use of boron-[6] and sulfur-substituted[7] carbanions as olefin-forming reagents.

Although the details of the mechanisms for these reactions are too complex for discussion herein, it is reasonable to consider the phosphorus olefination reactions, at least, in terms of the generalized eq 1.



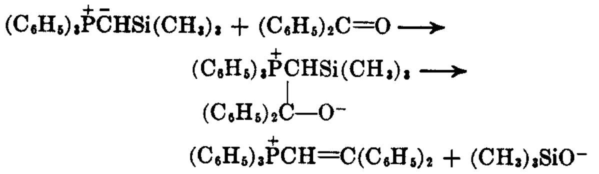
(1)

Thus, the essential features of the reaction involve formation of the alkoxide (**5**), attack of this alkoxide on the phosphorus atom to form a pentacovalent intermediate (**6a**) or, possibly, an intermediate in which the α-carbon atom bears some negative charge (**6b**), and, finally, extrusion of the phosphoryl moiety with concommitant formation of the olefin. The major driving force for reaction is provided by phosphoryl bond formation.

Upon consideration of this information it was felt that similar over-all conversions of carbonyl compounds to olefins could be effected using silicon-substituted carbanions since silicon, like phosphorus, (a) is readily attacked by alkoxides, (b) forms strong bonds with oxygen, and (c) has d orbitals which can conceivably enter into pentacovalent bond formation.[8] Also, interrelated with (b) is the fact that the silanolate moiety, like the phosphoryl moiety, is a good leaving group (eq 2).

$$\gtrdot\mathrm{SiCR_2M} + {>}\mathrm{C{=}O} \longrightarrow \gtrdot\mathrm{SiCR_2}(\mathrm{-C(OM)<}) \longrightarrow \gtrdot\mathrm{SiOM} + \mathrm{R_2C{=}C{<}} \quad (2)$$

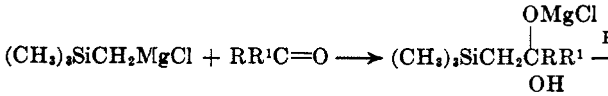
Additional information in support of the feasibility of effecting β-silyl-substituted alkoxide to olefin conversion reactions was provided by the report[9] of Gilman and Tomasi in 1962 describing the formation of tetraphenylallene from the reaction of $(C_6H_5)_3\overset{+}{P}\overset{-}{C}HSi(CH_3)_3$ with benzophenone. To rationalize the formation of the allene, these workers proposed a reaction scheme involving the elimination process given in eq 3. However, a similar reaction attempt with 4,4′-bis(dimethylamino)benzophenone was unsuccessful. Furthermore, no effort was made to extend the olefin-forming reaction to include silanes other than the atypical phosphorus-substituted silicon compound.



$$(C_6H_5)_3\overset{+}{P}\overset{-}{C}HSi(CH_3)_3 + (C_6H_5)_2C{=}O \longrightarrow (C_6H_5)_3\overset{+}{P}CH(C(C_6H_5)_2O^-)Si(CH_3)_3 \longrightarrow (C_6H_5)_3\overset{+}{P}CH{=}C(C_6H_5)_2 + (CH_3)_3SiO^- \quad (3)$$

We now report the results of a study which clearly demonstrate that carbonyl olefination reactions can be effected by utilizing common silyl-substituted carbanions.

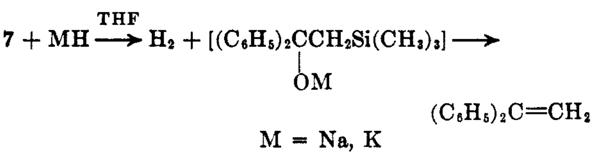
A series of four β-silylcarbinols (**7**–**10**) was prepared by reactions of trimethylsilylmethylmagnesium chloride with the appropriate carbonyl compound. In accordance with the literature,[10] each of the carbinols was obtained in fair yield and, consequently, it is apparent that the magnesium alkoxides are not prone to undergo the desired elimination process (eq 4).



$$(CH_3)_3SiCH_2MgCl + RR^1C{=}O \longrightarrow (CH_3)_3SiCH_2C(OMgCl)RR^1 \xrightarrow{H^+} (CH_3)_3SiCH_2C(OH)RR^1 \quad (4)$$

7, $R,R^1 = C_6H_5$
8, $R = H; R^1 = C_6H_5$
9, $R = H; R^1 = n\text{-}C_7H_{15}$
10, $R = R^1 = CH_3$

To test the relative stability of the corresponding sodium and potassium alkoxides, **7** was treated with both sodium and potassium hydrides in tetrahydrofuran (eq 5). In contrast to the magnesium alkoxide,



$$\mathbf{7} + MH \xrightarrow{THF} H_2 + [(C_6H_5)_2C(OM)CH_2Si(CH_3)_3] \longrightarrow (C_6H_5)_2C{=}CH_2 \quad (5)$$

$$M = Na, K$$

the sodium and potassium salts underwent the desired decompositions to give 1,1-diphenylethylene in yields of 67 and 86%, respectively (see Table I, expt 1 and 2).

TABLE I
β-SILYLCARBINOL TO OLEFIN CONVERSIONS

Expt no.	Carbinol	Base	Olefin	Yield, %
1	$(C_6H_5)_2C(OH)CH_2Si(CH_3)_3$	KH	$(C_6H_5)_2C{=}CH_2$	86
2	$(C_6H_5)_2C(OH)CH_2Si(CH_3)_3$	NaH	$(C_6H_5)_2C{=}CH_2$	67[a,b]
3	$C_6H_5C(OH)HCH_2Si(CH_3)_3$	KH	Polystyrene	91
4	$n\text{-}C_7H_{15}C(OH)HCH_2Si(CH_3)_3$	KH	$n\text{-}C_7H_{15}CH{=}CH_2$	70
5	$(CH_3)_2C(OH)CH_2Si(CH_3)_3$	$t\text{-}C_4H_9OK$	$(CH_3)_2C{=}CH_2$	35[c,d]

[a] Reaction incomplete after 20 hr at *ca.* 50° in tetrahydrofuran. [b] Pure compound not isolated; yield determined by H^1 nmr and glpc analyses. [c] Yield based on isolated 1,2-dibromo-2-methylpropane; therefore the yield from the original reaction was probably significantly higher; no starting material recovered. [d] Room-temperature reaction in tetrahydrofuran.

The potassium alkoxide elimination reaction was essentially complete within 6 hr at room temperature, while the sodium alkoxide elimination had not gone to completion within 20 hr at 50°. This order of reactivity of the alkoxides, *i.e.*, $K \cong Na \gg Mg$, is

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[4] E. J. Corey and G. T. Kwiatkowski, *J. Am. Chem. Soc.*, **88**, 5652 (1966).

[5] E. J. Corey and G. T. Kwiatkowski, *ibid.*, **88**, 5654 (1966).

[6] G. Cainelli, G. Dal Bello, and G. Zubiani, *Tetrahedron Letters*, 4315 (1966).

[7] E. J. Corey and T. Durst, *J. Am. Chem. Soc.*, **88**, 5656 (1966).

[8] See, for example, A. G. Brook, G. E. LeGrow, and D. M. MacRae, *Can. J. Chem.*, **45**, 239 (1967), and references cited therein.

[9] H. Gilman and R. A. Tomasi, *J. Org. Chem.*, **27**, 3647 (1962).

[10] C. R. Hauser and C. R. Hance, *J. Am. Chem. Soc.*, **74**, 5091 (1952).

reasonable from the standpoint of effective electron density on oxygen.

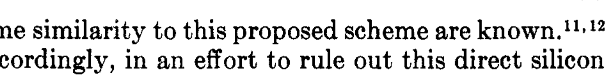
The β-silylcarbinol to olefin conversion reaction was also effected using potassium *t*-butoxide (Table I, expt 5) as the base.

The trimethylsilyl group from reactions of **7–10** with base was isolated as trimethylsilanol, hexamethyldisiloxane, or mixtures of the two.

Although potassium hydride proved to be satisfactory as the base for the conversion process, with the possible exception of the elimination reaction of **8** in which the resulting styrene polymerized, it should be noted that it is also possible to effect the olefin formation reaction by using acid catalysis. Thus, Whitmore and coworkers have demonstrated that propylene formation occurred readily when β-hydroxypropyltrimethylsilane was treated with dilute acid.[11] Since these workers did not report the yield of propylene from their reaction, a tetrahydrofuran solution of **9** was treated with a few drops of concentrated sulfuric acid. It was found that 1-nonene was formed slowly at room temperature, but rapidly at 65°. From this single run, 1-nonene was isolated in 73% yield.

A similar reaction of **8**, but with 10% sulfuric acid, afforded styrene (which polymerized on work-up) in apparent quantitative yield during 3 hr at 60°.

There is the remote possibility that the olefination reaction did not proceed by the scheme outlined in eq 2 but occurred by an alternate pathway involving nucleophilic attack of hydrides (eq 6, where $N^- = H^-$) on the silicon atom. Elimination reactions bearing



$$\text{HOCCH}_2\text{Si}\lessdot + \text{N}^- \longrightarrow \,\gtrdot\text{SiN} + \text{H}_2\text{C}{=}\text{C}{-} + \text{HO}^-$$
$$\gtrdot\text{SiN} + \bar{\text{O}}\text{H} \longrightarrow \text{HN} + \,\gtrdot\text{SiO}^- \qquad (6)$$

some similarity to this proposed scheme are known.[11,12] Accordingly, in an effort to rule out this direct silicon attack mechanism, **9** was treated with triphenylmethylpotassium. The products of the reaction were 1-nonene, triphenylmethane, and trimethylsilanol. There was no evidence for triphenylmethyltrimethylsilane which would result from direct attack on silicon. Therefore, since it appears reasonable to extrapolate the results of this experiment to those reactions in which N^- is a weak nucleophile but a strong base (eq 6), it is unlikely that direct nucleophilic attack on silicon is operational in reactions of MH or *t*-BuOK with the β-silylcarbinols.

The usefulness of the methylene extension reaction using silylalkyl-Grignard reagents is limited by the availability of the precursory chloroalkylsilanes. However, the recent finding[13] that trimethylsilylmethyllithium and *n*-butyldimethylsilylmethyllithium could be obtained from metalations of the parent silanes using the highly reactive *n*-C_4H_9Li·TMEDA (N,N,N′,N′-tetramethylethylenediamine) complex[14–16] suggested that perhaps the silicon olefination method could be made more general by employing this metalation technique to prepare the required precursory silyl-substituted carbanions.

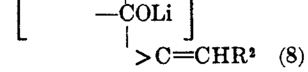
For this purpose, the three silanes, **11–13**, were chosen as model compounds for study. As predicted from earlier studies of the metalations of silanes,[13] sulfides,[17] and phosphines,[16] **11** and **12** underwent rapid, quantitative reactions with *n*-butyllithium to give $(CH_3)_3SiCHLiR^2$ (eq 7). Benzyltrimethylsilane,

$$(CH_3)_3SiCH_2R^2 + n\text{-}C_4H_9Li \longrightarrow (CH_3)_3SiCHLiR^2 \qquad (7)$$

11, $R^2 = (C_6H_5)_2P$
12, $R^2 = CH_3S$
13, $R^2 = C_6H_5$

although relatively unreactive toward *n*-butyllithium, was readily metalated by the *n*-BuLi·TMEDA complex.

Additions of the metalated **11–13** to benzophenone and benzaldehyde resulted in immediate formation of the expected olefins in moderate to high yields (see Table II).



$$(CH_3)_3SiCHLiR^2 + {>}C{=}O \longrightarrow \left[\begin{array}{c}(CH_3)_3SiCHR^2\\ -\text{COLi}\end{array}\right] \longrightarrow {>}C{=}CHR^2 \qquad (8)$$

TABLE II

REACTIONS OF $(CH_3)_3SiCHLiR^2$ WITH CARBONYL COMPOUNDS

Expt no.	R^2 group	Carbonyl	Olefin	Yield,[a] %
1	C_6H_5	$(C_6H_5)_2CO$	$(C_6H_5)_2C{=}CHC_6H_5$	77
2	C_6H_5	C_6H_5CHO	$C_6H_5CH{=}CHC_6H_5$	72[b]
3	C_6H_5	$CH_3C(O)CH_3$	$C_6H_5CH{=}C(CH_3)_2$	50
4	C_6H_5	*c*-$C_5H_{10}CO$	*c*-$C_5H_{10}C{=}CHC_6H_5$[c]	52
5	$(C_6H_5)_2P$	C_6H_5CHO	$(C_6H_5)_2PCH{=}CHC_6H_5$[d]	53[b]
6	$(C_6H_5)_2P$	$(C_6H_5)_2CO$	$(C_6H_5)_2PCH{=}C(C_6H_5)_2$	65
7	$(C_6H_5)_2P(S)$	$(C_6H_5)_2CO$	$(C_6H_5)_2P(S)CH{=}C(C_6H_5)_2$	80
8	CH_3S	C_6H_5CHO	$CH_3SCH{=}CHC_6H_5$[e]	64[b]
9	CH_3S	$(C_6H_5)_2CO$	$CH_3SCH{=}C(C_6H_5)_2$	56

[a] Yields based on isolated, pure compounds with exceptions of expt 3 and 4; the yields of the latter were determined by spectroscopic and glpc analyses of mixtures of starting silane and product. [b] The ratios of the *cis* to *trans* isomers were found to be, within the limits of experimental error, 1:1. [c] S. Trippett and D. M. Walker, *J. Chem. Soc.*, 1266 (1961). [d] Isolated as the corresponding phosphine sulfides. [e] M. C. Caserio, R. E. Pratt, and R. J. Holland, *J. Am. Chem. Soc.*, **88**, 5747 (1966).

The formation of β,β-dimethylstyrene and benzylidenecyclohexane in moderate yields (Table II, expt 3 and 4) from reactions of α-lithiobenzyltrimethylsilane with acetone and cyclohexanone, respectively, demonstrates the feasibility of converting carbonyl compounds having enolizable hydrogens into olefins by the silane method.

It is of interest to note that, from the reactions (Table II above, expt 2, 5, and 8) in which geometrical isomerism was possible, little, if any, stereoselectivity was realized. With the data presently available it is not possible to determine which of several factors are responsible for this lack of stereoselectivity.

The reaction of the trimethylsilyl-substituted phosphorus ylide with benzophenone to give a (diphenylethylidene)triphenylphosphonium salt, as proposed by Gilman and Tomasi[9] (reaction 3), is of interest since the intermediate betaine is potentially capable of undergoing two modes of decomposition, *i.e.*, alkoxide

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[11] F. C. Whitmore, L. H. Sommer, J. Gold, and R. E. Van Strien, *J. Am. Chem. Soc.*, **69**, 1551 (1947).

[12] F. C. Whitmore and L. H. Sommer, *ibid.*, **68**, 481 (1946).

[13] D. J. Peterson, *J. Organometal. Chem.*, **9**, 373 (1967).

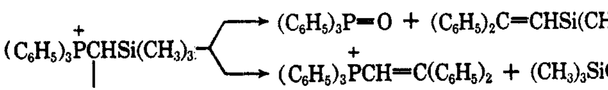
[14] G. G. Eberhardt and W. A. Butte, *J. Org. Chem.*, **29**, 2928 (1964).

[15] A. W. Langer, Jr., *Trans. N. Y. Acad. Sci.*, [II] **27**, 741 (1965).

[16] D. J. Peterson, *J. Organometal. Chem.*, **8**, 199 (1967).

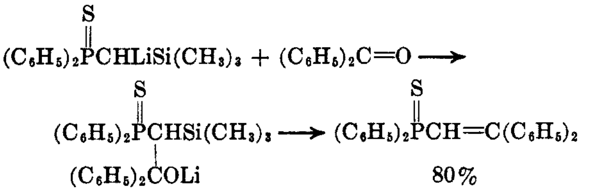
[17] D. J. Peterson, *J. Org. Chem.*, **32**, 1717 (1967).

attack on phosphorus to give a vinylsilane (a normal Wittig reaction), or alkoxide attack on silicon to give the vinylphosphonium salt (eq 9).



$$(C_6H_5)_3\overset{+}{P}CH(C(C_6H_5)_2O^-)Si(CH_3)_3 \rightarrow (C_6H_5)_3P{=}O + (C_6H_5)_2C{=}CHSi(CH_3)_3 \quad\text{or}\quad (C_6H_5)_3\overset{+}{P}CH{=}C(C_6H_5)_2 + (CH_3)_3SiO^- \tag{9}$$

Although the isolation of tetraphenylallene by these workers was indeed consistent with alkoxide attack on silicon, as proposed, the results of their study do not afford information concerning possible competitive attack on phosphorus. In an effort to shed some light on this question, and with the intent of obtaining supporting evidence for the Gilman–Tomasi proposal, (α-lithiotrimethylsilylmethyl)diphenyl sulfide was treated with benzophenone to give an alkoxide which, like the silylbetaine, has two possible pathways for decomposition (eq 10). The isolation of (diphenylethylidene)diphenylphosphine sulfide in 80% yield and the failure to obtain evidence for the formation of the corresponding vinylsilane clearly demonstrates highly selective, if not exclusive, attack on silicon. This finding then, in conjunction with the Gilman–Tomasi results, provides some insight into the ease with which β-silyl-substituted alkoxides undergo the olefination reaction.



$$(C_6H_5)_2\overset{S}{\overset{\|}{P}}CHLiSi(CH_3)_3 + (C_6H_5)_2C{=}O \longrightarrow (C_6H_5)_2\overset{S}{\overset{\|}{P}}CH(C(C_6H_5)_2OLi)Si(CH_3)_3 \longrightarrow (C_6H_5)_2\overset{S}{\overset{\|}{P}}CH{=}C(C_6H_5)_2 \;\; 80\% \tag{10}$$

Experimental Section

All reactions and manipulations involving organometallic compounds and phosphines were performed under an atmosphere of oxygen-free argon. Nmr spectra were obtained on Varian Associates HR-60 (phosphorus) and HA-100 (proton) spectrometers.

The trimethylsilylmethylmagnesium chloride was prepared by a reported procedure,[10] but with tetrahydrofuran substituted for diethyl ether as solvent. Compounds **8**,[10] **10**,[10] and **12**[17] were prepared by reported procedures. Alcohols **7** and **9** were obtained from reactions of trimethylsilylmethylmagnesium chloride with the appropriate carbonyl compound. The physical properties and analyses of these compounds are described below.

Reactions of alcohols **7–10** with alkali metal hydrides are typified by the experiments described for **7** and **9**. For yield data on the reactions not described in the Experimental Section, see Tables I and II.

2-Hydroxy-2,2-diphenylethyltrimethylsilane.—The crude alcohol was purified by crystallizations from hexane, mp 76–78°. The nmr spectrum of the compound in $CDCl_3$ showed a complex multiplet centered (relative to H_2SO_4 capillary reference) at τ 2.6 and singlets at 7.9, 8.1, and 10.05 corresponding to aromatic protons (10), hydroxylic proton (1), methylene protons (2), and silylmethyl protons (9), respectively.

Anal. Calcd for $C_{17}H_{22}OSi$: C, 75.6; H, 8.15. Found: C, 76.3; H, 8.3.

2-Hydroxynonyltrimethylsilane.—The alcohol distilled at 82–83° (1 mm), $n^{25}D$ 1.4400. A proton nmr spectrum of the compound exhibited signals centered (relative to H_2SO_4 capillary reference) at τ 6.27 (HCO), 8.42 (HO), 8.72 [$(CH_2)_6$], 9.13 (CCH_3), 9.22 ($SiCH_2$), and 9.97 [$Si(CH_3)_3$] in the correct area ratios. A mass spectrum of the alcohol was also consistent with the structure assignment with intense peaks at *m/e* 198 ($M - H_2O$), 183 (base peak, $M - CH_3 - H_2O$), and 143 [$M - (CH_3)_3Si$].

Anal. Calcd for $C_{12}H_{28}OSi$: C, 66.6; H, 13.0. Found: C, 66.5; H, 13.1.

Preparation of Diphenylethylidene Methyl Sulfide.—A solution of 5.36 g (0.04 mole) of methylthiomethyltrimethylsilane[17] in 6 ml of tetrahydrofuran was treated with 27 ml of 1.5 *M* *n*-butyllithium (in hexane). Subsequent to stirring for 2 hr, the metalation mixture was added slowly to 7.3 g (0.04 mole) of benzophenone dissolved in 10 ml of THF (exothermic reaction). After stirring for 3 hr, the reaction mixture was hydrolyzed with aqueous ammonium chloride. The ether extracts were combined and concentrated to give an oil that was chromatographed on alumina (Baker's neutral). Hexane eluted 5.2 g of compound melting over the range of 50–56°. Crystallizations from hexane gave 4.8 g (56%) of diphenylethylidene methyl sulfide, mp 72–73°. A proton nmr spectrum of the compound in $CDCl_3$ confirmed the structure assignment with signals (relative to TMS) centered at τ 2.65 and 2.77 for nonequivalent phenyl groups, 3.47 for the vinylic proton (singlet), and 7.7 for the methyl group protons (singlet) in the correct area ratios.

Anal. Calcd for $C_{15}H_{14}S$: C, 79.6; H, 6.2; S, 14.2. Found: C, 79.8; H, 6.13; S, 14.3.

Preparation of (Trimethylsilylmethyl)diphenylphosphine Sulfide.—(Trimethylsilylmethyl)diphenylphosphine, bp 139–143° (0.6 mm) and P^{31} nmr chemical shift (relative to 85% H_3PO_4) of +22.5 ppm, prepared by reaction of the silyl-Grignard with chlorodiphenylphosphine, was converted quantitatively into the phosphine sulfide by treatment with sulfur dispersed in benzene at room temperature. The resulting phosphine sulfide, melting over the range 75–83°, was purified by crystallizations from hexane to give the analytical sample, mp 87–89°. The compound exhibited a P^{31} nmr chemical shift (relative to 85% H_3PO_4) of −38.8 ppm in $CHCl_3$ and proton nmr signals ($CDCl_3$) centered (relative to H_2SO_4 capillary reference) at τ 2.42 (aromatic), 7.95 (doublet, J = 16 cps, methylene), and 9.90 (singlet, silylmethyl) in the correct area ratios.

Anal. Calcd for $C_{16}H_{21}PSSi$: C, 63.1; H, 6.9; P, 10.2; S, 10.5. Found: C, 62.5; H, 7.3; P, 10.2; S, 10.3.

Reaction of (α-Lithiotrimethylsilylmethyl)diphenylphosphine Sulfide with Benzophenone.—To a solution of 6.08 g (0.02 mole) of (trimethylsilylmethyl)diphenylphosphine sulfide in 30 ml of tetrahydrofuran (cooled to 0°) there was added dropwise 14 ml of 1.5 *M* *n*-butyllithium in hexane. Subsequent to the addition the reaction mixture was stirred at 0° for 1.5 hr and was then added to 3.64 g (0.02 mole) of benzophenone dissolved in 10 ml of tetrahydrofuran. After 0.5 hr, the reaction mixture was hydrolyzed by pouring into aqueous ammonium chloride. The ether extracts on concentration afforded 7.6 g of compound melting over the range of 110–125°. A P^{31} nmr spectrum of the crude material in $CHCl_3$ gave rise to a single signal at −31 ppm (relative to 85% H_3PO_4).

Chromatography of the material on alumina (Baker's neutral) using benzene as eluent gave 4.2 g of (diphenylethylidene)diphenylphosphine sulfide, mp 128–130°, and 1.3 g of less pure compound, mp 115–131°, which corresponds to an 80% yield.

A proton nmr of the phosphine sulfide in $CDCl_3$ confirmed the structure assignment with signals centered (relative to TMS) at τ 2.2 (*ortho* protons of C_6H_5P), 2.9 (remaining aromatic protons), and 3.2 (doublet, J = 18 cps, vinyl proton). Also, the compound was identical in all respects with the phosphine sulfide prepared by reaction of (diphenylethylidene)diphenylphosphine with sulfur.

Anal. Calcd for $C_{26}H_{21}PS$: C, 78.8; H, 5.3; S, 8.1. Found: C, 78.5; H, 5.3; S, 8.2.

Reaction of (α-Lithiotrimethylsilylmethyl)diphenylphosphine with Benzophenone.—To a solution of 8.1 g (0.03 mole) of (trimethylsilylmethyl)diphenylphosphine in 10 ml of tetrahydrofuran there was added 20 ml of 1.5 *M* *n*-butyllithium in hexane. The reaction was complete within 2 hr as evidenced by P^{31} nmr spectral analysis of the reaction mixture; *i.e.*, the signal at +22.5 ppm for the starting phosphine had completely disappeared and a single signal for the desired lithium compound was apparent at +3.8 ppm (relative to 85% H_3PO_4).

The metalation mixture was then added to 5.46 g (0.03 mole) of benzophenone dissolved in 8 ml of tetrahydrofuran. Subsequent to stirring for 1 hr, the reaction mixture was hydrolyzed with aqueous ammonium chloride. The ether extract gave a yellow solid that was crystallized from an ethanol-benzene solvent mixture to afford 6.5 g (60%) of (diphenylethylidene)-diphenylphosphine, mp 114–116° (sealed capillary). The phosphine gave rise to a P^{31} nmr signal ($CHCl_3$) at +24.2 ppm (relative to 85% H_3PO_4) and proton nmr signals ($CDCl_3$) centered (relative to TMS) at τ 2.6 (aromatic) and 3.1 (doublet, J = 3 cps, vinyl) in the correct area ratios.

Anal. Calcd for $C_{26}H_{21}P$: C, 85.7; H, 5.7. Found: C, 85.4; H, 5.9.

The mother liquor from the above crystallization was chromatographed on alumina (Baker's neutral) under argon atmosphere. Benzene eluted an additional 1.5 g of semisolid material that was triturated with hexane and subsequently filtered to give 0.7 g of crude phosphine, mp 112–115°.

Reactions of 2-Hydroxynonyltrimethylsilane. A. With Potassium Hydride.—To a slurry of 5 g of 40% potassium hydride (freed of its protective coating by hexane washings) dispersed in 50 ml of tetrahydrofuran there was added 10.9 g (0.05 mole) of **9**. Within a few minutes the hydrogen evolution was complete (1.22 l.). Subsequent to stirring for 6 hr at room temperature, the reaction mixture was *carefully* hydrolyzed by pouring into chilled aqueous ammonium chloride. The ether extracts were concentrated and distilled to give 0.55 g of impure 1-nonene, bp 126–143°, and 4.03 g of pure product, bp 143–145°. The yield, based on 4.4 g, was 70%.

B. With Triphenylmethylpotassium.—To a red solution of triphenylmethylpotassium in 25 ml of 1,2-dimethoxyethane, prepared from 6.37 g (0.027 mole) of triphenylmethane, 3.4 g (0.05 mole) of isoprene, and 1 g (0.025 g-atom) of potassium by the method of House,[18] there was added 5.4 g (0.025 mole) of **9** which resulted in a decolorization of the solution. Subsequent to stirring for 1 hr, the reaction mixture was carefully hydrolyzed with aqueous ammonium chloride. Concentration of the ether extracts afforded a semisolid that was shown not to contain triphenylmethyltrimethylsilane by glpc analysis. A proton nmr spectrum of the mixture (in $CDCl_3$) revealed it to be composed of triphenylmethane, 1-nonene, an isoprene dimer,[18] and a small amount of hexamethyldisiloxane. No attempt was made to resolve the mixture.

C. With Sulfuric Acid.—To a solution of 8.68 g (0.04 mole) of **9** in 40 ml of THF there was added 3 drops of concentrated sulfuric acid. The formation of 1-nonene was slow at room temperature (reaction mixture analyzed by glpc), but became quite rapid upon heating to 65°. After 2 hr at the higher temperature, the reaction mixture was water washed and worked up in the usual manner to give 3.68 g (73%) of 1-nonene, bp 143–145°, and 0.9 g of a distillation residue which was composed of starting alcohol and small amounts of three unidentified compounds.

Reaction of (2-Hydroxy-2,2-diphenylethyl)trimethylsilane with Sodium Hydride.—A mixture of 2.7 g (0.01 mole) of the alcohol, 0.6 g (0.012 mole) of 50% sodium hydride, and 20 ml of tetrahydrofuran was heated at *ca.* 50° for 3 hr and then stirred overnight at room temperature. The reaction mixture was then carefully hydrolyzed with aqueous ammonium chloride and concentrated to give an oil that consisted of *ca.* 67% 1,1-diphenylethylene and 33% starting alcohol (infrared and proton nmr spectroscopy and gas phase chromatographic analyses).

Registry No.—**7**, 15096-08-9; **9**, 15096-09-0; diphenylethylidene methyl sulfide, 15096-10-3; (trimethylsilylmethyl)diphenylphosphine sulfide, 4451-97-2; (diphenylethylidene)diphenylphosphine sulfide, 15096-12-5; (diphenylethylidene)diphenylphosphine, 15096-13-6; 1-nonene, 124-11-8; **11**, 4451-96-1.

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Conformational Analysis. LIX. The Relative Stabilities of the *cis*- and *trans*-Dimethylcyclohexanes[1,2]

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The equilibration of the *cis* and *trans* isomers of the 1,2-, 1,3-, and 1,4-dimethylcyclohexanes has been carried out using palladium catalyst at elevated temperatures. The thermodynamic quantities for the isomerization of the diequatorial to the equatorial-axial conformations are as follows: for the 1,2 isomer, $\Delta H°$ = +1.72 kcal/mole, $\Delta S°$ = +0.79 eu; for the 1,3 isomer $\Delta H°$ = +1.81 kcal/mole, $\Delta S°$ = +1.16; and for the 1,4 isomer, $\Delta H°$ = +1.78 kcal/mole, $\Delta S°$ = +1.14 eu. The experimental values for the 1,3 and 1,4 isomers are in agreement with both theoretical and thermochemical values. The values for the 1,2 isomer are somewhat anomalous with reference to the theoretical quantities but in agreement with the thermochemical data.

The conformational energies of the simple alkyl groups are of considerable importance in quantitative conformational analysis, and that of the methyl group is really the cornerstone of the whole subject.[4] From calorimetric studies on the isomers of the 1,3- and 1,4-dimethylcyclohexanes, the conformational enthalpy of the methyl group was determined to be 1.94 ± 0.2 kcal/mole in the gas phase,[5] and 1.66 ± 0.2 kcal/mole in the liquid phase.[6] By direct equilibration methods the value in the liquid phase was determined from these same compounds as 1.97 ± 0.3 kcal/mole.[7]

Results and Discussion

Since we have obtained considerable experience in the equilibrium method during the last few years, it seemed that it would now be desirable to redetermine the value in this way with a higher accuracy. In the present work, the type of experiment and the measurements were the same in principle as previously, but great attention was paid to achieving accuracy. The equilibrations were carried out in sealed tubes with a small amount of palladium catalyst at elevated tem-

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[2] This research was supported by grant PRF 2916 from the Petroleum Research Fund administered by the American Chemical Society.

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