April, 1979] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (4), 1197—1202 (1979) 1197

Carbon-Carbon Bond Formation by Use of Chloroiodomethane as a C_1 Unit. I. Formation of Chloromethyltriphenylphosphonium Iodide, and Its Application for the Wittig Chloromethylenation of Aldehydes and Ketones[1)]

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(Received September 12, 1978)

Chloromethyltriphenylphosphonium iodide has been prepared by the reaction of chloroiodomethane with triphenylphosphine. Upon treatment with potassium *t*-butoxide in *t*-butyl alcohol, the phosphonium iodide was converted into chloromethylenetriphenylphosphorane; this in turn was used for the Wittig reaction of aldehydes and ketones into the corresponding chloroolefins of the type RCH=CHCl and RR′C=CHCl in good to moderate yields. The configurations of these chloroolefins were assigned on the basis of NMR spectral studies. Direct conversion of benzaldehyde into phenylacetylene was also achieved using the phosphonium salt and excess potassium *t*-butoxide.

Chloroiodomethane can be easily obtained in large quantities from dichloromethane *via* a halogen exchange reaction with sodium iodide in dipolar aprotic media,[2,3)] or under phase-transfer conditions.[4)] It is useful as a methylene source for the cyclopropanation[5)] of olefins as well as for the methylenation[6)] of aldehydes *via* organozinc intermediates.

As is well recognized, the Wittig olefination reaction of carbonyl function is one of the most successful synthetic routes to a wide variety of unsaturated compounds. Chloroolefins are also accessible by the chloromethylenation of carbonyl compounds with chloromethylenetriphenylphosphorane ($Ph_3P{=}CHCl$, **2**).[7)] However, the requisite precursor chloromethyltriphenylphosphonium salts ($(Ph_3\overset{+}{P}CH_2Cl)\overset{-}{X}$) have only been prepared by somewhat complicated procedures, such as those described by Seyferth *et al.*,[8)] by Wittig and Schlosser,[9)] and by Appel and Morbach.[10)] Chlorocarbene: CHCl generated from dichloromethane and butyllithium adds to triphenylphosphine to form the phosphorane (**2**),[8,11)] but it is said that troublesome isolation of the phosphorane from residual triphenylphosphine is necessary to obtain chloroolefins in good yields.[8b)] This problem can be avoided to some extent by use of (bromochloromethyl)phenylmercury as the carbene source; nevertheless, the yields are moderate.[12)]

During the course of our investigation on the carbon-carbon bond formation utilizing chloroiodomethane as a C_1 unit, we found that it smoothly reacts with triphenylphosphine to afford chloromethyltriphenylphosphonium iodide (**1**) as a white precipitate.[1)] We report here another convenient method for the conversion of aldehydes and ketones into chloroolefins using the phosphonium iodide (**1**) for the Wittig reaction.**

Results and Discussion

Formation of Chloromethyltriphenylphosphonium Iodide (1) from Chloroiodomethane and Triphenylphosphine. Table 1 shows the results of the reaction of chloroiodomethane and triphenylphosphine in several solvents. When the reaction was carried out in THF, **1** began to precipitate as white solids in the course of the initial 1/2 h heating at reflux. The phosphonium salt amounted to a 60% isolated yield after an 8 h reaction, and to a 70% yield after 20 h (Eq. 1):

$$\mathrm{CH_2ClI} + \mathrm{Ph_3P} \longrightarrow \underset{\mathbf{1}}{(\mathrm{Ph_3\overset{+}{P}CH_2Cl})\overset{-}{\mathrm{I}}} \qquad (1)$$

TABLE 1. PREPARATION OF CHLOROMETHYLTRIPHENYLPHOSPHONIUM IODIDE (**1**)

Ph_3P (mmol)	CH_2ClI (mmol)	Solvent	(ml)	Temp (°C)	Time (h)	Yield of **1**[a)] (%)
10	12	Et_2O	20	20—25	20	8
10	11	THF	10	50	20	34
120	150	THF	150	67	8	60
120	150	THF	150	67	20	70
50	70	*t*-BuOH	50	83	6	72
100	110	DMF	120	100	8	0

a) Isolated yield based on Ph_3P.

This phosphonium salt showed an IR spectrum quite similar to that of chloromethyltriphenylphosphonium chloride over the range from 4000 to 625 cm^{-1}.[13)] It gave satisfactory elemental analysis data, and was converted into the known tetraphenylborate.[8,9)] In refluxing *t*-butyl alcohol, the reaction time was somewhat shortened, probably due to a higher reaction temperature, while the resulting precipitate had to be washed well with THF to remove residual triphenylphosphine. When a mixture of chloroiodomethane and triphenylphosphine in DMF was heated, it turned dark brown, but no precipitate was formed.

Chloromethylenation of Aldehydes and Ketones with Chloromethyltriphenylphosphonium Iodide (1) and Base. Tables 2 and 3 summarize the results of the chloromethylenation of several carbonyl compounds by the Wittig reaction. It can be seen that some aldehydes and ketones can be easily converted into the corresponding chloroolefins of the type RCH=CHCl and RR′C=CHCl in good to moderate yields by use of **1** and potassium *t*-butoxide in *t*-butyl alcohol (Scheme 1).

** After this work had been submitted for publication, the authors learned that fluoromethylenation with $(Ph_3\overset{+}{P}CH_2F)\overset{-}{I}$ had been reported: D. J. Burton and P. E. Greenlimb, *J. Org. Chem.*, **40**, 2796 (1975).

TABLE 2. CHLOROMETHYLENATION OF KETONES[a)]

	R $\mathrm{C{=}O}$ $\mathrm{R'}$		Base	Solvent	Products and yield (%)[b)]		
	R–	–R′			R $\mathrm{C{=}CHCl}$ $\mathrm{R'}$ (**3**)	*E*/*Z* Ratio[c)]	R $\mathrm{C{=}CH_2}$ $\mathrm{R'}$ (**4**)
a	$-(\mathrm{CH_2})_5-$		*t*-BuOK	*t*-BuOH	94		3.4
			t-BuOLi	*t*-BuOH	58		trace
			EtONa	EtOH	92		0
			t-BuOK	THF	62		7.9
			$\mathrm{K_2CO_3}$[d)]	THF	trace		0
b	$-(\mathrm{CH_2})_6-$		*t*-BuOK	*t*-BuOH	55		
			t-BuOK	*t*-BuOH	86[e)]		
			EtONa	EtOH	56		
c	$-\underset{\mathrm{CH_3}}{\mathrm{CH}}(\mathrm{CH_2})_4-$		*t*-BuOK	*t*-BuOH	89	92/8	
			EtONa	EtOH	49	55/45	
d	$-\underset{\mathrm{CH(CH_3)_2}}{\mathrm{CH}}(\mathrm{CH_2})_2\underset{\mathrm{CH_3}}{\mathrm{CH}}\mathrm{CH_2}-$[f)]		*t*-BuOK	*t*-BuOH	61	72/28	13
			EtONa	EtOH	trace		
e	$\mathrm{C_6H_5}-$	$-\mathrm{CH_3}$	*t*-BuOK	*t*-BuOH	75	56/44	13
			EtONa	EtOH	38	68/32	1
f	p-$\mathrm{ClC_6H_4}-$	$-\mathrm{CH_3}$	*t*-BuOK	*t*-BuOH	59	53/47	13
			EtONa	EtOH	8	75/25	1
g	p-$\mathrm{CH_3C_6H_4}-$	$-\mathrm{CH_3}$	*t*-BuOK	*t*-BuOH	65	57/43	17
			EtONa	EtOH	2		trace

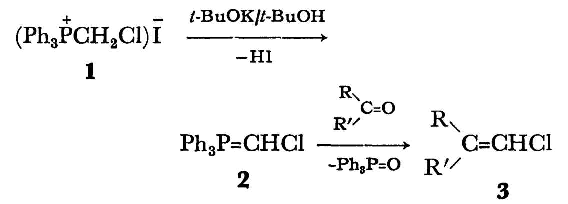
a) Solvent, 50—70 ml; RR′C=O, 20 mmol; **1**, 25 mmol; base, 30 mmol; temp, 20—25 °C; time, 4 h; under a nitrogen atmosphere. b) GLC yield based on RR′C=O. c) Peak area of each isomer on GLC was approximated to the molar ratio. d) The reaction was carried out on the scale of 1/2 using 18-crown-6 (70 mg) as the phase-transfer catalyst under reflux for 9 h. e) Cycloheptanone, 10 mmol. f) Menthone.

TABLE 3. CHLOROMETHYLENATION OF ALDEHYDES[a)]

	RCHO	Reaction conditions			Products and yield (%)[b)]		
	R–	Base (mmol)		Temp (Time, h)	RHC=CHCl (**3**)	*E*/*Z* Ratio	RC≡CH (**5**)
h	$\mathrm{C_6H_5}-$	EtONa	50[c)]	Ambient (4)	77	78/22	1
		EtONa	50[c)]	Ambient (4), then reflux (3)	60	100/0	16
		EtOK	40[c)]	Ambient (4), then reflux (3)	66	100/0	27
		t-BuOK	55	Ambient (1)	81	46/54	7
		t-BuOK	55	Ambient (1), then reflux (2)	20	100/0	71
		t-BuOK	55	Ambient (1), then reflux (8)	trace	—	91
		t-BuOK	30	Ambient (2)	45	62/38	28
i	p-$\mathrm{ClC_6H_4}-$	*t*-BuOK	30	Ambient (4)	69	38/62	3
j	o-$\mathrm{ClC_6H_4}-$	*t*-BuOK	30	Ambient (4)	66	50/50	5
k	p-$\mathrm{CH_3OC_6H_4}-$	*t*-BuOK	30	Ambient (4)	60	d)	10
l	p-$\mathrm{CH_3C_6H_4}-$	*t*-BuOK	30	Ambient (4)	62	d)	15
m	n-$\mathrm{C_8H_{17}}-$	*t*-BuOK	30	Ambient (4)	45	44/56	trace

a) *t*-BuOH (50—70 ml) was used as solvent unless otherwise noted. RCHO,20 mmol; **1**, 25 mmol. In the case of benzaldehydes (**h**—**l**), the styrene $\mathrm{ArCH{=}CH_2}$ was also detected in 3—5% yield. b) See footnotes b) and c) in Table 2. c) Solvent, EtOH, 50 ml. d) The *E*- and *Z*-isomer could not be sufficiently well separated from each other on GLC (but $E < Z$).

Upon addition of **1** to a potassium *t*-butoxide solution in *t*-butyl alcohol under nitrogen, the orange-red color characteristic of phosphinemethylene reagents developed. To this mixture was added *ca.* 0.8 molar equivalent amount of a carbonyl compound. For example, after 4 h stirring at ambient temperature, all of the cyclohexanone reacted to afford chloromethylenecyclohexane (**3a**) in as high as 94% yield. Small amounts of methylenecyclohexane was also formed a sa by-product, showing some reduction had occurred during the process. The exact nature of the reduction is not yet clear,[14)] but the methylenation reaction was dependent



Scheme 1.

on the substrate carbonyl compounds as well as on the reaction medium; menthone and acetophenones gave relatively large amounts of methylenated products, and the EtONa/EtOH system seemed to suppress the reduction.

When the chloromethylenation was carried out in ethyl alcohol using sodium ethoxide as the base, the chloromethylenephosphorane (**2**) showed diminished reactivity. Thus, with this solvent-base combination, reactive substrates such as cyclohexanone and benzaldehyde gave chloroolefins in good yields, but almost all of the menthone was recovered unchanged. A solid-liquid two phase system16) using 18-crown-6 as the phase-transfer catalyst and sodium carbonate powder as the base did not work well. Organolithium reagents have been used conventionally in the Wittig chloromethylenation reaction under rather severe reaction conditions.8,9,11) In preliminary experiments, however, chloromethylenation of cyclohexanone with butyllithium was complicated by the occurrence of an alkylation reaction to pentylidenecyclohexane, and no further investigation was conducted.

The Wittig methylenation of cycloheptanone is reported to have resulted in poor yields,17) but chloromethylenecycloheptane (**3b**) was obtained in a reasonable yield by use of about twice as much of the phosphorane (**2**).

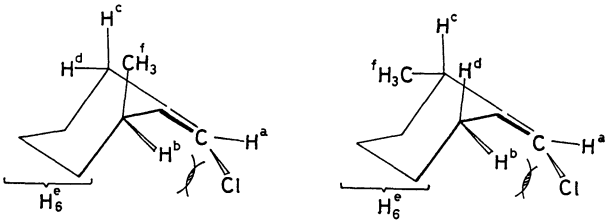
NMR Spectral Studies of 1-Chloroolefins. In the reaction with aldehydes and unsymmetrical ketones, two geometric isomers of 1-chloroolefins were formed in roughly comparable yields, showing that the chloromethylenephosphorane (**2**) is one of the semistabilized ylids.18) In a given pair of isomeric chloroolefins, the component which eluted first on GLC (Apiezon Grease L column) was assigned to the *Z*-configuration on the

Table 4. NMR spectral data of 1-chloroolefins (**3**)a)

Compound	Chemical shifts and assignments	
	=CHCl	Other protons
3a	5.63 (m)b)	1.4—1.8 (6H, br, $-(CH_2)_3-$), 1.8—2.5 (4H, m, $\left.\begin{array}{l}-CH_2\\-CH_2\end{array}\right\rangle C{=}C$)
3b	5.69 (m)b)	1.3—1.8 (8H, br, $-(CH_2)_4-$), 2.0—2.5 (4H, m, $\left.\begin{array}{l}-CH_2\\-CH_2\end{array}\right\rangle C{=}C$)
E-**3d**	5.63 (m)b)	0.7—1.2 (9H, m, 3-CH_3), 1.2—2.4 (8H, m), 2.4—2.7 (1H, m)
Z-**3e**	5.96 (q, *J*=1.4)	2.0 (3H, d, *J*=1.4, $-CH_3$), 7.2 (5H, s, $-C_6H_5$)
E-**3e**	6.15 (q, *J*=1.3)	2.1 (3H, d, *J*=1.3, $-CH_3$), 7.2 (5H, s, $-C_6H_5$)
Z-**3f**	5.98 (q, *J*=1.5)	2.0 (3H, d, *J*=1.5, $-CH_3$), 7.2 (4H, s, $-C_6H_4$)
E-**3f**	6.19 (q, *J*=1.4)	2.1 (3H, d, *J*=1.4, $-CH_3$), 7.1 (4H, s, $-C_6H_4$)
Z-**3g**	5.95 (q, *J*=1.6)	2.0 (3H, d, *J*=1.6, $=C-CH_3$), 2.3 (3H, s, Ph-CH_3), 7.1 (4H, s(br), $-C_6H_4$)
E-**3g**	6.15 (q, *J*=1.5)	2.1 (3H, d, *J*=1.5, $=C-CH_3$), 2.3 (3H, s, Ph-CH_3), 7.0 (4H, s, $-C_6H_4$)
Z-**3h**	6.07 (d, *J*=8.2)	6.5 (1H, d, *J*=8.2, =CH-Ph), 7.1—7.6 (5H, m, $-C_6H_5$)
E-**3h**	6.43 (d, *J*=15)	6.7 (1H, d, *J*=15, =CH-Ph), 7.1—7.6 (5H, m, $-C_6H_5$)
Z-**3i**	6.11 (d, *J*=8.2)	6.4 (1H, d, *J*=8.2, =CH-Ph), 7.1—7.6 (4H, q-like, $-C_6H_4$)
E-**3i**	6.41 (d, *J*=13.3)	6.7 (1H, d, *J*=13.3, =CH-Ph), 7.1 (4H, s, $-C_6H_4$)
Z-**3j**	6.28 (d, *J*=8.0)	6.8 (1H, d, *J*=8.0, =CH-Ph), 7.0—7.4 (3H, m, $-C_6H_3$), 7.6—7.9 (1H, m, $-C_6H$)
E-**3j**	6.46 (d, *J*=13.4)	7.0 (1H, d, 13.4, =CH-Ph), 7.0—7.4 (4H, m, $-C_6H_4$)
Z-**3k**	5.98 (d, *J*=8.0)	3.7 (3H, s, $-OCH_3$), 6.4 (1H, d, *J*=8.0, =CH-Ph), 6.5—7.6 (4H, m, $-C_6H_4$)
E-**3k**	6.31 (d, *J*=13.8)	3.7 (3H, s, $-OCH_3$), 6.7 (1H, d, *J*=13.8, =CH-Ph), 6.6—7.3 (4H, q-like, $-C_6H_4$)
Z-**3l**	5.95 (d, *J*=8.4)	2.2 (3H, s(br), $-CH_3$), 6.4 (1H, d, *J*=8.4, =CH-Ph), 6.8—7.5 (4H, m, $-C_6H_4$)
E-**3l**	6.33 (d, *J*=16)	2.2 (3H, s(br), $-CH_3$), 6.55 (1H, d, *J*=16, =CH-Ph), 6.8—7.5 (4H, m, $-C_6H_4$)
Z-**3m**	5.91 (dt, $J_{cis}=7.2$, $J_{H,CH_2}\leq 1$	0.7—1.0 (3H, t, CH_3), 1.0—1.7 (12H, br, $-(CH_2)_6-$), 1.8—2.4 (2H, m, $-CH_2-C{=}C$), 5.7 (1H, dt, $J_{cis}=7.2$, $J_{vis}=7.2$, =CH-Alkyl)
E-**3m**	5.77 (m)b)	0.7—1.1 (3H, t, $-CH_3$), 1.1—1.6 (12H, br, $-(CH_2)_6-$), 1.7—2.3 (2H, m, $-CH_2-C{=}C$), 5.8 (1H, br, =CH-Alkyl)

a) CCl_4 (5—10%); chemical shift, δ (ppm) from internal hexamethyldisiloxane; coupling constant, *J*(Hz).
b) Rather sharp signal.

basis of NMR studies (Table 4). Chemical shifts of vinylic protons of these 1-chloroolefins were correlated well with the known empirical formula of Pascual, Meier, and Simons.[19] In the case of β-chlorostyrenes (**3e**—**3l**), in general, the proton which locates in the *geminal* position to the chlorine atom in the *E*-isomer resonanced at a lower magnetic field than that in the *Z*-isomer. The NMR spectra of (*E*)- and (*Z*)-chloromethylene-2-methylcyclohexane (**3c**) were assigned as summarized in Scheme 2:



Z-**3c**

H_a: δ5.63 (d, J_{ac}=1.8 Hz)
H_b: 2.9—3.4 (m)
H_c+H_d: 1.9—2.4 (m)
H_e: 1.3—1.9 (m)
H_f: 1.05 (d, J_{bf}=7 Hz)

E-**3c**

H_a: δ5.62 (m, J_{ac}=1.5 Hz)
H_b: 2.5—2.9 (m)
H_c: 2.0—2.3 (m)
H_d+H_e: 1.2—2.0 (m)
H_f: 1.02 (d, J_{cf}=7 Hz)

Scheme 2.

The PCK model shows considerable steric interaction between the Cl and the H_b atom. Thus, the methyl substituent attached to the C_2 atom of the *Z*-isomer seemed to be restrained to the axial position. The remarkable downfield shift of the H_b protons of each isomer can be explained by the steric compression effect (van der Waal's shift) and/or the anisotropic effect of the nearby Cl atom.[20,21] The H_a proton of the *E*-isomer showed a multiplet, but rather narrow signal; this was sharpened by irradiation of the H_c proton, showing a magnetic interaction between H_c and H_a. Similar allylic long-range couplings are documented.[22]

The vinylic protons of (*E*)-1-chloro-1-decene (*E*-**3m**) showed a somewhat confusing NMR spectrum. It can be characterized as shown in the last line of Table 4 on the assumption that each vinylic proton resonanced at almost the same magnetic field, reducing the apparent J_{trans} to zero.[23]

Conversion of Benzaldehyde into Phenylacetylene. From benzaldehydes, phenylacetylenes as well as β-chlorostyrenes were formed in the chloromethylenation reaction (Table 3). From the results of the reaction of benzaldehyde conducted in the presence of excess amounts of alkoxides and employing longer reaction periods, it is concluded that the phenylacetylene was formed *via* dehydrochlorination of the initially formed β-chlorostyrenes, the *Z*-isomer reacting much faster than the *E*-counterpart. The dehydrochlorination with sodium or potassium ethoxide in ethyl alcohol consumed only the *Z*-isomer under the reaction conditions, leaving the other chloride intact, while both were converted to phenylacetylene by refluxing with *t*-butoxide in *t*-butyl alcohol.[24] It is known that dehydrohalogenation from olefinic halides with alkoxides proceeds mainly through an E2 mechanism *via trans*-elimination, and in many instances the relative rate ratio of *Z*- to *E*-isomer ranges from 10^4 to 10^6.[25] On the other hand, Schlosser and Ladenberger reported that (*E*)-β-chlorostyrenes are more sensitive to phenyllithium than the corresponding *Z*-isomer, suggesting an E2cB mechanism for the dehydrochlorination.[26]

Irrespective of the precise mechanism involved, it is noteworthy that the formyl function of benzaldehydes can be converted into the acetylenic grouping in a one-pot reaction. Further studies are now in progress. Multistep formyl to ethynyl conversions have been reported by Villieras *et al.*[27] and by Corey and Fuchs.[28]

Experimental

The IR spectra were recorded on a Shimadzu IR 430 spectrometer. The NMR spectra were determined using a Hitachi R-24A spectrometer (60 MHz), with hexamethyldisiloxane as an internal standard. GLC analyses were carried out with a Shimadzu GC-3AF or a Shimadzu GC-3BT apparatus using a Silicone DC 550 (20%), an Apiezon Grease L (20%), or a Silicone DC 410 (20%) on Diasolid M (60—80 meshes) column. A Shimadzu GC-2C apparatus was used for the preparative GLC using an Apiezon Grease L column.

Materials. Chloroiodomethane was obtained by the procedure described before.[2] Commercial ketones and aldehydes except *p*-chlorobenzaldehyde, which was used as purchased, were dried over magnesium sulfate, and distilled at reduced pressure and stored under nitrogen. Triphenylphosphine (mp 80.5 °C), sodium tetraphenylborate, and 18-crown-6 were used without further purification. Solvents were purified as usual before use.

Preparation of Chloromethyltriphenylphosphonium Iodide (1). Triphenylphosphine (120 mmol) was dissolved in 150 ml of THF in a 500 ml round-bottomed flask equipped with a magnetic stirrer, a pressure-equilibrating dropping funnel, a thermometer, and a Widmer reflux condenser topped with a nitrogen inlet tube. The mixture was stirred rapidly while chloroiodomethane (150 mmol) was added. The flask was immersed in an oil bath and the mixture was heated at reflux for *ca.* 20 h. The resulting white precipitate was filtered, and

Table 5. NMR spectral data of methylenation products (**4**) and acetylenes (**5**)[a]

Compound	Chemical shifts and assignments
4d	0.8—1.1 (9H, m, 3-CH_3), 1.2—2.5 (9H, m), 4.4—4.5 (1H, br), 4.5—4.6 (1H, br)
4f	2.1 (3H, d, $-CH_3$), 5.0 (1H, q, =CH *trans* to Ph), 5.2 (1H, d, =CH *cis* to Ph), 7.2 (4H, s, $-C_6H_4$)
4g	2.0 (3H, dd, =C–CH_3), 2.2 (3H, s, Ph–CH_3), 4.8 (1H, m, =CH *trans* to Ph), 5.2 (1H, m, =CH *cis* to Ph), 6.8—7.3 (4H, q-like, $-C_6H_4$)
4k	3.7 (3H, s, $-OCH_3$), 5.0 (1H, dd, =CH *trans* to Ph), 5.5 (1H, dd, =CH *cis* to Ph), 6.6 (1H, dd, =CH *gem* to Ph), 6.6—7.4 (4H, q-like, $-C_6H_4$), J_{trans}=17.4, J_{cis}=10.4, J_{gem}=1.5
5i	2.9 (1H, s, CH), 7.1—7.4 (4H, m, $-C_6H_4$)
5j	3.1 (1H, s, ≡CH), 6.9—7.6 (4H, m, $-C_6H_4$)
5k	3.7 (3H, s, $-OCH_3$), 2.7 (1H, s, ≡CH), 6.5—7.4 (4H, q-like, $-C_6H_4$)
5l	2.2 (3H, s(br), $-CH_3$), 2.8 (1H, s, ≡CH), 6.8—7.3 (4H, m, $-C_6H_4$)

a) See footnote a) in Table 4.

TABLE 6. ANALYTICAL DATA

Compound	Molecular formula	C Found(Calcd)	H Found(Calcd)	Cl Found(Calcd)
3a	$C_7H_{11}Cl$	64.67(64.37)	8.92(8.49)	26.58(27.14)
3b	$C_8H_{13}Cl$	66.77(66.43)	8.76(9.06)	24.18(24.51)
E-**3c**	$C_8H_{13}Cl$	66.06(66.43)	9.17(9.06)	24.79(24.51)
3d[a]	$C_{11}H_{19}Cl$	71.23(70.76)	10.60(10.26)	17.41(18.98)
Z-**3e**	C_9H_9Cl	70.90(70.83)	5.69(5.94)	23.64(23.23)
E-**3e**	C_9H_9Cl	70.76(70.83)	5.58(5.94)	23.72(23.23)
3f[a]	$C_9H_8Cl_2$	57.18(57.79)	4.35(4.31)	38.65(37.90)
Z-**3g**	$C_{10}H_{11}Cl$	71.94(72.07)	6.96(6.65)	21.50(21.27)
E-**3g**	$C_{10}H_{11}Cl$	72.29(72.07)	6.68(6.65)	21.04(21.27)
3h[a]	C_8H_7Cl	69.26(69.33)	5.51(5.09)	24.92(25.58)
Z-**3i**	$C_8H_6Cl_2$	55.44(55.53)	3.08(3.49)	41.13(40.98)
E-**3j**	$C_8H_6Cl_2$	55.61(55.53)	3.73(3.49)	41.28(40.98)
Z-**3k**	C_9H_9ClO	63.78(64.11)	5.31(5.38)	20.56(21.02)
3l[a]	C_9H_9Cl	70.44(70.83)	5.85(5.94)	23.73(23.23)
Z-**3m**	$C_{10}H_{19}Cl$	68.71(68.75)	10.59(10.96)	20.65(20.29)
4g	$C_{10}H_{12}$	90.74(90.85)	8.91(9.15)	
5l	C_9H_8	93.18(93.06)	6.53(6.94)	

a) A mixture of *E*- and *Z*-isomer.

the solids were washed thoroughly with 5×50 ml of THF in a nitrogen atmosphere. The phosphonium salt was dried *in vacuo* at 50—60 °C for several hour; it was then stored in a Schlenk tube under nitrogen. The dried product weighed 37 g (70 % yield based on triphenylphosphine). Mp 185—187 °C (dec). Found: C, 51.58; H, 3.82 %. Calcd for $C_{19}H_{17}ClIP$: C, 52.02; H, 3.91 %. IR (KBr, cm^{-1}): 3030 (w), 2890 (m), 2850 (m), 2770 (w, sh), 1580 (m), 1480 (m), 1440 (s), 1350 (w), 1330 (w), 1250 (w), 1170 (m), 1125 (vs), 1005 (m), 940 (w), 920 (w), 880 (m), 820 (w), 770 (s), 750 (m), 740 (m), 730 (m), 705 (s), 545 (s), 530 (s), 505 (m), 506 (w, sh).

Chloromethyltriphenylphosphonium Tetraphenylborate. A sample of the phosphonium iodide (**1**) (1.0 mmol) was placed in 30 ml of water and stirred vigorously. To this suspension was added a solution of sodium tetraphenylborate (1.5 mmol) in 20 ml of 1: 1 ethyl alcohol–water. Another 250 ml of ethyl alcohol was added, and then the mixture was stirred at reflux for 2 h. After filtration, the filtrate was kept overnight at −78 °C. The resulting white precipitate was collected, recrystalized from ethyl alcohol (150 ml)–ether (150 ml), washed several times with small portions of alcohol–ether, and dried *in vacuo*. Mp 190—193 °C (dec) (lit, mp 189—192 °C (dec),[8a] 222—223.8 °C[9]). Found: C, 81.85; H, 6.22; Cl, 4.90 %. Calcd for $C_{43}H_{37}BClP$: C, 81.85; H, 5.91; Cl, 5.62 %.

Generation of Chloromethylenetriphenylphosphorane (2) and the Wittig Chloromethylenation of Carbonyl Compounds. The general procedure is described below. Under a nitrogen atmosphere, *t*-butyl alcohol (25 ml) was placed in a 100 ml three-neck round-bottomed flask equipped with a magnetic stirrer, a thermometer, and a Widmer reflux condenser topped with a nitrogen inlet tube. Potassium (30 mg-atom) was added, and the mixture was heated at reflux for *ca.* 1 h to afford a potassium *t*-butoxide solution. The reaction flask was then immersed in a water bath. A powder dropping funnel[29] which contained 25 mmol of **1** was attached to the flask, and the **1** was dropped to the solution over 5 min. The funnel was washed with another 15 ml of *t*-butyl alcohol to bring the residual phosphonium salt into the reaction flask. The mixture was stirred for 1.5 h at ambient temperature; during this time it turned from white to an orange-red slurry. After the formation of **2** was completed, the powder dropping funnel was replaced with a pressure-equilibrating dropping funnel which contained a substrate carbonyl compound (20 mmol) in 10 ml of *t*-butyl alcohol. The carbonyl compound was added over 20 min, while retaining the reaction temperature below 25 °C. The mixture was stirred for another 3 h 40 min at ambient temperature (20—25 °C). At the end of the reaction, the mixture was shaken with 50 ml of pentane and 50 ml of water, filtered, and the layers were separated. The aqueous layer was extracted with 3×50 ml of pentane. The combined organic phase was washed with 3×30 ml of water, and dried over magnesium sulfate. An aliquot of the sample was used for the quantitative determination of the reaction products by GLC, employing experimentally determined calibration curves. After removal of the solvents by distillation *in vacuo*, the volatile products were collected in a cold trap, and subjected to a preparative GLC for the recovery of each component. Reaction products were identified and characterized by means of GLC, NMR (Tables 4 and 5), and IR spectrometry, and elemental analyses (Table 6).

Financial support of this work by a Grant-in-Aid (C-35536) from the Ministry of Education, Japan, is gratefully acknowledged (S. M.).

References

1) Preliminary communication: S. Miyano, Y. Izumi, and H. Hashimoto, *J. Chem. Soc., Chem., Commun.*, **1978**, 446.

2) S. Miyano and H. Hashimoto, *Bull. Chem. Soc. Jpn.*, **44**, 2864 (1971).

3) N. Altabev, R. D. Smith, and S. I. Suratwala, *Chem. Ind.*, **1973**, 331.

4) D. Landini and F. Rolla, *Chem. Ind.*, **1974**, 533.

5) a) S. Miyano and H. Hashimoto, *Bull. Chem. Soc. Jpn.*, **46**, 892 (1973); b) S. Miyano, Y. Izumi, H. Fujii, and H. Hashimoto, *Synthesis*, **1977**, 700.

6) S. Miyano, M. Hida, and H. Hashimoto, *J. Organomet. Chem.*, **12**, 263 (1968).

7) See for example, A. Maercker, "Organic Reactions," (1965), Vol. 14, p. 270.

8) a) D. Seyferth, S. O. Grim, and T. O. Read, *J. Am. Chem. Soc.*, **82**, 1510 (1960); b) D. Seyferth, S. O. Grim, and

T. O. Read, *J. Am. Chem. Soc.*, **83**, 1617 (1961).

9) G. Wittig and M. Schlosser, *Chem. Ber.*, **94**, 1373 (1961).

10) R. Appel and W. Morbach, *Synthesis*, **1977**, 699.

11) G. Wittig and M. Schlosser, *Angew. Chem.*, **72**, 324 (1960).

12) D. Seyferth, J. K. Heeren, G. Singh, S. O. Grim, and W. B. Hughes, *J. Organomet. Chem.*, **5**, 267 (1966).

13) C. J. Pouchert, "The Aldrich Library of Infrared Spectra," Aldrich Chemical Co., Inc., Spectrum No. 867B.

14) *Cf.* Köbrich *et al.* ascribed the formation of the methylenated products to the halogen-metal interconversion on the halomethyltriphenylphosphonium salts by organolithium reagents used as the base for the ylid formation.[15)]

15) G. Köbrich, H. Trapp, K. Flory, and W. Drischel, *Chem. Ber.*, **99**, 689 (1966).

16) R. M. Boden, *Synthesis*, **1975**, 784.

17) A. Schriesheim, R. J. Muller, and C. A. Rowe, Jr., *J. Am. Chem. Soc.*, **84**, 3164 (1962).

18) S. Nishida, "Shin Zikken Kagaku Koza," Maruzen, Tokyo (1977), Vol. 14, p. 224.

19) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, London (1969), p. 184.

20) R. C. Fort, Jr., G. W. H. Cheeseman, and E. C. Taylor, *J. Org. Chem.*, **29**, 2440 (1964).

21) Ref. 19), pp. 71, 80.

22) Ref. 19), p. 316.

23) For example, M. Hesse, W. von Philipsborn, D. Schumann, G. Spiteller, M. Spiteller-Friedmann, W. I. Taylor, H. Schmid, and P. Karrer, *Helv. Chim. Acta*, **47**, 878 (1964).

24) *Cf.* L. A. Paquette, L. S. Wittenbrook, and V. V. Kane, *J. Am. Chem. Soc.*, **89**, 4487 (1967).

25) D. V. Banthorpe, "Reaction Mechanisms in Organic Chemistry," ed by E. D. Hughes, Elsevier Publ. Co., New York, N. Y. (1963), Vol. 2, p. 142.

26) M. Schlosser and V. Ladenberger, *Chem. Ber.*, **100**, 3901 (1967).

27) J. Villieras, P. Perriot, and J. F. Normant, *Synthesis*, **1975**, 458.

28) E. J. Corey and P. L. Fuchs, *Tetrahedron Lett.*, **1972**, 3769.

29) T. Suehiro, K. Tokumaru, and M. Yoshida, "Gendai no Yukikagaku Zikken," Gihodo, Tokyo (1971), p. 139.