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The Preparation and ^{13}C-NMR Spectra of Alkoxymethyltriphenylphosphonium Salts

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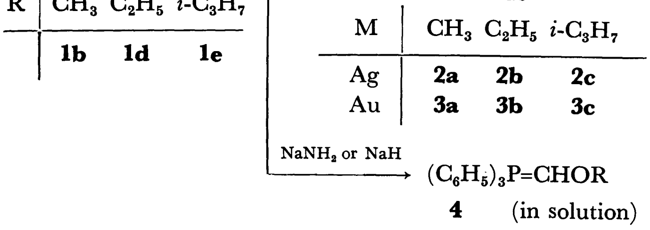
Alkoxymethyltriphenylphosphonium salts, $[(C_6H_5)_3PCH_2OR]X$, X: Cl, Br, and I, R: CH_3, C_2H_5, and *i*-C_3H_7, have been obtained from the reaction of the triphenylphosphine and the corresponding alkyl halomethyl ether. In the ^{13}C-NMR spectra of these salts, the coupling constant (J_{CP}) is 68—71 Hz, which is larger than that (J_{CP}: 48—56 Hz) of $[(C_6H_5)_3PCH_2R]Br$, R: H, CH_3, and *i*-C_3H_7, $Me_3P{=}S$ and $Me_3P{=}Se$, while it is close to that (66—69 Hz) of $Me_3P{=}O$ and $Et_3P{=}O$. The coupling constant (J_{CP}) of these salts can be caused by the oxygen atom in the salts.

Although the ^{1}H-NMR spectra of methoxymethyltriphenylphosphonium chloride[1] has already been described, the ^{13}C-NMR spectra of alkoxymethyltriphenylphosphonium salts and alkyltriphenylphosphonium salts, except for methyltriphenylphosphonium salt,[2,3] have been the subject of little research.

Previously we have reported on several ylides and Ib-group (Cu,[4] Ag,[4] and Au[5]) or IIb-group[6] (Zn, Cd, and Hg) metal complexes. The present paper will deal with the preparation and ^{13}C-NMR measurements of alkoxymethyltriphenylphosphonium salts, $[(C_6H_5)_3PCH_2OR]X$, X: $[Ag(CN)_2]$, $[Au(CN)_2]$, Cl, Br, and I, R: CH_3, C_2H_5, and *i*-C_3H_7, and with the ^{13}C-NMR measurements of alkyltriphenylphosphonium salts, $[(C_6H_5)_3PCH_2R]Br$, R: H, CH_3, and *i*-C_3H_7.

Results and Discussion

Synthesis and Properties. Methoxymethyltriphenylphosphonium salt[1,7] (**1a**, **1b**, and **1c**) and ethoxymethyltriphenylphosphonium salt (**1d**) were prepared by the reaction of triphenylphosphine and the corresponding alkyl halomethyl ether. Isopropoxymethyltriphenylphosphonium bromide (**1e**) was prepared by the reaction of the triphenylphosphine and the bromomethyl isopropyl ether. The alkoxymethyltriphenylphosphonium dicyanoargentate(I) (**2a**—**2c**) and alkoxymethyltriphenylphosphonium dicyanoaurate(I) (**3a**—**3c**) were synthesized by the reaction of **1b**, **1d**, or **1e** and potassium dicyanoargentate(I)[8] or potassium dicyanoaurate(I)[9] respectively.



$$[(C_6H_5)_3PCH_2OR]Br \xrightarrow{K[M(CN)_2]} [(C_6H_5)_3PCH_2OR][M(CN)_2]$$

R	CH_3	C_2H_5	*i*-C_3H_7
	1b	**1d**	**1e**

M: Ag, Au

M	R: CH_3	C_2H_5	*i*-C_3H_7
Ag	**2a**	**2b**	**2c**
Au	**3a**	**3b**	**3c**

$$\xrightarrow{NaNH_2 \text{ or } NaH} (C_6H_5)_3P{=}CHOR$$

4 (in solution)

These salts are soluble in most organic solvents, but are insoluble in ether, ethyl acetate, and benzene.

Attempts at the isolation of the alkoxymethylidenetriphenylphosphorane (**4**) from the reaction mixture of **1a**—**1e** and $NaNH_2$ or NaH in dry THF have been unsuccessful, probably because the electron density of ylide carbanion of **4** is too high, as compared with other unstable alkylidenetriphenylphosphoranes,[4,10] to allow its existence. At present, the ylide **4**[7,11,12] can never be isolated from the solution.

NMR Spectra. The ^{1}H-NMR spectra of **1a**—**1e**, **2a**—**2c**, and **3a**—**3c** were measured in $CDCl_3$ at room temperature. In the ^{1}H-NMR spectrum of **3a**, the signal (3.67 ppm) at the highest field is assigned to the methyl protons of the OCH_3 group. The signal of 5.28 ppm is assigned to the methylene protons of the PCH_2 group. The multiplet signal of 7.8 ppm at the lowest field is assigned to the protons of the phenyl groups. The coupling constants (J_{HCP}: 4 Hz) of the methylene protons of **1a**—**1e**, **2a**—**2c**, and **3a**—**3c** are much smaller than those ($J_{HCP}\approx 13$ Hz) of the alkyltriphenylphosphonium salts, $[(C_6H_5)_3\overset{+}{P}CH_2R]$, R: H (**5a**),[3,13] CH_3 (**5b**),[13] and *i*-C_3H_7 (**5c**),[13] of tetracovalent phosphorus, as is shown in Table 1. Hendrickson, *et al.*[1] explained the small coupling constant (4 Hz) of **1b** by assuming that the oxygen was partially bound to the positive phosphorus. The coupling constant (J_{HCP}) of $[(C_6H_5)_3PCH_2SeC_6H_5]Br$ (**6**) is 7 Hz,[14] which is also small. The selenium atom in **6** may interact with the positive phosphorus center, but the interaction can be weaker than that of **1a**—**1e**, **2a**, and **3a**, because the coupling constant of **6** is larger than those of these salts.

The ^{13}C-NMR spectra of **1a**—**1e**, **2a**, **3a**, and **5b**—**5c** have also been measured in $CDCl_3$ at room temperature. The doublet signals (10.1—29.2 ppm) at the highest field of **5a**—**5c** are assigned to the carbon of the $PCH_{2(3)}$ group. The chemical shift (10.1 ppm) of the methyl carbon of **5a** is much higher than that (29.2 ppm) of the methylene carbon of **5c**, while the coupling constant (J_{CP}: 56.6 Hz) of the methyl carbon of **5a** is larger than that (47.9 Hz) of the methylene carbon of **5c**. These changes seem to be due to the substituent (R) effect of $[(C_6H_5)_3\overset{+}{P}CH_2R]$; *i.e.*, the isopropyl group of the substituent in **5c** has a greater electron-donating effect than does the hydrogen of **5a**. In the ^{13}C-NMR spectra of **3a**, the doublet signal of 62.9 ppm is assigned to the carbon of the OCH_3 group, and the doublet signal of 66.3 ppm is assigned to the carbon of the PCH_2 group, while the singlet signal of 151.2 ppm is assigned to the cyano carbon of the $[Au(CN)_2]$ ion. The chemical shifts (δ CH_2P: 62—66 ppm) of **1a**—**1e**, **2a**, and **3a** are much lower than those of **5a**—**5c**. The coupling constants (J_{CP}) of these salts are 68—71 Hz, larger than those (48—56 Hz) of **5a**—**5c**, $Me_3P{=}S$,[15] and $Me_3P{=}Se$,[15] but close to that (66—69 Hz) of

TABLE 1. ^{1}H-NMR SPECTRA OF ALKOXYMETHYLTRIPHENYLPHOSPHONIUM SALTS

	OH_2P δ/ppm	J_{HCP}/Hz	OCH_{1-3} δ/ppm	CH_3 δ/ppm	J_{HCCH}/Hz	C_6H_5 δ/ppm
1a	5.83 d (2H)	4.0	3.67 s (3H)			7.80m(15H)
1b	5.80 d (2H)	4.0	3.73 s (3H)			7.83m(15H)
1c	5.70 d (2H)	4.0	3.73 s (3H)			7.83m(15H)
1d	5.80 d (2H)	4.0	3.93 q (2H)	1.17 t (3H)	7.2	7.80m(15H)
1e	5.75 d (2H)	4.0	4.13m(1H)	1.20 d (6H)	6.0	7.80m(15H)
2a	5.28 d (2H)	4.5	3.64 s (3H)			7.80m(15H)
2b	5.28 d (2H)	4.0	3.83 q (2H)	1.24 t (3H)	7.2	7.80m(15H)
2c	5.24 d (2H)	5.0	3.94m(1H)	1.23 d (6H)	6.0	7.80m(15H)
3a	5.28 d (2H)	4.5	3.67 s (3H)			7.80m(15H)
3b	5.31 d (2H)	4.0	3.89 q (2H)	1.25 t (3H)	7.2	7.80m(15H)
3c	5.23 d (2H)	5.0	3.94m(1H)	1.22 d (6H)	6.0	7.80m(15H)

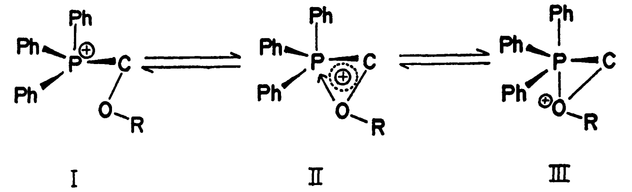
Solvent and standard: $CDCl_3$ (int. TMS).

TABLE 2. ^{13}C-NMR SPECTRA OF **1a**—**1e**, **2a**, **3a**, AND **5a**—**5c**

No.	PCH_{2-3} δ/ppm	$^1J_{CP}$/Hz	OCH_{1-3} [CH] δ/ppm	$^3J_{COCP}$/Hz	$^2J_{CCP}$/Hz	CH_3 δ/ppm	C_6H_5 δ/ppm (J_{CP}/Hz) c-1	*o*	*m*	*p*	CN δ/ppm
1a	65.7 d	68.4	62.5 d	13.7			116.3	133.9	130.2	135.2	
							(85.9)	(11.7)	(11.7)	(—)	
1b	65.1 d	70.3	61.8 d	13.7			115.4	133.1	129.6	134.4	
							(85.9)	(9.8)	(13.7)	(—)	
1c	66.0 d	69.3	62.5 d	13.7			115.8	133.7	127.2	135.2	
							(86.9)	(10.7)	(12.7)	(2.9)	
1d	63.3 d	68.4	69.8 d	13.7		13.9 s	115.4	132.9	129.9	134.4	
							(85.9)	(9.8)	(13.7)	(3.9)	
1e	62.0 d	70.3	76.3 d	11.7		21.2 s	116.1	133.6	129.9	134.8	
							(85.8)	(9.8)	(11.7)	(—)	
2a	66.2 d	71.3	62.7 d	13.7			115.8	133.8	130.8	135.9	153.4s
							(86.9)	(9.8)	(12.7)	(2.9)	
3a	66.3 d	70.3	62.9 d	13.7			115.8	133.8	130.7	135.9	151.2s
							(86.9)	(9.8)	(12.7)	(2.9)	
5a	10.1 d	56.6					118.5	132.7	130.0	134.7	
							(87.9)	(11.7)	(11.7)	(—)	
5b	16.1 d	51.8			4.9	5.9 d	116.9	132.6	129.6	134.2	
							(85.9)	(10.7)	(12.7)	(2.9)	
5c	29.2 d	47.9	[23.0 d]		3.9	23.4 s	117.4	132.4	129.4	133.9	
							(85.9)	(10.7)	(12.7)	(2.9)	
$K[Ag(CN)_2]$a)											149.7s
$K[Au(CN)_2]$a)											154.1s

Solvent and standard: $CDCl_3$ (δ=77.1 ppm). a) D_2O and internal dioxane (δ=67.4 ppm).

$Me_3P{=}O$[16] and $Et_3P{=}O$.[16] The large coupling constants (J_{CP}) of these salts can be caused by the highly electronegative[17] oxygen in salts. As the oxygen atom and the positive phosphorus center in these salts come close to each other and interact, the 2p electrons of the oxygen atom are partially bound to the 3d-orbital of the positive phosphorus. Thus, the positive charge is delocalized over the $\underset{\nwarrow O \diagup}{P\text{——}C}$ system, and the phosphorus is considered to be formally pentacovalent (Formulae II and III) with the dsp^3 configuration from the Formulae I—III. The chemical shifts and the coupling constants of **1a**—**1e**, **2a**, and **3a** receive less influence from the substituent. The anion in these salts has no effect on the chemical shift or the coupling constant. The ^{13}C-NMR data of these salts are collected in Table 2.



I II III

Experimental

Measurements. The NMR spectra were measured with an FX-60 spectrometer (JEOL) for ^{13}C-NMR, and with JNMPMX-60 (JEOL) and R-40 (Hitachi) spectrometers for ^{1}H-NMR.

Starting Materials. Alkyl halomethyl ether were prepared by Vousi,[18] Lapkina,[19] and Marvel's[20] methods.

*Methoxymethyltriphenylphosphonium Chloride, [$(C_6H_5)_3PCH_2OCH_3$]Cl (**1a**), Methoxymethyltriphenylphosphonium Bromide (**1b**), Methoxymethyltriphenyl phosphonium Iodide [$(C_6H_5)_3PCH_2OCH_3$]I (**1c**), Ethoxymethyltriphenylphosphonium Bromide (**1d**), and Isopropoxymethyltriphenylphosphonium Bromide (**1e**)*: The corresponding alkyl halomethyl ether (7.55 g (95 mmol dm^{-3}) for **1a**. 39.0 g (314 mmol dm^{-3}) for **1b**, 1.83 g (10.7 mmol dm^{-3}) for **1c**, 14.00 g (101 mmol dm^{-3}) for **1d**, and 18.00 g (118 mmol dm^{-3}) for **1e**) was added to a benzene solution of triphenylphosphine (25 g (95 mmol dm^{-3}) for **1a**, 82.1 g (312 mmol dm^{-3}) for **1b**, 2.8 g (10.7 mmol dm^{-3}) for **1c**, 26.4 g (101 mmol dm^{-3}) for **1d** and 31.0 g (118 mmol dm^{-3}) for **1e**). The solution was then stirred for 24 h at room temperature. The white salt thus precipitated was filtered off, washed with benzene, and dried under vacuum. The crude products were recrystallized from chloroform and ethyl acetate. Yield: 30.0 g (92.1%) for **1a**, 106.0 g (87.7%) for **1b**, 3.47 g (74.7%) for **1c**, 37.1 g (91.5%) for **1d**, and 41.0 g (83.7%) for **1e**. Found: C, 69.89; H, 5.80% for **1a**, C, 61.84; H, 5.06% for **1b**, C, 55.40; H, 4.50% for **1c**, C, 62.73; H, 5.83% for **1d**, and C, 63.54; H, 5.70% for **1e**. Calcd for $C_{20}H_{20}OClP$ (MW 342.81) C, 70.07; H, 5.88 for **1a**, $C_{20}H_{20}OBrP$ (MW 387.26) C, 62.03; H, 5.21 for **1b**, $C_{20}H_{20}OIP$ (MW 434.26) C, 55.32; H, 4.64 for **1c**, $C_{21}H_{22}OBrP$ (MW 401.28) C, 62.87; H, 5.53 for **1d**, and $C_{22}H_{24}OBrP$ (MW 415.33) C, 63.62; H, 5.82% for **1e**. Mp: 198—199 for **1a**, 208—210 for **1b**, 189—190 for **1c**, 227—229 for **1d**, and 190—191 °C for **1e**.

Methoxymethyltriphenylphosphonium Dicyanoargentate (I) (2a), Ethoxymethyltriphenylphosphonium Dicyanoargentate (I) (2b), and Isopropoxymethyltriphenylphosphonium Dicyanoargentate (I) (2c): **1b** (0.387 g, 1.0 mmol dm^{-3}), **1d** (0.40 g, 1.0 mmol dm^{3}), and **1e** (0.415 g, 1.0 mmol dm^{-3}) were dissolved in 1 cm^3 of methanol. Potassium dicyanoargentate (I) (0.2 g, 1.0 mmol dm^{-3}) was dissolved in 0.7 cm^3 of water. The methanol solution was added to an aqueous solution, and the new mixture was stirred; the white complex thus precipitated was filtered, washed with cooled water, and dried. Yield: 0.38 g (81.4%) for **2a**, 0.40 g (83.2%) for **2b**, and 0.40 g (80.8%) for **2c**. Found: C, 56.54; H, 4.52 for **2a**, C, 57.26; H, 4.59 for **2b**, and C, 58.32; H, 4.88% for **2c**. Calcd for $C_{22}H_{20}N_2OAgP$ (MW 467.28) C, 56.55; H, 4.31 for **2a**, $C_{23}H_{22}N_2OAgP$ (MW 481.31) C, 57.40; H, 4.01 for **2b**, and $C_{24}H_{24}N_2OAgP$ (MW 495.33) C, 58.20; H, 4.88% for **2c**. Mp: 122—124 for **2a**, 133—135 for **2b** and 126—127 °C for **2c**.

Methoxymethyltriphenylphosphonium Dicyanoaurate (I) (3a), Ethoxymethyltriphenylphosphonium Dicyanoaurate (I) (3b), and Isopropoxymethyltriphenylphonium Dicyanoaurate (I) (3c): 0.194 g (0.5 mmol dm^{-3}) of **1b**, 0.20 g (0.5 mmol dm^{-3}) of **1c**, and 0.207 g (0.5 mmol dm^{-3}) of **1d** was soluble in 0.5 cm^3 methanol. Potassium dicyanoaurate (I) (0.15 g, 0.5 mmol dm^{-3}) was soluble in water of 0.7 cm^3. The above methanol solution was added to an aqueous solution, the mixture was stirred; the white complex thus precipitated was filtered, washed with cooled water, and dried. Yield: 0.2 g (71.9%) for **3a**, 0.2 g (70.1%) for **3b** and 0.23 g (78.7%) for **3c**. Found: C, 47.52; H, 3.84 for **3a**, C, 48.44; H, 3.99 for **3b**, and C, 49.76; H, 4.30% for **3c**. Calcd for $C_{22}H_{20}N_2OAuP$ (MW 556.38) C, 47.49; H, 3.62 for **3a**, $C_{23}H_{22}N_2OAuP$ (MW 570.41) C, 48.43; H, 3.89 for **3b**, and $C_{24}H_{24}N_2OAuP$ (MW 584.43) C, 49.32; H, 4.14% for **3c**. Mp: 143—145 for **3a**, 150—152 for **3b**, and 143—146 °C for **3c**.

Methyltrihpenylphosphonium Bromide[21] *(5a), Ethyltriphenylphosphonium Bromide*[21a,22] *(5b), and Isobuthyltriphenylphosphonium Bromide*[23] *(5c)*: They were prepared from triphenylphosphine and the corresponding alkyl bromide.

The Reaction of 1b and Base: **1b** (4.20 g, 10.8 mmol dm^{-3}) and sodium amide (0.42 g, 10.8 mmol dm^{-3}) were suspended in dry THF (12 ml) at room temperature, and the mixture was stirred for approximately 1 h. The orange solution[11] was filtered under nitrogen. Dry pentane was added to the solution and cooled. The yellow crystal was filtered under nitrogen and dried. The ^{1}H-NMR spectrum of that crystal in benzene-d_6 did not show the expected signal of the ylide carbanion at room temperature. ^{1}H-NMR spectrum of yellow crystals: δ 3.07 (s, 3H, OCH_3), 4.0 (d, 2H, J=6, PCH_2), 7.2—8.1 (m, 15H, C_6H_5), in C_6D_6.

A solution of 0.13 g of phLi (1.15 mmol dm^{-3}) in toluene-d_8 (5 ml) was slowly added to a suspension of **1b** (0.95 g, 2.45 mmol dm^{-3}) in 2 ml of toluene-d_8 at −70 °C under helium. The orange solution was filtered after 4 h at −70 °C under helium. The orange filtrate did not show the signal of the ylide carbanion from the ^{1}H-NMR spectrum.

The orange solutions from NaH and **1b** in solvents (THF or toluene) at the present temperatures (r.t. or −70 °C) did not show the signals of the ylide carbanion from the ^{1}H-NMR spectra.

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