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Syntheses of Cyano Derivatives of Triphenylphosphoniocyclopentadienide

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Bromo derivatives of triphenylphosphoniocyclopentadienide were found to react with copper cyanide in *N,N*-dimethylformamide to give the corresponding nitriles without decomposition. The mono- and dicyano derivatives were prepared under relatively mild reaction conditions, but no tricyano derivatives were obtained from the cyclopentadienide having more than three bromine atoms in the cyclopentadienyl ring.

Preceding papers contain reports on the electronic structures[1-3] and the syntheses[4-7] of various derivatives of triphenylphosphoniocyclopentadienide (**1**)[8] by the reactions of **1** with electrophiles and electron-deficient unsaturated compounds such as dialkyl acetylenedicarboxylate, tetracyanoethylene and maleimide. In the present research, the syntheses of the cyano derivatives of **1** have been attempted. Introduction of cyano groups into the five-membered ring might result in the stabilization of **1**, since cyano-substituted cyclopentadienide anions are known to be remarkably stable. Webster[9] synthesized tetra- and pentacyanocyclopentadienide salts from diazotetracyanocyclopentadiene prepared with use of 1,1,-2,3,4,4-hexacyano-2-butene dianion and observed that these highly cyano-substituted cyclopentadienides are very stable. For example, the potassium salt of pentacyanocyclopentadienide is so stable that it can be heated at 400 °C in the air without decomposition. The pK_a values of polycyanocyclopentadienes are extremely small as compared with those of 14—15 for cyclopentadiene,[10] indicating that the cyano group effectively stabilizes the cyclopentadienide anion. We have succeeded in introducing cyano groups into the cyclopentadienyl ring of **1** by cyano-debromination at the cyclopentadienyl ring (a different method from that of Webster). The reactions of the bromo derivatives of **1** with cuprous cyanide have been attempted in *N,N*-dimethylformamide(DMF). The cyanation products were obtained in good yields, when the derivatives substituted by two or three bromine atoms together with other substituents such as nitro, phenylazo, formyl, methoxycarbonyl and cyano groups in the cyclopentadienyl ring were employed as the bromo derivatives. The substitution reaction of bormine atom(s) in cyclopentadienyl ring with cyano group is a convenient method to introduce cyano group into cyclopentadienyl ring.

Results and Discussion

The bromo derivatives of **1** employed in the reaction were synthesized by the reactions of **1** and its derivatives with *N*-bromosuccinimide. The yields, melting points and analytical data are given in Table 1. The starting materials **2**, **3**, **4**, and **5** were prepared by nitration, diazo coupling and Vilsmeier reaction of **1**.[4,7] The substitution at 2-position was indicated by the reaction indices calculated from HMO treatment[7] and confirmed experimentally in the diazo coupling[11] and nitrosation reactions.[7] Triphenylphosphonio-2,5-bis(methoxycarbonyl)cyclopentadienide (**6**) was prepared by the oxidation of **5** and subsequent treatment with diazomethane. Refluxing of the oxime of **5** in acetic anhydride afforded triphenylphosphonio-2,5-dicyanocyclopentadienide (**7**). The remaining hydrogens in the cyclopentadienyl ring of these derivatives (**2**, **3**, **4**, **5**, **6**, and **7**) were easily bromainted by *N*-bromosuccinimide.

Triphenylphosphonio-2,5-dibromocyclopentadienide (**8**) was prepared by treatment of **1** with cyanogen bromide. Cyanogen bromide is known as a reagent for direct cyanation of aromatic compounds in the presence of Lewis acid.[12] However, the reaction of **1** with cyanogen bromide in the presence of aluminum trichloride gave the 2,5-dibrominated one(**8′**) but no cyanation product. Compound **8′** is not as stable as the other bromo drivatives, but diazo coupling reaction of **8′** led to the formation of a stable compound, **9′**. All the bromo derivatives (**2′**, **3′**, **4′**, **5′**, **6′**, **7′**, **8′**, and **9′**) are new compounds.

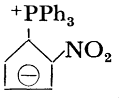
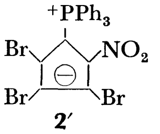
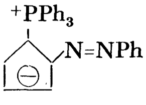
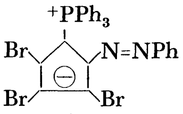
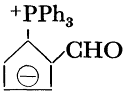
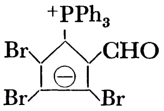
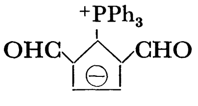
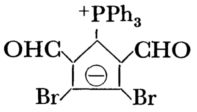
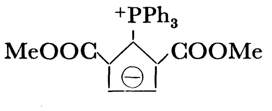
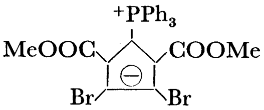
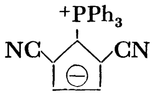
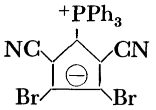
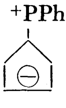
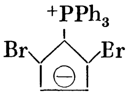
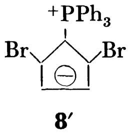
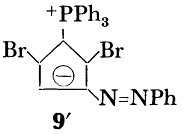
The reactions of these bromo derivatives with cuprous cyanide (Rosenmund-von Braun type reaction) were examined. The preparative method of aryl cyanides from aryl halides and cuprous cyanide was established,[13] its improvement[14,15] and mechanism[16,17] also being reported. Reactions of the bromo derivatives, **2′**, **3′**, **4′**, **5′**, and **6′** with cuprous cyanide in DMF under reflux resulted in the formation of the cyanation products, which showed the characteristic absorption due to the cyano groups in the IR spectrum. Elemental analyses indicated the products to be dicyano-substituted one, **2″**, **3″**, **4″**, **5″**, and **6″**. No tricyanation compounds were obtained even under reflux for a week. This can be attributed to the steric hindrance in the formation of the intermediate complex [RBr–CuCN], through which the reaction might proceed.

The chlorinated derivatives of **1** did not undergo Rosenmund-von Braun type reaction. For example, triphenylphosphonio-2,5-diformyl-3,4-dichlorocyclopentadienide with cuprous cyanide in DMF did not take place under reflux for several days.

The bromine atoms of 2,5-dicyano-3,4-dibromocyclopentadienide (**7′**) were not replaced with cyano groups. The result can be accounted for by the poor interaction between the copper metal and the bromine atom, presumably because of the dominant interaction of copper with the cyano groups attached to the 2,5-positions.

In the reaction of triphenylphosphonio-2,5-dibromocyclopentadienide (**8′**) with cuprous cyanide, decomposition immediately occurs to afford a tarry substance. The inherently unstable derivative **8′** was

TABLE 1. BROMO-SUBSTITUTED DERIVATIVES OF TRIPHENYLPHOSPHONIOCYCLOPENTADIENIDE

Starting material	Reagent	Bromo-derivative	Yield (%)	Mp (°C)	Formula	Elemental analysis (%)			
 **2**	NBS	 **2′**	81	190 (dec)	$C_{23}H_{15}Br_3NO_2P$		C	H	Br
						Calcd	45.43	2.49	39.43
						Found	45.34	2.54	39.52
 **3**	NBS	 **3′**	83	191 (dec)	$C_{29}H_{20}Br_3N_2P$		C	H	Br
						Calcd	52.21	3.02	35.93
						Found	52.10	3.25	36.01
 **4**	NBS	 **4′**	72	208 (dec)	$C_{24}H_{16}Br_3OP$		C	H	Br
						Calcd	48.76	2.72	40.55
						Found	48.65	3.02	40.31
 **5**	NBS or Br_2	 **5′**	89	186 (dec)	$C_{25}H_{17}Br_2O_2P$		C	H	Br
						Calcd	55.58	3.17	29.58
						Found	55.14	3.30	28.30
 **6**	NBS	 **6′**	90	232 (dec)	$C_{27}H_{21}Br_2O_4P$		C	H	Br
						Calcd	54.03	3.53	5.16
						Found	53.72	3.55	5.10
 **7**	NBS	 **7′**	92	258 (dec)	$C_{25}H_{15}Br_2N_2P$		C	H	P
						Calcd	56.21	2.83	29.91
						Found	56.20	3.07	31.56
 **1**	BrCN/ $AlCl_3$	 **8′**	68	122 (dec)	$C_{23}H_{17}Br_2P$		C	H	P
						Calcd	57.05	3.53	6.40
						Found	57.15	3.72	6.66
 **8′**	PhN_2Cl	 **9′**	83	228 (dec)	$C_{29}H_{21}Br_2N_2P$		C	H	Br
						Calcd	59.21	3.60	27.16
						Found	58.89	3.72	27.92

not recovered. More stable derivative **9′** reacts with cuprous cyanide to give the monocyano-substituted product, **9″**. The results are summarized in Table 2. Although the positions of the cyano-debromination in the five-membered ring were not experimentally determined for **2″**, **3″**, **4″**, and **9″**, most probable structures were deduced from examination of the intermediate complex in the reaction by the use of CPK atomic models.

Attempt to replace the bromine atoms in the five-membered ring of **2′**—**9′** with cyano groups using sodium cyanide was unsuccessful, but treatment of the bromo derivatives with sodium cyanide in the presence of cuprous bromide gave the cyano-substituted derivatives. The reaction of the bromo derivatives with cupric cyanide also afforded the cyanated products. Thus, it is obvious that copper is important as a catalyst in the substitution of the bromine by cyano group on the five-membered ring of triphenylphosphoniocyclopentadienide. The reaction is considered to proceed *via* a complex of copper with bromine atom and cyanide ion.

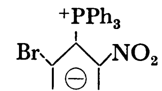
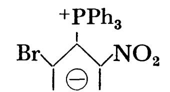
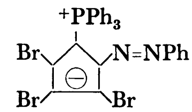
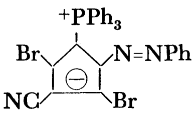
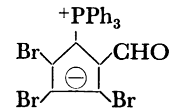
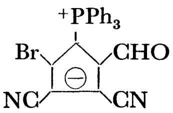
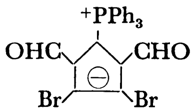
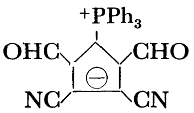
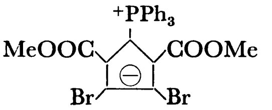
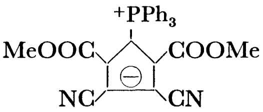
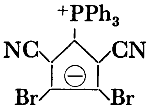
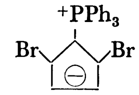
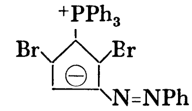
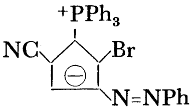
All the cyano-substituted products synthesized are stable in the air as well as in acidic and basic media.

Experimental

Spectra. Ultraviolet spectra were taken on a Hitachi EPS-3T recording photometer. Infrared spectra were recorded on a Hitachi grating infrared spectrophotometer, Model 215, and NMR spectra on a JNM C-60H NMR spectrometer with tetramethylsilane as an internal standard.

*Preparation of Triphenylphosphoniocyclopentadienide and Its Derivatives, **1**—**7** (Starting Materials in Table 1).* Triphenylphosphoniocyclopentadienide (**1**) and the derivatives (**2**, **3**, **4**, and **5**) were prepared according to the methods reported.[4-8] The derivative **6** was prepared by the oxidation of **5** and subsequent treatment with diazomethane. Mp 244 °C; IR(KBr) 1695 cm^{-1} (C=O); NMR ($CDCl_3$), $\delta=7.5$—8.0 (15H, m, phenyl), 6.85 (2H, d, $J_{P-H}=5.0$ Hz, cyclopentadienyl), 3.80 (6H, s, methyl).

Table 2. Reactions of bromo derivatives (**2′**—**9′**) with cuprous cyanide in *N*,*N*-dimethylformamide

Bromo derivatives	Reaction temperature	Reaction time (h)	Cyanation product.	Yield (%)	Mp (°C)
 **2′**	Reflux	2	 **2″**	47	259 (dec)
 **3′**	130—135 °C	0.5	 **3″**	68	266 (dec)
 **4′**	Reflux	2	 **4″**	32	257 (dec)
 **5′**	Reflux	2	 **5″**	75	263 (dec)
 **6′**	Reflux	2	 **6″**	74	273—274 (dec)
 **7′**	Reflux	12	No reaction	—	
 **8′**	110—115 °C	1	Decomposition	—	—
 **9′**	130—135 °C	4	 **9″**	84	191 (dec)

Found: C, 73.21; H, 5.20; P, 6.85%. Calcd for $C_{27}H_{23}O_4P$: C, 73.29; H, 5.23; P, 7.00%.

The 2,5-dicyano derivative **7** was prepared by the reaction of acetic anhydride with the dialdehyde oxime derived from **5** under reflux for 1 h. The IR spectrum showed and absorption band at 2250 cm^{-1} due to the cyano group; NMR ($CDCl_3$) δ=7.4—7.9 (15H, m, phenyl), 3.45 (2H, d, J_{P-H}=5.5 Hz, cyclopentadienyl).

Found: C, 72.83; H, 5.09; N, 6.79%. Calcd for $C_{25}H_{17}N_2P$: C, 72.54; H, 5.37; N, 6.86%.

Bromination of Triphenylphosphoniocyclopentadienide Derivatives. A solution of *N*-bromosuccinimide was added to a solution of triphenylphosphonio-2-nitro, 2-phenylazo, 2-formyl, 2,5-diformyl, 2,5-bis(methoxycarbonyl), and 2,5-dicyano-substituted cyclopentadienides (**2**—**7**). Stirring was continued for 30 min at room temperature and the precipitate was collected and recrystallized from dichloromethane–methanol.

Triphenylphosphonio-2,5-dibromocyclopentadienide (**8′**) was prepared by the following procedure. 0.750 g (0.70 mol) of cyanogen bromide in 20 ml of dichloromethane was added at 0—5 °C for 10 min to a solution of 1.141g (0.035 mol) of **1** in 100 ml of dichloromethane. After being stirred for 1 h at 110—115 °C the solvent was evaporated and the residue was chromatographed on alumina using dichloromethane as an eluent. A solid product precipitated when hexane was added to the dichloromethane solution. The precipitate was collected and purified by recrystallization from dichloromethane-methanol. The product **8′** is unstable, and accordingly the successive reaction should be carried out in mild conditions. However, triphenylphosphonio-2,5-dibromo-3-phenylazocyclopentadienide (**9′**) prepared by the diazo coupling reaction of **8′** is stable.

The yields, melting points and analytical data of **2′**—**9′** are summarized in Table 1.

*Reaction of Bromo-substituted Phosphoniocyclopentadienide (**2′**—**9′**) with Cuprous Cyanide.* The reactions of the bromo derivatives with cuprous cyanide in DMF were carried out under the reaction conditions given in Table 2. The reaction mixture was poured into water and the procut precipitated was collected, washed with water and purified by column chromatography on alumina using dichloromethane–methanol as eluents. The yields and the melting points are summarized in Table 2. The spectral and analytical data of each product are as follows.

Triphenylphosphonio(2-nitro-3,4-dicyano-5-bromo)cyclopentadienide (**2″**): mp 295 °C (dec); IR (KBr) 2220 cm^{-1} ($C\equiv N$); NMR ($CDCl_3$) $\delta=7.4$—8.0 (m, phenyl); UV_{max} (CH_3CN) 222 nm (log ε 4.54), 393 (4.08).

Found: C, 60.29; H, 3.25; N, 8.28: P, 5.88%. Calcd for $C_{25}H_{15}N_3O_2Br$: C, 60.01; H, 3.03; N, 8.48; P, 6.11%.

Triphenylphosphonio(2-phenylazo-3,5-dibromo-4-cyano)-cyclopentadienide (**3″**): mp 266 °C (dec); IR (KBr) 2210 cm^{-1} ($C\equiv N$); NMR ($CDCl_3$) $\delta=6.6$—7.2 (5H, m, phenylazo), 7.4—8.0 (15H, m, P-phenyl); UV_{max} (CH_3CN) 223 nm (log ε 4.64), 432 (4.32).

Found: C, 58.96; H, 3.23; N, 6.97%. Calcd for $C_{30}H_{20}N_3PBr_2$: C, 58.75; H, 3.29; N, 6.85%.

Triphenylphosphonio(2-formyl-3,4-dicyano-5-bromo)cyclopentadienide (**4″**): mp 257 °C (dec); IR (KBr) 2210 ($C\equiv N$) 1665 cm^{-1} ($C=O$): NMR ($CDCl_3$) $\delta=7.3$—8.0 (15H, m, phenyl), 9.81 (1H, formyl); UV_{max} (CH_3CN) 232 nm (log ε 4.61), 254 (4.57), 316 (4.18).

Found: C, 64.63; H, 3.49; N, 5.67%. Calcd for $C_{26}H_{16}N_2OPBr$: C, 64.41; H, 3.34; N, 5.80%.

Triphenylphosphonio(2,5-diformyl-3,4-dicyano)cyclopentadienide (**5″**): mp 263 °C (dec); IR (KBr) 2210 ($C\equiv N$), 1670 cm^{-1} ($C=O$); NMR ($CDCl_3$) $\delta=7.4$—8.1 (15H, m, phenyl), 10.39 (2H, s, formyl): UV_{max} (CH_3CN) 269 nm (log ε 4.61), 278 (4.69), 327 (3.92).

Found: C, 74.64; H, 4.11; N, 6.47%. Calcd for $C_{27}H_{17}N_2O_2P$: C, 74.99; H, 3.97; N, 6.48%.

Triphenylphosphonio-2,5-bis(methoxycarbonyl)-3,4-dicyanocyclopentadienide (**6″**): mp 273.5—274.0 °C; IR (KBr) 2200 ($C\equiv N$), 1710 cm^{-1} ($C=O$); NMR ($CDCl_3$) $\delta=7.6$—8.0 (15H, m, phenyl), 3.90 (6H, s, methyl); UV_{max}(CH_3CN) 233 nm (log ε 4.63), 253 (4.65), 276 (4.15), 292 (4.11).

Found: C, 70.45; H, 4.45; N, 5.76; P, 6.21%. Calcd for $C_{29}H_{21}N_2O_4P$: C, 70.73; H, 4.30; N, 5.69; P, 6.29%.

Triphenylphosphonio(2-bromo-3-phenylazo-5-cyanocyclopentadienide (**9″**); mp 191 °C (dec); IR (KBr) 2210 cm^{-1} ($C\equiv N$); NMR ($CDCl_3$) $\delta=5.80$ (1H, d, $J_{P-H}=6.0$ Hz, cyclopentadienyl), 6.7—7.3 (5H, m, phenylazo), 7.3—8.0 (15H, m, phenyl); UV_{max} (CH_3CN) 220 nm (log ε 4.53), 4.28 (4.08).

Found: C, 67.15; H, 3.87; N, 7.56%. Calcd for $C_{30}H_{21}N_3PBr$: C, 67.42; H, 3.97; N, 7.86%.

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