of **5**, the carbon dioxide trapped amounted to 17%, the aniline found was 44%,[33] and the nitrosobenzene detected[36] was 4%. A third reaction with 4.0 mmol of **5** also gave carbon dioxide (11%), aniline (44%),[33] and nitrosobenzene (4%).[36]

**Registry No.**—**2**, 33479-92-4; **3**, 33482-90-5; **4**, 33537-34-7; **4** (phenylthiourea derivative), 33482-91-6; **5**, 18129-63-0; **6**, 33479-90-2; **7b**, 33519-79-8; **11**, 33479-91-3; dodecacarbonyltriiron, 15444-70-9; methanol, 67-56-1; nitrobenzene, 98-95-3; aniline, 62-53-3; *o*-nitrobiphenyl, 86-00-0; nitrosobenzene, 586-96-9.

---

# The Isomerization and Disproportionation of Acylcobalt Carbonyls

WOLFGANG RUPILIUS AND MILTON ORCHIN*

*Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221*

*Received August 27, 1971*

When acylcobalt carbonyls, $RCOCo(CO)_4$, are left standing under a nitrogen atmosphere, they not only slowly isomerize but disproportionate irreversibly to yield a mixture of aldehydes and olefins. Thus when R is $n$-$C_3H_7$, the products are *n*- and isobutyraldehyde and propylene, formed in accordance with the reaction scheme shown in Chart I. The report that nonpolar solvents inhibit the isomerization of acylcobalt carbonyls is confirmed, but this failure is now shown to arise because of the competing disproportionation reaction. In nonpolar solvents the olefin–metal hydride $\pi$ complex required as an intermediate for the isomerization reacts with the acyl compounds to produce the aldehyde and olefin. With polar solvents, however, the $\pi$ complex is rapidly converted to the $\sigma$ complex and thence to the isomerized acylcobalt compound. The implications of these reactions for the mechanism of the oxo reaction in which the acylcobalt carbonyls play a vital role are discussed.

Although the room temperature, spontaneous interconversion of branched and straight chain acylcobalt carbonyls (eq 1) is well documented,[1–6] certain features

$$RCH_2CH_2COCo(CO)_n \rightleftharpoons \underset{COCo(CO)_n}{\overset{RCHCH_3}{|}} \quad (n = 3 \text{ or } 4) \qquad (1)$$

of the isomerization are difficult to explain. Furthermore, these acyl compounds are intermediates in the oxo reaction and whether such interconversions affect the product distribution of the aldehydes, especially in the stoichiometric hydroformylation, has not been explicitly ascertained. Accordingly we undertook an investigation of this reaction in an effort to elaborate the details of the interconversion.

In our initial experiments we planned to prepare the acylcobalt carbonyls by the published procedure (eq 2)

$$RCOX + NaCo(CO)_4 \longrightarrow RCOCo(CO)_4 + NaX \qquad (2)$$

and, after a lapse of time during which interconversion of the acyl compounds would be permitted to proceed, we planned to hydrogenolyze the resulting mixture with $HCo(CO)_4$ (eq 3) in order to duplicate the last step of the stoichiometric hydroformylation.

$$RCOCo(CO)_n + HCo(CO)_4 \longrightarrow RCHO + Co_2(CO)_{4+n} \qquad (3)$$

In the course of studying this reaction, we found, much to our surprise, that aldehydes were formed even before the $HCo(CO)_4$ was added, and that in addition, olefins possessing one carbon less than the starting acyl compound were also formed. This observation indicated that not only were the acylcobalt carbonyls undergoing isomerization but they were disproportionating as well.

## Results and Discussion

Treatment of *n*- and isobutyrylcobalt tetracarbonyl under three different sets of conditions gave the results shown in Table I. These results are most conveniently discussed in terms of the reaction scheme shown in Chart I.

TABLE I

ISOMERIZATION AND DISPROPORTIONATION OF *n*- AND ISOBUTYRYLCOBALT CARBONYL[a]

| Butyrylcobalt carbonyl | Atm | Solvent | Butyraldehydes<br>Yield, mmol[b] | Butyraldehydes<br>*n*, % | Butyraldehydes<br>Iso, % |
|---|---|---|---|---|---|
| *n* | CO | Pentane | 0.15 | 95 | 5 |
| Iso | CO | Pentane | 0.08 | 0 | 100 |
| *n* | $N_2$ | Pentane | 0.55 | 77 | 23 |
| Iso | $N_2$ | Pentane | 0.55 | 8 | 92 |
| *n* | $N_2$ | Ethyl ether | 0.27 | 51 | 49 |
| Iso | $N_2$ | Ethyl ether | 0.07 | 21 | 79 |

[a] 2.6 mmol of $NaCo(CO)_4$, 2 mmol of acyl chloride in 10 ml of solvent for 24 hr. [b] The yields of propylene were proportional to the yields of aldehydes.

Under 1 atm of CO, relatively little of anything happens in 24 hr to either of the acylcobalt carbonyls, probably because the first steps in the reaction sequence involve the loss of CO and hence the reaction is inhibited. However, when the reaction is repeated under $N_2$ rather than under CO, extensive isomerization and disproportionation occurs. The total yield of aldehydes is the same (perhaps fortuitously, exactly the same, 55%) regardless of the structure of the starting isomer. The yield is based on the stoichiometry

$$2RCOCo(CO)_n \longrightarrow RCHO + R_{-H} + Co_2(CO)_{2n} \qquad (4)$$

Under our conditions, the reaction does not go to completion because of the self-inhibiting effect of the CO liberated during the reaction. When ethyl ether rather than pentane is used as a solvent, there is much more extensive interconversion of isomers but appreciably less disproportionation; with isobutyrylcobalt carbonyl, practically no disproportionation occurs.

---

(1) Y. Takegami, C. Yokokowa, Y. Watanabe, H. Masada, and Y. Okuda, *Bull. Chem. Soc. Jap.*, **37**, 1190 (1964).

(2) Y. Takegami, C. Yokokowa, Y. Watanabe, and Y. Okuda, *ibid.*, **37**, 181 (1964).

(3) Y. Takegami, C. Yokokowa, Y. Watanabe, H. Masada, and Y. Okuda, *ibid.*, **38**, 787 (1965).

(4) Y. Takegami, Y. Watanabe, H. Masada, Y. Okuda, K. Kubo, and C. Yokokowa, *ibid.*, **39**, 1495 (1966).

(5) Y. Takegami, C. Yokokowa, and Y. Watanabe, *ibid.*, **39**, 2430 (1966).

(6) Y. Takegami, Y. Watanabe, H. Masada, and T. Mitsudo, *ibid.*, **42**, 206 (1969).

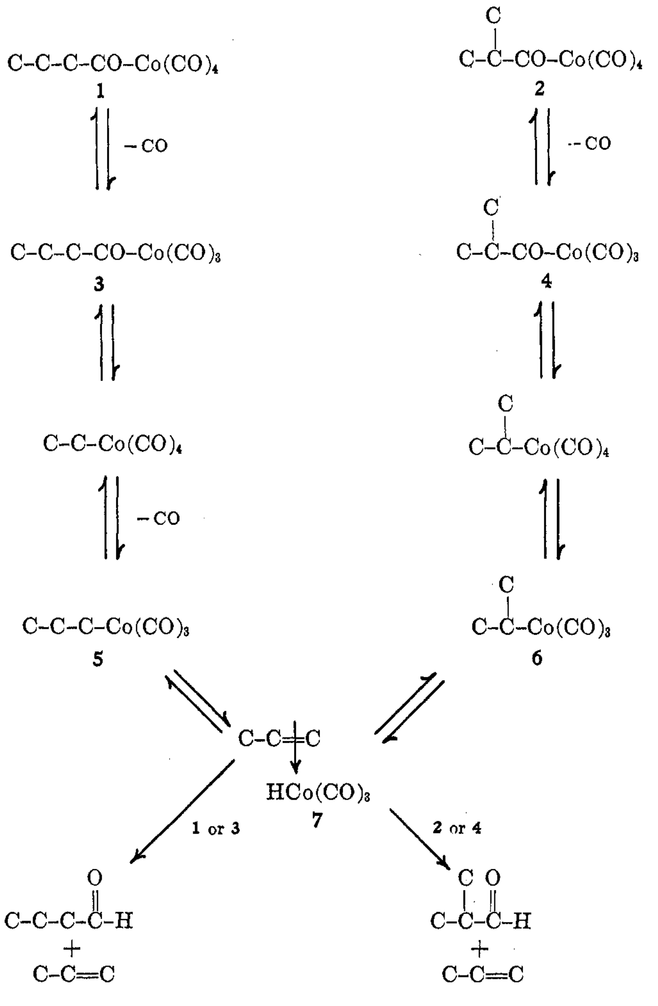
TABLE II

ISOMERIZATION AND DISPROPORTIONATION OF $RCOCo(CO)_4$ [R = $n$-$C_4H_9$ AND $CH_3CH(CH_3)CH_2$][a]

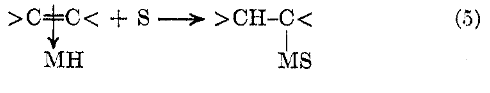
| | | | C₅ Aldehydes | | | Butenes | | | |
|---|---|---|---|---|---|---|---|---|---|
| $RCOCo(CO)_4$ | Hexane, ml | 1-Pentene, mmol | Yield[b] | st[c] | br[d] | Yield[b] | 1- | *cis*-2- | *trans*-2- |
| Pentanoyl | 10 | 0 | 0.30 | 75.0 | 25.0 | 0.47 | 29.7 | 28.1 | 42.2 |
| 2-Methylbutanoyl | 10 | 0 | 0.40 | 3.0 | 97.0 | 0.31 | 35.7 | 25.5 | 38.8 |
| Pentanoyl | 10 | 10 | 0.28[e] | 31.5 | 68.5 | 0.48 | 29.0 | 28.6 | 42.4 |
| 2-Methylbutanoyl | 10 | 10 | 0.21[e] | 32.0 | 68.0 | 0.56 | 29.5 | 27.4 | 43.1 |
| Pentanoyl | 0 | 100[f] | 0.01 | *g* | *g* | 0.26 | 31.6 | 29.7 | 38.7 |
| 2-Methylbutanoyl | 0 | 100[f] | 0.03 | *g* | *g* | 0.13 | 33.3 | 29.8 | 36.0 |

[a] 2.6 mmol of $NaCo(CO)_4$ and 2 mmol of acyl chloride under $N_2$ for 24 hr. [b] mmol. [c] Per cent straight chain. [d] Per cent branched chain. [e] A small amount of $C_6$ aldehydes was observed. [f] The recovered pentene was largely (>95%) 1-pentene and some pentane was present. [g] Too small for accurate determination but approximately 90% branched.

CHART I



It is well known[7] that coordinating solvents (S) promote the rearrangement of metal hydride–$\pi$ olefin complexes to the corresponding $\sigma$ complexes (eq 5). In



$$\underset{\text{MH}}{>C{\downarrow}C<} + S \longrightarrow \underset{\text{MS}}{>CH\text{-}C<} \qquad (5)$$

pentane, there is a relatively high concentration of $\pi$ complex **7** (Chart I) which furnishes the MH required for the hydrogenolysis of $RCOCo(CO)_n$ to aldehyde. In ether, the $\sigma$ complexes **5** and **6** are favored, relative to the $\pi$ complex, and the relative unavailability of MH reduces the rate of hydrogenolysis to aldehyde. Previous reports[8] that propionylcobalt tetracarbonyl does not undergo disproportionation at room temperature are probably in error because ethyl ether was used as a solvent and the reaction time of 30 min was probably too short to observe the slow disproportionation.

Although the disproportionation of $C_4$ acylcobalt carbonyls leads to propylene as the only olefin, similar disproportionation of $C_5$ acylcobalt carbonyls can lead to a mixture of $C_4$ olefins. The results obtained from the disproportionation of pentanoyl- and 2-methylbutanoyl cobalt carbonyls are shown in Table II. One surprising feature of these data is that approximately the same mixture of butenes is obtained from the disproportionation of either of the isomeric acyl compounds. This mixture of butenes does not result from the interconversion of butenes catalyzed by $HCo(CO)_4$, since, if 1-pentene (1.1 ml = 10 mmol) is added to the mixture, essentially no isomerization to 2-pentene can be detected. The results can be rationalized on the basis of an extension of the scheme shown in Chart I. The interconversion of $\sigma \rightleftharpoons \pi$ complexes is very fast compared to the final displacement of the butenes; thus the same mixture of butenes is obtained independent of the starting acyl compound. When 1-pentene is used as solvent (Table II), appreciable butenes are still formed but no aldehydes are produced because, although the liberated $HCo(CO)_3$ is tightly bound in $\pi$ complexes, the large excess of olefin traps the hydrocarbonyl. The possibility that $\sigma$ alkylcobalt carbonyls react with acylcobalt carbonyls to form alkenes and aldehydes in the disproportionation reaction, although unlikely, cannot be completely ruled out. The dramatic effect on the change in aldehyde distribution produced by the presence of 1-pentene is very puzzling and requires further investigation.

When the stoichiometric hydroformylation is carried out under CO, the yield of aldehyde depends on the relative rates of the two major reactions,[9] eq 6 and 7. In

$$RCH{=}CH_2 + HCo(CO)_4 + CO \longrightarrow RCH_2CH_2COCo(CO)_4 \qquad (6)$$

$$RCH_2CHCOCo(CO)_4 + HCo(CO)_4 \longrightarrow RCH_2CH_2CHO + Co_2(CO)_8 \qquad (7)$$

the presence of excess olefin reaction 6 is accelerated and the yield of aldehyde is depressed because the $HCo(CO)_4$ required for reaction 7 is consumed in reaction 6. As a result, when all the $HCo(CO)_4$ has disappeared, substantial cobalt is present as acylcobalt carbonyls. We have demonstrated above that, in the absence of an atmosphere of CO, the acylcobalt compounds isomerize and disproportionate. Thus we might expect that at

---

(7) M. Tsutsui, M. Hankock, J. Ariyoshi, and M. N. Levi, *Angew. Chem., Int. Ed. Engl.*, **8**, 410 (1968).

(8) R. F. Heck and D. S. Breslow *J. Amer. Chem. Soc.*, **83**, 4023 (1961).

(9) L. Kirch and M. Orchin, *ibid.*, **81**, 3597 (1959).

the conclusion of a stoichiometric reaction conducted with excess olefin under CO, were the CO replaced with $N_2$, enhanced yields of aldehyde might be observed. This prediction was fully confirmed, as the data in Table III show. It will be noted from this table that the additional aldehyde formed (17%) after replacement of CO by $N_2$ is relatively richer in branched aldehyde. We have found that the distribution of aldehydes in the stoichiometric reaction carried out from its inception under $N_2$ favors the branched aldehydes; a 37% yield of total aldehydes consisting of 44% straight-chain and 56% branched-chain aldehyde is obtained. Incidentally, if this reaction is allowed to stand for an additional long period (44 hr), there is, as expected, no further change in yield or product distribution.

TABLE III

STOICHIOMETRIC HYDROFORMYLATION OF 1-PENTENE[a]

| Reaction time, hr | Yield of hexanals, % | Composition of hexanals, %: Straight | Branched |
|---|---|---|---|
| 16[b] | 60.5 | 78.2 | 21.8 |
| 19 | 73.4 | 70.8 | 29.2 |
| 24 | 77.5 | 69.1 | 30.9 |
| 42 | 77.5 | 68.4 | 31.6 |

[a] 1.8 mmol of $HCo(CO)_4$, 10 mmol of 1-pentene, 13 ml of pentane. [b] After 16 hr the CO was replaced by $N_2$.

We have commented earlier on the effect of solvents on the isomerization and disproportionation of acylcobalt compounds. The effect of solvents on the stoichiometric hydroformylation reaction should be consistent with their effect on the isomerization and disproportionation of the acylcobalt compounds. We have written the formation of the acylcobalt carbonyls in one step as eq 6. In considering the yield of aldehydes in the stoichiometric reaction under $N_2$ and in the presence of excess olefin, the intermediate steps to the acylcarbonyl are important and require analysis. The first step is unquestionably the loss of CO and the complexation between olefin and $HCo(CO)_3$. The presence of CO or other nucleophiles should slow this reaction. On the other hand, the presence of ether solvents results in the acceleration of the rate of the $\pi \rightarrow \sigma$ conversion and the equilibrium is strongly in favor of the $\sigma$ complex. The concentration of uncomplexed $HCo(CO)_3$ is relatively high, thereby increasing the yield of aldehyde. The data of Table IV show that the presence of ether does increase the yield of aldehydes in the stoichiometric hydroformylation of both 1- and 2-pentene.

TABLE IV

STOICHIOMETRIC HYDROFORMYLATION OF 1- and *cis*-2-PENTENE IN PENTANE. EFFECT OF ETHYL ETHER[a]

| Ether, ml | Pentene | Aldehydes: Yield, % | st,[b] % | br,[c] % |
|---|---|---|---|---|
| 0 | 1- | 42 | 43 | 57 |
| 0 | 2- | 30 | 41 | 59 |
| 4 | 1- | 51 | 53 | 47 |
| 4 | 2- | 38 | 47 | 53 |
| 7 | 1- | 62 | 58 | 42 |
| 7 | 2- | 41 | 50 | 50 |

[a] 1.8 mmol of $HCo(CO)_4$; 10 mmol of pentene; total solvent 10 ml; 4 hr under $N_2$ and then quenched with $PPh_3$. [b] Straight chain. [c] Branched chain.

The stoichiometric hydroformylation of terminal olefins under $N_2$ in the presence of excess olefin is characterized by extensive isomerization of the olefin. The double bond isomerization catalyzed by $HCo(CO)_4$ involves a series of $\sigma \rightleftharpoons \pi$ interconversions and displacement of the $\pi$-complexed olefin by free, starting olefin. The less favored the $\pi$ complexes are relative to $\sigma$ complexes, the less opportunity for isomerization, and vice versa. Accordingly, one might expect that a hydroformylation reaction conducted in ether solvents should lead to less olefin isomerization than similar reactions conducted in a nonpolar solvent. The results shown in Table V confirm this expectation.

TABLE V

EFFECT OF SOLVENT ON ISOMERIZATION OF 1-PENTENE[a]

| Solvent | $HCo(CO)_4$, mmol | Recovered pentene: 1- | 2-(*cis*- + *trans*-) |
|---|---|---|---|
| Pentane | 0.3 | 7 | 93 |
| Pentane | 0.6 | 5 | 95 |
| Ethyl ether | 0.3 | 94 | 6 |
| Ethyl ether | 0.6 | 78 | 22 |
| Tetrahydrofuran | 0.3 | 97 | 3 |
| Tetrahydrofuran | 0.6 | 94 | 6 |
| Dioxane[b] | 0.6 | 100 | 0 |

[a] 10 ml of solvent; 10 mmol of 1-pentene; under $N_2$. After 4 hr, the reaction was quenched with $PPh_3$. [b] Evolution of a small amount of gas was observed.

Finally, it should be noted that the rate of acylcobalt carbonyl isomerization is so slow that such interconversion would not normally affect the distribution of products in either the catalytic reaction carried out under at least 30 atm of CO or in the stoichiometric reaction carried out under CO.

## Experimental Section

Acyl chlorides were commercial products and were distilled before use. $NaCo(CO)_4$ solutions in absolute tetrahydrofuran (THF) were prepared from NaOH and $Co_2(CO)_8$.[10] Most experiments reported in the tables were repeated about three times.

**A. Isomerization and Disproportionation of Acylcobalt Carbonyls Prepared from Acyl Chlorides and $NaCo(CO)_4$.**—A solution of $NaCo(CO)_4$ in dry THF was introduced into a 100-ml flask fitted with a side arm. This operation was carried out in a drybox under $N_2$. The THF was eliminated by distillation *in vacuo* and replaced by the desired solvent. In order to eliminate all the THF it was necessary to heat the $NaCo(CO)_4$ to 60–80° in a good vacuum (oil pump). The desired solvent was then introduced, and again eliminated, by evacuation at 60–80°. This operation was repeated three times. When pentane was the solvent of choice, the $NaCo(CO)_4$ was insoluble and hence the yields of aldehydes and olefins were more difficult to reproduce than when ether solvents were employed. However, the ratios of aldehydes and of olefins in all cases were obtained with good precision. The $NaCo(CO)_4$ and solvent, together with a known quantity of reference compound (for the determination of yields), was connected to a gas burette. After filling the burette and the flask with 1 atm of CO or $N_2$, the acyl chloride was introduced by means of a syringe. The reaction was stopped by adding $PPh_3$ in ethyl ether; the phosphine converts all cobalt carbonyls to insoluble phosphine derivatives. When butenes were present, the mixture was cooled with Dry Ice-acetone and liquid samples were removed for analysis. The reaction product was then distilled at room temperature at low pressure (about 1 mm) and the aldehydes were analyzed by glc. All transfers were carried out in a drybox and in the absence of oxygen, and magnetic stirring was used in all reactions.

**B. Isomerization and Disproportionation of Acylcobalt**

---

[10] W. F. Edgell and J. Lyford, *Inorg. Chem.*, **9**, 1932 (1970).

**Carbonyls during the Stoichiometric Hydroformylation.**—Solvent, olefin, and reference compound were introduced into the 100-ml flask connected to a gas burette. The flask and the burette were filled with 1 atm of CO and then a solution of $HCo(CO)_4$ was introduced. After 16 hr of stirring, the flask was cooled with Dry Ice-acetone and $N_2$ was flushed through until complete elimination of CO took place. The solution was stirred at room temperature and the samples, which were taken after treatment with $PPh_3$, were analyzed by glc.

**Registry No.**—*n*-BuCOCo$(CO_4)$, 33520-58-0; *i*-BuCOCo$(CO_4)$, 33520-59-1; 1-pentene, 109-67-1.

**Acknowledgment.**—The authors are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this investigation.

---

# Silicon-Containing Carbanions. I. Synthesis of Vinyl Thioethers and Vinylphosphonates *via* Silicon-Modified Organolithium Reagents

FRANCIS A. CAREY* AND A. S. COURT

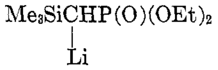
*Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901*

*Received September 9, 1971*

Reactions of diethyl 1-lithio-1-trimethylsilylmethylphosphonate (1) and 1-trimethylsilyl-1-phenylthiomethyllithium (2) with representative aldehydes and ketones are reported which provide useful routes to diethyl vinylphosphonates (**6a–g**) and vinyl phenylthioethers (**18a–g**) by loss of $Me_3SiOLi$ from the presumed intermediate resulting from attack of the organolithium reagent at the carbonyl group. It was found that the exocyclic vinylphosphonate **6e** from cyclohexanone and **1** isomerized to the endocyclic isomer **7** under the reaction conditions. The reactions are not highly stereoselective in that **1** and **2** usually give cis–trans mixtures of olefins from aldehydes and unsymmetrical ketones. Methylation and benzoylation of **1** are described. Reaction of $Me_3SiCH_2OCH_3$ resulted in nucleophilic attack at silicon when *n*-butyllithium was used and proton abstraction from the methyl group when *tert*-butyllithium was used.

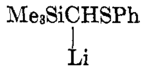
A number of silicon-containing ylides[1] and organometallics[2] have been described in which electron delocalization into silicon 3d orbitals may be important. While the extent of this delocalization remains to be established, the synthetic versatility of carbanions and the expectation of stabilization with modification of chemical reactivity resulting from silicon bonded directly to the carbanionic center suggests the desirability of thorough examination into the reactions of such intermediates.

This report describes the generation and some reactions of diethyl 1-lithio-1-trimethylsilylmethylphosphonate (1) and 1-trimethylsilyl-1-phenylthiomethyllithium (2).



$Me_3SiCH(Li)P(O)(OEt)_2$

1



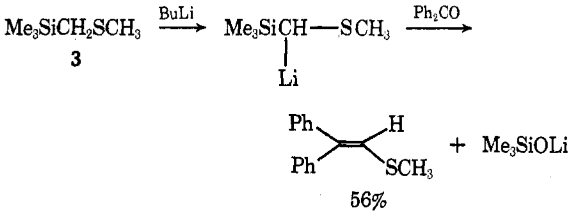
$Me_3SiCH(Li)SPh$

2

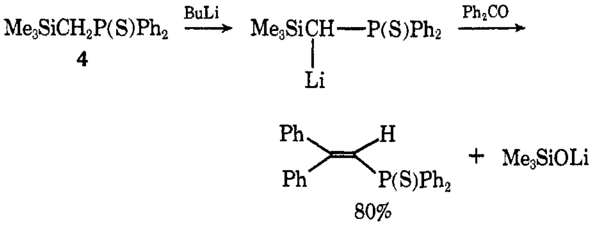
Peterson[3] made the important discoveries that metalation of methylthiomethyltrimethylsilane (**3**) and (trimethylsilylmethyl)diphenylphosphine sulfide (**4**) occurred readily using *n*-butyllithium and that the resulting lithio reagents reacted with benzophenone to afford olefins resulting from loss of $Me_3SiOLi$ (eq 1 and 2).

The lithio reagent from **3** yielded equal amounts of *cis*- and *trans*-2-phenylvinyl methylthioether (64%) when treated with benzaldehyde.

As will be seen from the results to be described these reactions are very general and provide convenient routes to a number of interesting hetero-substituted olefins.



(1)



(2)

## Results and Discussion

**Synthesis of Diethyl Vinylphosphonates.**—Diethyl trimethylsilylmethylphosphonate (**5**) is conveniently prepared by the Arbusov reaction between chloromethyltrimethylsilane and triethyl phosphite.[4] Treatment of **5** in tetrahydrofuran with *n*-butyllithium in *n*-hexane generates the lithio derivative **1**, which reacts with aldehydes and ketones to give good yields of substituted diethyl vinylphosphonates (**6**) according to eq 3. The results are summarized in Table I.

Most of the compounds listed in Table I have previously been prepared by Wysocki and Griffin by the Wadsworth–Emmons procedure employing $CH_2[P(O)(OEt)_2]_2$ in KO-*tert*-Bu-THF.[5] The structures of **6a–e** were confirmed by comparison of their physical

---

[1] (a) N. E. Miller, *J. Amer. Chem. Soc.*, **87**, 390 (1965); (b) N. E. Miller, *Inorg. Chem.*, **4**, 1458 (1965); (c) N. E. Miller and D. R. Mathiason, *ibid.*, **7**, 709 (1968); (d) H. Schmidbaur and W. Malisch, *Chem. Ber.*, **103**, 3448 (1970), and previous papers in this series; (e) D. Seyferth and G. Singh, *J. Amer. Chem. Soc.*, **87**, 4156 (1965); (f) H. Gilman and R. A. Tomasi, *J. Org. Chem.*, **27**, 3647 (1962).

[2] (a) D. J. Peterson, *J. Organometal. Chem.*, **9**, 373 (1967); (b) M. A. Cook, C. Eaborn, A. E. Jukes, and D. R. M. Walton, *ibid.*, **24**, 529 (1970); (c) T. H. Chan, E. Chang, and E. Vinokur, *Tetrahedron Lett.*, 1137 (1970).

[3] D. J. Peterson, *J. Org. Chem.*, **33**, 780 (1968).

[4] A. R. Gilbert, U. S. Patent 2,768,193 (Oct 23, 1956); *Chem. Abstr.*, **51**, 5816 (1957).

[5] D. C. Wysocki, Ph.D. Thesis, University of Pittsburgh, 1967; C. E. Griffin, adviser. See *Diss. Abstr. B*, **28**, 1437 (1967), for a summary.