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HALOMETHYL–METAL COMPOUNDS

LXIII*. DIETHYL LITHIODICHLOROMETHYLPHOSPHONATE AND TETRAETHYL LITHIOCHLOROMETHYLENEDIPHOSPHONATE

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SUMMARY

The action of n-butyllithium in THF at low temperature on diethyl trichloromethylphosphonate and tetraethyl dichloromethylenediphosphonate gave the reagents $LiCCl_2P(O)(OEt)_2$ and $[(EtO)_2(O)P]_2CClLi$, respectively. The hydrolyses of these reagents, some coupling reactions with dimethyl sulfate, allyl bromide and trimethylchlorosilane and their use in the synthesis of chloroolefins are described.

INTRODUCTION

In previous studies we have examined the generation and reactions of functional halomethyllithium reagents such as $(CH_3)_3SiCCl_2Li$ and $[(CH_3)_3Si]_2CClLi$[2], $(CH_3)_3SiCBr_2Li$[3], $(CH_3)_3SiCI_2Li$[1] and $(CH_3)_3SnCX_2Li$ (X = Cl, Br)[4]. We report here concerning the extension of these investigations to similar derivatives of phosphorus, $(EtO)_2(O)PCCl_2Li$ and $[(EtO)_2(O)P]_2CClLi$.

RESULTS AND DISCUSSION

Diethyl lithiodichloromethylphosphonate

Reaction of the readily available[5] diethyl trichloromethylphosphonate with n-butyllithium in THF at −80° proceeded readily as shown in eqn. (1)**. The reagent formed showed normal organolithium reactivity (Chart 1). Also studied was its addition to the C=O bond of aldehydes and ketones. The initial adduct formed underwent elimination of phosphate anion at higher temperatures, similar to the process already known through the pioneering work of Horner[8], and Wadsworth and

$$CCl_3P(O)(OEt)_2 + n\text{-}C_4H_9Li \xrightarrow{\text{THF, }-80^\circ} (EtO)_2(O)PCCl_2Li + n\text{-}C_4H_9Cl \quad (1)$$

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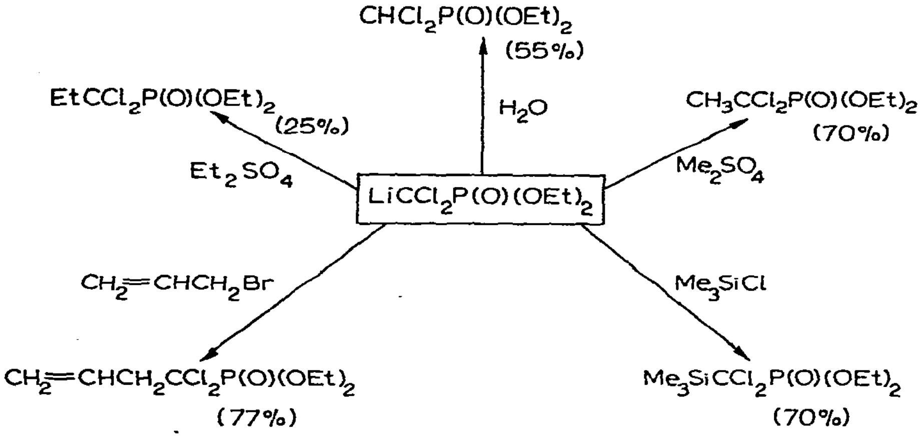
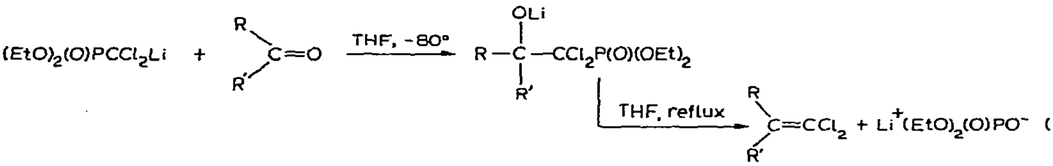
* For Part LXII see ref. 1.

** The formation of reagents of type $LiCH_2P(Y)X_2$ in THF at low temperature by lithium–hydrogen exchange has been reported: $LiCH_2P(O)(OMe)_2$ and $LiCH_2P(S)(OMe)_2$[6]; $LiCH_2P(O)(NMe_2)_2$[7].

CHART 1



Emmons[9]. The 1,1-dichloroolefin yields were moderate (47% with acetone, 55% with pivaldehyde, 69% with benzophenone).



(2)

In the lithiation of $CCl_3P(O)(OEt)_2$ an excess of n-butyllithium must be avoided since polylithiation to give $Li_2CClP(O)(OEt)_2$ appears to be possible. In one experiment where a slight excess of n-butyllithium was used, a ca. 6/1 mixture of $CH_3CCl_2P(O)(OEt)_2$ and $(CH_3)_2CClP(O)(OEt)_2$ was obtained after the mixture had been treated with dimethyl sulfate. It was possible to prepare $(CH_3)_3CP(O)(OEt)_2$ in 57% yield by repeated stepwise lithiation and methylation of diethyl trichloromethylphosphonate without isolation of intermediates.

Tetraethyl lithiochloromethylenediphosphonate

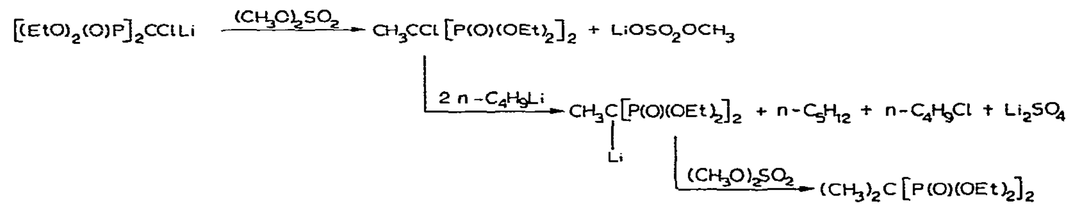
Tetraethyl dichloromethylenediphosphonate, now readily available by the reaction of tetraethyl methylenediphosphonate with sodium hypochlorite solution[10], also was found to undergo lithium–chlorine exchange with n-butyllithium in THF at −80° (eqn. 3). Hydrolysis of the lithium reagent solution gave $HCCl[P(O)(OEt)_2]_2$

$$[(EtO)_2(O)P]_2CCl_2 + n\text{-}C_4H_9Li \xrightarrow{\text{THF, }-80°} [(EtO)_2(O)P]_2CClLi + n\text{-}C_4H_9Cl \quad (3)$$

in 79% yield. Alkylation with dimethyl sulfate and with allyl bromide resulted in $CH_3CCl[P(O)(OEt)_2]_2$ and $CH_2{=}CHCH_2CCl[P(O)(OEt)_2]_2$, respectively. These reactions in general proceeded more slowly than the corresponding reactions of $LiCCl_2P(O)(OEt)_2$. In contrast to the latter, $[(EtO)_2(O)P]_2CClLi$ was stable at room temperature. This was as expected, since similar sodium reagents, *e.g.* $(EtO)_2(O)PCBrNaCO_2C_2H_5$[9], are stable at room temperature. Multiple methylation to give

$(CH_3)_2C[P(O)(OEt)_2]_2$ was also possible with tetraethyl dichloromethylenediphosphonate, but enough n-butyllithium to quench the lithium methyl sulfate formed in the first stage had to be added (Scheme 1).

SCHEME 1



Reaction of tetraethyl lithiochloromethylenediphosphonate with aldehydes and unhindered ketones gave α-chlorovinylphosphonate esters in high yield (eqns. 4 and 5). Little or no reaction occurred with benzophenone.

$$LiCCl[P(O)(OEt)_2]_2 + Me_2C{=}O \xrightarrow[THF]{-80°} \xrightarrow[21h]{reflux} Me_2C{=}CClP(O)(OEt)_2 \quad (85\%) \qquad (4)$$

$$LiCCl[P(O)(OEt)_2]_2 + Me_3CCH{=}O \xrightarrow[THF]{-80°} \xrightarrow[19h]{reflux} Me_3CCH{=}CClP(O)(OEt)_2 \ (83\%) \ (cis/trans \text{ mixture}) \qquad (5)$$

Although this investigation was of limited scope, it is apparent that the two reagents described, $LiCCl_2P(O)(OEt)_2$ and $LiCCl[P(O)(OEt)_2]_2$, will make possible the preparation of many new α-chloroalkyl- and α-chloroalkenylphosphonate esters.

EXPERIMENTAL

General comments

Organolithium reactions were carried out under nitrogen in three-necked flasks of appropriate volume equipped with a stirring unit, an addition funnel, a low temperature thermometer, a nitrogen inlet tube and, if needed, a reflux condenser. Tetrahydrofuran was distilled from lithium aluminum hydride. IR spectra were obtained using a Perkin–Elmer 457A IR spectrophotometer, NMR spectra using a Varian Associates T60 spectrometer. Chemical shifts are reported in δ units, ppm downfield from internal tetramethylsilane.

The new compounds prepared in this study are collected in Table 1.

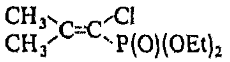
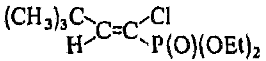
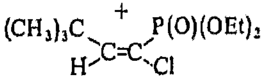
Preparation of tetraethyl dichloromethylenediphosphonate

A modified procedure based on the method of Quimby *et al.*[10] was used. In our hands the NaOCl chlorination of tetraethyl methylenediphosphonate proceeded smoothly only when the reaction mixture was buffered with added sodium bicarbonate.

TABLE 1

PHOSPHONATE ESTERS PREPARED

Compound	*B.p.* [°C (*mmHg*)]	n_D^{25}	*Analysis, found (calcd.) (%)*			*NMR (in* CCl_4*)* δ *(ppm)*
			C	*H*	*Cl*	
$CH_3CCl_2P(O)(OEt)_2$	52–54 (0.07)	1.4480	30.69 (30.66)	5.57 (5.57)	29.93 (30.17)	1.40 (t, *J* 7Hz, 6H), 2.20 (d, *J* 12.5Hz, 3H), 4.27 (quintet with fine splitting, *J* ≈ 7Hz, 4H)
$C_2H_5CCl_2P(O)(OEt)_2$	54 (0.03)	1.4540	33.82 (33.75)	6.10 (6.07)		1.25 (partially obscured t, *J* 7Hz, 3H), 1.43 (t, *J* 7Hz, 6H), 2.35 (quintet, *J* 7Hz, 2H), 4.30 (quintet with fine splitting, *J* ≈ 7Hz, 4H)
$(CH_3)_3CP(O)(OEt)_2$	54 (1.5)	1.4160	49.49 (49.47)	9.86 (9.86)		1.12 (d, *J* 16Hz, 9H), 1.36 (t, *J* 7Hz, 6H), 4.12 (quintet with fine splitting, *J* ≈ 7, 4H)
$CH_2{=}CHCH_2CCl_2P(O)(OEt)_2$	73–74 (0.08)	1.4643	36.78 (36.80)	5.85 (5.79)	27.32 (27.16)	1.40 (t, *J* 7Hz, 6H), 3.03 (t with fine splitting, *J* ≈ 7Hz, 2H), 4.32 (quintet with fine splitting, *J* ≈ 7Hz, 4H), 5.1–5.5 and 5.7–6.5 (m, 3H, vinyl H)
$Me_3SiCCl_2P(O)(OEt)_2$	90–92 (0.9)	1.4614	32.85 (32.77)	6.66 (6.53)	24.22 (24.18)	0.0 (s, 9H), 1.07 (t, *J* 7Hz, 6H), 3.90 (quintet with fine splitting, *J* ≈ 7Hz, 4H)

$[(EtO)_2(O)P]_2CHCl$	108 (0.05)	1.4534			10.90 (10.99)	1.37 (t, *J* 7Hz, 12H), 3.8–4.6 (m, with buried P_2CH, 9H)
$[(EtO)_2(O)P]_2CClCH_3$	95 (0.05)	1.4491	35.93 (35.67)	7.10 (6.88)		1.36 (t, *J* 7Hz, 12H), 1.79 (t, *J* 15Hz, 3H), 4.0–4.5 (m, 8)
$[(EtO)_2(O)P]_2C(CH_3)_2$	86 (0.03)	1.4375	42.71 (41.77)	8.44 (8.29)		1.33 (two t with overlapping center peaks, *J* 7Hz, (CH_2CH_3) and *J* 16Hz $(PCCH_3)$, 18H), 4.13 (quintet with fine splitting, $J \approx 7$Hz, 8H)
$[(EtO)_2(O)P]_2CClCH_2CH{=}CH_2$	102–106 (0.03)	1.4577	39.59 (39.73)	7.04 (6.95)	9.74 (9.78)	1.37 (t, *J* 7Hz, 12H), 2.89 [d of t, *J*(HCCH) 7Hz, *J*$(HCCP_2)$ 13.5Hz, 2H], 4.0–4.6 (m, 8H), 4.9–5.3 and 5.6–6.4 (m, 3H, vinyl H).
	63–67 (0.27)	1.4602	42.46 (42.39)	7.33 (7.12)	15.40 (15.64)	1.33 (t, *J* 7Hz, 6H), 2.00 (d, J_P 3Hz, 3H), 2.26 (d, J_P 3Hz, 3H), 4.03 (quintet with fine splitting, $J \approx 7$Hz, 4H)
 (65 parts) +  (35 parts)	64–66 (0.10)	1.4515	47.05 (47.15)	7.87 (7.92)	13.62 (13.92)	[1.28 (s, t-Bu, *trans* to P), 1.32 (s, t-Bu *cis* to P), 1.34 (t, *J* 7Hz) 15H], 3.8–4.5 (two q, finely split, 4H), [6.81 (d, J_P 38Hz, H *trans* to P), 6.88 (d, J_P 16Hz, H *cis* to P) 1H].

A solution of 25.2 g (0.30 mol) of sodium bicarbonate in "Clorox" (commercial 5.25% aqueous NaOCl solution) (86 ml, 0.06 mol) was stirred in an ice bath while tetraethyl methylenediphosphonate[11] (5.75 g, 0.02 mol) was added dropwise over a 3 min period. The mixture was stirred at 0° for 30 min and for another 30 min at room temperature. Extraction with 50 ml and with two 25 ml portions of chloroform followed. The combined organic phase was extracted with 25 ml of saturated aqueous NaCl, dried and evaporated at reduced pressure to leave 9.7 g of a colorless oil. Distillation (short path) gave 6.08 g (85%) of the title compound, b.p. 117–123° at 0.08 mmHg (lit.[10] b.p. 119–120°/0.05 mmHg). NMR (in CCl_4): δ 1.39 (t, J 7 Hz, 6H, CH_3) and 4.33 ppm (quintet with fine splitting, J 7 Hz, 4H, CH_2). n_D^{25} 1.4615 (lit.[10] n_D^{25} 1.4619). (Found: C, 29.96; H, 5.56; Cl, 20.33. $C_9H_{20}Cl_2O_6P_2$ calcd.: C, 30.27; H, 5.65; Cl, 19.86%.)

In the absence of the sodium bicarbonate, base-induced cleavage of one $P(O)(OEt)_2$ group occurred, giving $CHCl_2P(O)(OEt)_2$. Essentially the same procedure was used in the reaction of 86 ml (0.06 mol) of "Clorox" with 20 mmol of tetraethyl methylenediphosphonate at 0° (no $NaHCO_3$). Distillation of the chloroform layer upon work-up gave 1.8 g (41%) of $CHCl_2P(O)(OEt)_2$, b.p. 60°/0.08 mmHg, n_D^{24} 1.4530 (lit.[12] b.p. 82°/0.2 mmHg, n_D^{25} 1.4513). (Found: C, 27.56; H, 5.06; Cl, 31.96. $C_5H_{11}Cl_2O_3P$ calcd.: C, 27.17; H, 5.02; Cl, 32.08%.) NMR (in CCl_4): δ 1.40 (t, J 7 Hz, 6H, CH_3), 4.30 (quintet with fine splitting, J 7 Hz, 4H, OCH_2) and 6.12 ppm (d, J 1.5 Hz, 1H, $CHCl_2$).

Reactions of diethyl lithiodichloromethylphosphonate

A solution of 5.11 g (20 mmol) of $CCl_3P(O)(OEt)_2$ in 80 ml of THF under nitrogen was cooled to −80° and 13.8 ml of 1.6 *M* n-butyllithium (22 mmol) in hexane was added dropwise with stirring during 10 min. The mixture was stirred at −85° for 5 min and then quenched with 24 mmol of water in 10 ml of THF at this temperature. The reaction mixture was allowed to warm slowly to room temperature. Water (100 ml) was added. The resulting mixture was concentrated at reduced pressure and the remaining liquid was extracted with three 20 ml portions of ether. The ether extracts were dried, concentrated and the residue was short path distilled to give 2.41 g (55%) of diethyl dichloromethylphosphonate, b.p. 66°/0.02 mmHg, n_D^{25} 1.4521.

In another reaction, a 10 mmol preparation of $LiCCl_2P(O)(OEt)_2$ was treated at −85° with 1.14 ml (12 mmol) of dimethyl sulfate. The reaction mixture was stirred at this temperature for 1 h, allowed to warm to room temperature and treated with 20 ml of half-saturated $NaHCO_3$ solution. Distillation of the organic phase gave 1.64 g (70%) of $CH_3CCl_2P(O)(OEt)_2$, b.p. 52–54°/0.07 mmHg. GLC examination of the distillate (F&M 720) indicated that it contained only one component.

In another reaction (20 mmol of $CCl_3P(O)(OEt)_2$, 24 mmol of n-butyllithium, followed by 24 mmol of dimethyl sulfate) 3.44 g of product was obtained which GLC analysis showed to be an approximately 86/14 mixture of $CH_3CCl_2P(O)(OEt)_2$ and $(CH_3)_2CClP(O)(OEt)_2$. GLC collection gave an impure but enriched sample of the latter which was characterized by NMR only. $(CH_3)_2CClP(O)(OEt)_2$, NMR (in CCl_4): δ 1.37 (t, J 7 Hz, 6H, OCH_2CH_3), 1.67 [d, J 14 Hz, 6H, $(CH_3)_2C$] and 4.15 ppm (quintet with fine splitting, $J \approx 7$ Hz, 4H, OCH_2).

Treatment of a 20 mmol preparation of $LiCCl_2P(O)(OEt)_2$ at −85° with 24 mmol of diethyl sulfate gave, using essentially the same procedure, a mixture of diethyl sulfate and $EtCCl_2P(O)(OEt)_2$, which was resolved by GLC. The latter was collected (1.24 g, 25%) and characterized.

Diethyl 1,1-dichloro-3-butenylphosphonate was obtained in 77% yield when a 10 mmol preparation of $LiCCl_2P(O)(OEt)_2$ at −85° was treated with 12 mmol of freshly distilled allyl bromide. The product was purified by distillation and microchromatography (Woelm neutral alumina).

Silylation of 20 mmol of $LiCCl_2P(O)(OEt)_2$ at −85° with 24 mmol of freshly distilled trimethylchlorosilane (Union Carbide) gave $Me_3SiCCl_2P(O)(OEt)_2$ in 70% yield.

In another experiment, a 10 mmol preparation of $LiCCl_2P(O)(OEt)_2$ in THF at −85° was treated with 12 mmol of dry acetone in 2 ml of THF. The mixture was stirred at −85° for 1h, allowed to warm to room temperature and then stirred and heated at reflux for 1 h. Precipitation of lithium diethyl phosphate occurred during the reflux period. Trap-to-trap distillation of the reaction mixture was followed by concentration of the distillate to a head temperature of 69°. GLC analysis of the residue (6 ft. DC-200 silicone oil at 40°) showed the presence of $Me_2C{=}CCl_2$ in 47% yield. A GLC-collected sample had b.p. 108° and n_D^{25} 1.4572 (lit.[13] b.p. 109° and n_D^{20} 1.4580). A lower yield of product (32%) was obtained in a similar reaction in which the reflux period was omitted.

In a similar reaction, a 10 mmol preparation of $LiCCl_2P(O)(OEt)_2$ was treated with 12 mmol of $Me_3CCH{=}O$, first at −85° for 1 h, then at room temperature for 24 h. The reaction mixture was treated with 20 ml of half-saturated $NaHCO_3$ solution. The dried organic layer was trap-to-trap distilled *in vacuo* and the distillate was analyzed by GLC (6 ft. DC-200 at 80°). 1,1-Dichloro-3,3-dimethyl-1-butene, n_D^{25} 1.4510 (lit.[14] n_D^{25} 1.4537) was present in 55% yield. (Found: C, 47.01; H, 6.66; Cl, 46.06. $C_6H_{10}Cl_2$ calcd.: C, 47.08; H, 6.59; Cl, 46.33%.) NMR (in CCl_4): δ 1.20 (s, 9H, CH_3) and 5.90 ppm (s, 1H, CH=).

Finally, a 10 mmol preparation of $LiCCl_2P(O)(OEt)_2$ in THF at −85° was treated with 10 mmol of benzophenone. The reaction mixture was stirred at −85° for 1 h and then at reflux for another h. Similar work-up gave 2.26 g of distillate at 93–97° (0.04 mmHg) which crystallized in the receiver, m.p. 65–70°. Recrystallization from hexane with 76% recovery gave white, air-sensitive needles, m.p. 77–79° (69% yield), identified as $Ph_2C{=}CCl_2$, lit.[15] m.p. 79–80°. An IR spectrum was identical with that of authentic material[16].

Preparation of diethyl tert-butylphosphonate

A solution of $LiCCl_2P(O)(OEt)_2$ (20 mmol) in 75 ml of THF and 25 ml of diethyl ether at −95° and was treated with 21 mmol of dimethyl sulfate. Subsequently, another 21 mmol of n-butyllithium was added to prepare $CH_3CClLiP(O)(OEt)_2$ *in situ*, and this reagent was treated with 21 mmol of dimethyl sulfate. This treatment with n-butyllithium and dimethyl sulfate was repeated two more times, at −90° to −75° and at −75° to −50°, to ensure complete methylation. Work-up and distillation as described in the experiments above gave 3.49 g of liquid at 49–60° at 1.8 mmHg, which was stirred overnight with 25 ml of ethanol and 25 ml of saturated sodium bicarbonate solution to remove unconverted dimethyl sulfate. Redistillation gave 2.22 g (57%) of the desired product at 57.5–58.5° at 1.8 mmHg. Although it exhibited a satisfactory NMR spectrum, a satisfactory C, H analysis was not obtained.

Further purification was effected by chromatography on Woelm neutral alumina (95/5 ether/ethanol) and redistillation, b.p. 54° (1.5 mmHg).

Reactions of tetraethyl lithiochloromethylenediphosphonate

A solution of 3.57 g (10 mmol) of tetraethyl dichloromethylenediphosphonate in 50 ml of THF at −85° under nitrogen was treated dropwise over 2 min, with stirring, with 6.3 ml of 1.6 *M* n-butyllithium in hexane (10 mmol). The reaction mixture was stirred for 10 min at −80°, then was warmed to −60° and 10 ml of saturated $NaHCO_3$ was added. The resulting mixture was warmed to room temperature. The THF was removed at reduced pressure and the residue was extracted three times with 30 ml portions of ether. The dried ether extracts were distilled to give 2.55 g (79%) of tetraethyl chloromethylenediphosphonate. The IR spectrum of the product was identical to that of an authentic sample (above and ref. 17).

In another reaction, the lithium reagent thus prepared on a 5 mmol scale was treated with 5.5 mmol of dimethyl sulfate. A similar work-up gave $[(EtO)_2(O)P]_2CClCH_3$ in 81% yield.

Complete methylation also was possible. 10 mmol of the lithium reagent was treated with 10 mmol of dimethyl sulfate at −80°. The reaction mixture was allowed to warm to room temperature over 15 min and then was heated at reflux for 30 min. The resulting mixture was cooled to −80° and another 20 mmol of n-butyllithium solution was added. The reaction mixture was stirred at −70° to −60° for 2 h, warmed to room temperature and heated at reflux for 17 h. 60 ml of half-saturated $NaHCO_3$ solution was added and the reaction mixture was stirred for 24 h at room temperature. Work-up and distillation as above gave 1.79 g (57%) of $[(EtO)_2(O)P]_2CMe_2$, b.p. 94°/0.07 mmHg, n_D^{25} 1.4384. Further purification by chromatography (Woelm neutral alumina; 90/10 ether/ethanol) and redistillation gave a purer product.

In a further reaction, 10 mmol of the lithium reagent was treated with 20 mmol of allyl bromide at −80°. Similar work-up gave 0.685 g (19%) of $[(EtO)_2(O)P]_2CClCH_2CH{=}CH_2$.

In an olefin preparation, a reaction mixture containing ca. 10 mmol of the lithium reagent was treated at −80° with 11 mmol of dry acetone. Subsequently, the reaction mixture was heated at reflux for 21 h, during which time a precipitate of lithium diethyl phosphate formed. Work-up as in the olefination reactions described above yielded 1.93 g (85%) of $Me_2C{=}CClP(O)(OEt)_2$. In an experiment in which the reflux period was omitted, this olefin was obtained in 48% yield, together with a 35% yield of tetraethyl chloromethylenediphosphonate, the hydrolysis product of the lithium reagent.

A similar reaction in which pivaldehyde was the carbonyl substrate used (10 mmol scale) gave 2.11 g (83%) of the expected olefin as a mixture of *cis* and *trans* isomers (Table 1).

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REFERENCES

1 D. Seyferth and R. L. Lambert Jr., *J. Organometal. Chem.*, 54 (1973) 123.
2 D. Seyferth, E. M. Hanson and F. M. Armbrecht Jr., *J. Organometal. Chem.*, 23 (1970) 361.
3 D. Seyferth, R. L. Lambert Jr. and E. M. Hanson, *J. Organometal. Chem.*, 24 (1970) 647.
4 D. Seyferth, F. M. Armbrecht Jr., R. L. Lambert Jr. and W. Tronich, *J. Organometal. Chem.*, 44 (1972) 299.
5 G. M. Kosolapoff, *J. Amer. Chem. Soc.*, 69 (1947) 1002.
6 E. J. Corey and G. T. Kwiatkowski, *J. Amer. Chem. Soc.*, 88 (1966) 5654.
7 E. J. Corey and G. T. Kwiatkowski, *J. Amer. Chem. Soc.*, 88 (1966) 5652; 90 (1968) 6816.
8 (a) L. Horner, H. Hoffmann and H. G. Wippel, *Chem. Ber.*, 91 (1958) 61;
(b) L. Horner, H. Hoffmann, W. Klink, H. Ertel and V. G. Toscano, *Chem. Ber.*, 95 (1962) 581.
9 W. S. Wadsworth and W. D. Emmons, *J. Amer. Chem. Soc.*, 83 (1961) 1733.
10 O. T. Quimby, J. D. Curry, D. A. Nicholson, J. B. Prentice and C. H. Roy, *J. Organometal. Chem.*, 13 (1968) 199.
11 G. Schwarzenbach and J. Zurc, *Monatsh. Chem.*, 81 (1950) 202.
12 P. J. Bunyan and J. I. G. Cadogan, *J. Chem. Soc.*, (1962) 2953.
13 A. L. Henne and E. P. Plueddeman, *J. Amer. Chem. Soc.*, 65 (1943) 1272.
14 L. Schmerling, *J. Amer. Chem. Soc.*, 71 (1949) 701.
15 A. v. Baeyer, *Ber. Deut. Chem. Ges.*, 6 (1873) 223.
16 D. Seyferth, W. Tronich, R. S. Marmor and W. E. Smith, *J. Org. Chem.*, 37 (1972) 1537.
17 D. A. Nicholson and H. Vaughn, *J. Org. Chem.*, 36 (1971) 1835.