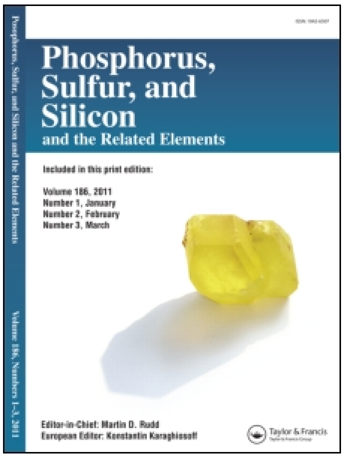

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THE PREPARATION OF ALKYLARYLDICHLOROCYCLOPROPANOL PHOSPHATES

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In the present article we report the preparation of alkylaryldichlorocyclopropanol phosphates by the addition of dichlorocarbene to enol phosphates of propiophenone and cyclohexanone with steric hinderance. The stereoselectivity of enol phosphates and the effect of substituents on the carbene addition rate are discussed.

Keywords: Addition; carbene; enol phosphate

Cyclopropanol is an important structure for the enzyme inhibitor,[1] its phosphates may be potential bioactive compounds. The easiest synthetic method is carbene addition to enol phosphates.

Due to the electron-withdrawing effect of the phosphoryl and phenyl group, aryl substituted enol phosphates can be regarded as electron-poor alkenes and relatively unreactive substrances, the carbene addition produces a complicated situation and gives a poor yield. Selms[2] obtained the dichlorocyclopropanol phosphates in an average yield of 25% by addition of carbene, generated from sodium trichloroacetate, to enol phosphates. Dichlorocarbene generated by phase-transfer reaction is exceptionally reactive toward substrates which hardly react.[3] To improve the addition reaction, Toke[4] studied the dichlorocarbene addition to enol phosphate under PTC condition.

In this article, we report on the addition of dichlorocarbene to more sterically hindered enol phosphates of propiophenone **2a–j** and cyclohexanone **2k** by the Toke method to prepare alkyl and aryl substituted cyclopropanol phosphates. The stereoselectivity of enol phosphates and the effect of substituents on the carbene addition rate are discussed.

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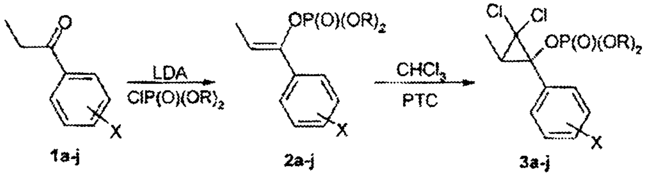

	a	b	c	d	e	f	g	h	i	j
X	H	4-Me	4-MeO	4-Cl	2,4-Me$_2$	H	4-Me	4-MeO	4-Cl	2,4-Me$_2$
R	Me	Me	Me	Me	Me	Et	Et	Et	Et	Et

RESULTS AND DISCUSSION

All enol phosphates used in the present work were prepared by reaction of dialkyl phosphorochloridate with enolate anion that formed from phenyl ethyl ketone and LDA under kinetically controlled condition as shown in Table I. LiBu and NEt$_3$ as base or the Atherton-Todd procedure gave poorer results.

We found that all of the propiophenones listed in Table I, except for compounds **2e** and **2j**, formed Z-isomers under the given conditions in a highly stereoselective manner. The structures of the products

TABLE I Preparation of Enol Phosphates

No.	Yield (%)[a] of **2**	Z:E[b] of **2**	Yield (%)[a] of **3**
a	70	>95:5	57
b	65	>95:5	70
c	58	>95:5	98
d	72	>95:5	60
e	59	4:6	59[c]
f	56	>95:5	68
g	54	>95:5	63
h	75	>95:5	98
i	90	>95:5	54
j	69	4:6	50[c]
k	78		75

[a] Isolated yield.

[b] The Z:E ratios were determined by ^{1}H-NMR analyses of the vinyl proton peaks of reaction products in the crude reaction mixture.

[c] The ratios of cis and trans isomers of cyclopropanol phosphates **3e** or **3j** are 3:7, the difference with **2e** and **2j** may be contributed to experimental and NMR error.

were assigned on the basis of ^{1}H-NMR spectral analysis; the spectrum did not show the vinyl proton peak of the E isomer. TLC monitoring did not show the presence of other products. In each case, this analysis was carried out on the crude product prior to purification by chromatography.

The stereoselectivity can be rationalized by the CIPE hypothesis (complex-induced proximity effect).[5] The more stable cis-conformation of propiophenones would lead to the formation of predominantly Z-isomer[6] of enol phosphates. In order to have more precise geometries PM3 semiempirical quantum mechanics calculation was performed. The binding energy and the heat of formation of cis conformations of the phenone **2d** are −2129.986 kcal/mol and 32.177 kcal/mol respectively; that of gauche conformation are −2125.623 kcal/mol and 36.540 kcal/mol. Cis-conformation is proved to be more stable than gauche.

In carbene addition reaction phase transfer catalysis was used to generate dichlorocarbene. A solution of the enol phosphates and TEBAC in chloroform was stirred with 50% aqueous sodium hydroxide at room temperature resulting in the formation of the adducts **3** as summarized in Table I.

The ^{1}H NMR spectra of all compounds showed that the two alkyl groups of phosphates are magnetic nonequivalent, because of the different relative position to the magnetically anisotropic benzene ring.[7]

Because the dichlorocarbene is a strong electronphile, electron-withdrawing group will decrease the reaction rate, but the range of relative rates is not great.[8] We examined relative rates of addition of dichlorocarbene to enol phosphates by the competing reaction, the results are shown in Table II, X represents the group at the benzene ring. The experimental results were consistent with the expectation.

EXPERIMENTS

All melting points were uncorrected. IR spectra were measured with a Shimadzu IR-440 spectrometer. ^{1}H-NMR spectra were recorded on

TABLE II Relative Addition Rates of Dichlorocarbene to Enol Phosphates

No.	X	Relative rates (GC)
3f	H	1.00
3g	4-methyl	1.04
3h	4-methoxyl	1.27
3i	4-chloro	0.91
3j	2,4-dimethyl	3.78

AM-300 or DPX-400 using TMS as internal standard and $CDCl_3$ as solvent. Mass and HRMS spectra were taken on a Finnigan GC-MS-4021 spectrometer. Elemental analyses were done by the Elemental Analyses Group of SIOC. The known compounds were identified in agreement with the literature data, and only the NMR data are reported here. Phenyl ethyl ketones and diethyl phosphochloriate were prepared by known methods with purity of >97% (GC).

General Procedure for the Preparation of Enol Phosphates

Under nitrogen atmosphere a multi-necked round bottom flask was charged with dry THF and $HN(i\text{-}Pr)_2$. The mixture was stirred and cooled to 0°C. The BuLi solution in hexane (1.5 M) was added. 30 min. Later, a solution of propiophenone in THF was added dropwise at −78°C. After 1 h phosphochloridate was added. The reaction temperature was allowed to warm to rt. When the reaction was completed as determined by TLC (about 2 h), the reaction mixture was neutralized with acetic acid and then filtered. The filtrate was washed with water, dried over Na_2SO_4, and concentrated in vacuo to give an oil. The pure product was obtained after flash chromatography on silica gel (using petroleum ether and ethyl acetate as eluent).

2a: ^1H NMR (300 MHz) δ: 7.49 (d, $J = 7.8$ Hz, 2H), 7.64 (m, 3H), 5.67 (q, $J = 7.0$ Hz, 1H), 3.72 (d, $J = 11$ Hz, 6H), 1.88 (d, $J = 7.0$ Hz, 3H). m/z: 242 (M^+, 19.50), 131 (1.49), 127 (100.00), 115 (65.34), 116 (34.13), 109 (13.58), 91 (4.28), 77 (13.97). IR (film): 2959, 2858, 1667, 1447, 1578, 1040, 852, 520 cm^{-1}. Anal. calcd. For $C_{11}H_{15}O_4P$: C, 54.55; H, 6.20. Found: C, 54.28; H, 6.40.

2b: ^1H NMR (300 MHz) δ: 7.38 (d, $J = 7.4$ Hz, 2H), 7.15 (d, $J = 7.4$ Hz, 2H), 5.14 (q, $J = 7.0$ Hz, 1H), 3.74 (d, $J = 11$ Hz, 6H), 2.34 (s, 3H), 1.87 (d, $J = 7.0$ Hz, 3 H). m/z: 257 ($M^+ + 1$, 26.11), 256 (M^+, 59.29), 245 (4.69), 130 (76.98), 127 (100.00), 115 (64.49), 109 (16.09), 91 (20.81). IR (film): 2958, 2858, 1668, 1513, 1277, 1035, 852, 525 cm^{-1}. Anal. cacld. for $C_{12}H_{17}O_4P$: C, 56.25; H, 6.64. Found: C, 56.07; H, 6.92.

2c: ^1H NMR (300 MHz) δ: 7.42 (d, $J = 7.0$ Hz, 2H), 6.85 (d, $J = 7.0$ Hz, 2H), 5.53 (q, $J = 7.0$ Hz, 1H), 3.75 (d, $J = 11$ Hz, 6H), 3.70 (s, 3H), 1.86 (d, $J = 7.0$ Hz, 3H). m/z: 272 (M^+, 24.32), 146 (100.00), 131 (45.31), 127 (20.75), 115 (9.40), 109 (14.19), 103 (39.02), 91 (5.82). IR (film): 2959, 2857, 1669, 1513, 1251, 1033, 850, 590 cm^{-1}. Anal. cacld. For $C_{12}H_{17}O_5P$: C, 52.94; H, 6.25. Found: C, 53.52; H, 6.46.

2d: ^1H NMR (300 MHz) δ: 7.39~7.44 (m, 4H), 5.67 (q, $J = 7.1$ Hz, 1H), 3.73 (d, $J = 11$ Hz, 6H), 1.84 (d, $J = 7.1$ Hz, 6 H). m/z: 276

(M^+, 7.72), 241 (2.04), 150 (11.58), 127 (100.00), 115 (37.37), 109 (27.69), 95 (4.36), 79 (5.25). IR (film): 2959, 2858, 1666, 1492, 1278, 1036, 852, 508 cm^{-1}. HRMS cacld. for $C_{11}H_{14}ClO_4P$: 276.0318; Found: 276.0325.

2e: ^1H NMR (300 MHz) δ: 6.70~7.71 (m, 3H), 5.63 (q, $J = 7.0$ Hz, 0.4 × 1H), 5.13(q, $J = 7.0$ Hz, 0.60 × 1H), 3.58 (d, $J = 11$ Hz, 0.40 × 6H), 5.07 (d, $J = 11$ Hz, 0.60 × 6H), 2.25~2.29 (m, 6H), 1.79 (d, $J = 7.0$ Hz, 0.60 × 3H), 1.44 (d, $J = 7.0$ Hz, 0.40 × 3H). m/z: 270 (M^+, 9.40), 144 (73.86), 130 (13.67), 129 (100.00), 127 (36.95), 115 (9.63), 105 (5.68), 77 (5.36). IR (film): 2957, 2858, 1615, 1450, 1280, 1041, 851, 570 cm^{-1}. Anal. cacld. For $C_{13}H_{19}O_4P$: C, 57.78; H, 7.04. Found: C, 57.61; H, 7.13.

2f[9]: ^1H NMR (300 MHz) δ: 7.51~7.24 (m, 5H), 5.65 (q, $J = 7.0$ Hz, 1H), 4.06 (m, 4H), 1.87 (d, $J = 7.0$ Hz, 3H), 1.20 (m, 6H).

2g: ^1H NMR (300 MHz) δ: 7.33 (d, $J = 12$ Hz, 2H), 7.07 (d, $J = 12$ Hz, 2H), 5.57 (q, $J = 7.0$ Hz, 1H), 4.01 (m, 4H), 2.27 (s, 3H), 1.80 (d, $J = 7.0$ Hz, 3H), 1.19 (m, 6H). m/z: 284 (M^+, 25.17), 257 (3.09), 155 (100.00), 129 (57.97), 127 (50.33), 115 (52.61), 99 (49.12), 91 (28.35). IR (film): 2984, 2934, 1668, 1445, 1270, 1031, 815, 519 cm^{-1}. HRMS cacld for $C_{14}H_{21}O_4P$: 284.1178; Found: 284.1174.

2h: ^1H NMR (300 MHz) δ: 7.38 (d, $J = 6.9$ Hz, 2H), 6.79 (d, $J = 6.9$ Hz, 2H), 5.47 (q, $J = 7.0$ Hz, 1H), 4.06 (m, 4H), 3.74 (s, 3H), 1.81 (d, $J = 7.0$ Hz, 3H), 1.20 (m, 3 H). m/z: 306 (M^+, 6.92), 155 (11.11), 146 (100.00), 131 (43.49), 115 (8.71), 103 (30.30), 99 (8.75), 77 (12.28). IR (film): 2986, 2840, 1668, 1610, 1513, 1250, 1032, 797 cm^{-1}. Anal. cacld. For $C_{14}H_{21}O_5P$: C, 56.00; H, 7.00. Found: C, 55.98; H, 7.05.

2i: ^1H NMR (300 MHz) δ: 7.20~7.39 (m, 4H), 5.60 (q, $J = 7.0$ Hz, 1H), 4.03 (m, 4H), 1.82 (d, $J = 7.0$ Hz, 3H), 1.19 (m, 6H). m/z: 306 ($M^+ + 2$, 16.08), 304 (M^+, 19.95), 277 (12.50), 155 (100.00), 127 (51.04), 115 (50.49), 99 (47.26), 81 (13.71). IR (film): 2894, 1666, 1492, 1396, 1270, 1093, 1031, 819 cm^{-1}. Anal. cacld. For $C_{13}H_{18}ClO_4P$: C, 51.15; H, 5.90. Found: C, 50.83; H, 6.22.

2j: ^1H NMR (300 MHz) δ: 6.91~7.17 (m, 3H), 5.67 (q, $J = 7.0$ Hz, 0.4 × 1H), 5.13 (q, $J = 7.0$ Hz, 0.60 × 1H), 3.93 (m, 4H), 2.27 (m, 6H), 1.81 (d, $J = 7.0$ Hz, 0.60 × 3H), 1.45 (d, $J = 7.0$ Hz, 0.40 × 3H), 1.18 (m, 6H). m/z: 299 (M^+, 11.57), 298 (14.62), 238 (5.54), 155 (100.00), 144 (61.93), 129 (83.19), 127 (20.36), 91 (7.91). IR (film): 2985, 1616, 1445, 1273, 1032, 969, 818, 543 cm^{-1}. Anal. cacld. For $C_{15}H_{23}O_4P$: C, 60.40; H, 7.72; Found: C, 60.48; H, 7.67.

2k[9]: ^1H NMR (300 MHz) δ: 5.42 (m, 1H), 4.10 (m, 4H), 2.0–2.3, 1.5–1.9 (m, 8H), 1.35 (t, 6H, $J = 7$ Hz).

General Procedure for the Preparation of 1-Aryl-2,2-dichlorocyclopropanol Phosphates

The solution of 2.4 mmol enol phosphate in 5 ml chloroform was added dropwise to the mixture of 0.11 g (0.50 mmol) of TEBAC, 10 ml of chloroform and 8 ml (50% NaOH) at rt. The mixture was stirred and followed by TLC until the reaction was finished. The organic layer was washed and dried. After concentration in vacuo the crude product was purified by flash column chromatography using a mixture of petroleum ether (bp 60–90°C) and ethyl acetate as eluent to give the desired products.

3a: ^{1}H NMR (300 MHz) δ: 7.58 (m, 2H), 7.43 (m, 3H), 3.63 (d, $J = 11$ Hz, 3H), 3.23 (d, $J = 11$ Hz, 3H), 2.25 (q, $J = 6.6$ Hz, 1H), 1.52 (d, $J = 6.6$ Hz, 3H). m/z: 325 (M^+, 1.50), 289 (5.80), 253 (8.42), 200 (3.32), 163 (100.00), 127 (50.45), 109 (38.01), 77 (35.90). IR (film): 2958, 1450, 1281, 1047, 1005, 854, 702, 486 cm^{-1}. Anal. cacld. For $C_{12}H_{15}Cl_2O_4P$: C, 44.33; H, 4.65. Found: C, 44.49; H, 4.86.

3b: ^{1}H NMR (300 MHz) δ: 7.47 (d, $J = 7.4$ Hz, 2H), 7.22 (d, $J = 7.4$ Hz, 2H), 3.65 (d, $J = 11$ Hz, 3H), 3.26 (d, $J = 11$ Hz, 3H), 2.36 (s, 3H), 2.23 (q, $J = 6.6$ Hz, 1H), 1.50 (d, $J = 6.6$ Hz, 3H). m/z: 339 (M^+, 0.78), 303 (5.31), 267 (6.80), 214 (4.30), 177 (100.00), 155 (38.12), 91 (22.30), 77 (3.25). IR (film): 2958, 1616, 1452, 1280, 1045, 1280, 1045, 848, 729, 538 cm^{-1}. Anal. cacld. For $C_{13}H_{17}Cl_2O_4P$: C, 46.02; H, 5.01; Found: C, 46.24; H, 5.27.

3c: ^{1}H NMR (400 MHz) δ: 7.42 (d, $J = 6.5$ Hz, 2H), 6.83 (d, $J = 6.5$ Hz, 2H), 3.69 (s, 3H), 3.56 (d, $J = 11$ Hz, 3H), 3.18 (d, $J = 11$ Hz, 3H), 2.13 (q, $J = 6.6$ Hz, 1H), 1.39 (d, $J = 6.6$ Hz, 3H). m/z: 355 (M^+, 4.88), 319 (33.57), 283 (5.75), 230 (4.96), 193 (100.00), 158 (4.36), 127 (30.88). IR (film): 2958, 1612, 1517, 1255, 1045, 1001, 848, 512 cm^{-1}. Anal. cacld. For $C_{13}H_{17}Cl_2O_5P$: C, 43.96; H, 4.82. Found: C, 44.23; H, 5.05.

3d: ^{1}H NMR (400 MHz) δ: 7.46 (d, $J = 8.6$ Hz, 2H), 7.33 (d, $J = 8.6$ Hz, 2H), 3.57 (d, $J = 11$ Hz, 3H), 3.26 (d, $J = 11$ Hz, 3H), 2.15 (q, $J = 6.6$ Hz, 1H), 1.42 (d, $J = 6.6$ Hz, 3H). m/z: 359 (M^+, 32.3), 323 (10.71), 287 (13.57), 235 (16.38), 197 (100.00), 127 (26.75), 109 (4.63), IR (film): 2958, 1598, 1493, 1294, 1047, 1005, 849, 514 cm^{-1}. Anal. cacld. For $C_{12}H_{14}Cl_3O_4P$: C, 40.06; H, 3.90. Found: C, 40.15; H, 4.12.

3e: ^{1}H NMR (400 MHz) δ: 7.00~7.28 (m, 3H), 3.69, 3.71 (2d, $J = 11$ Hz, cis/trans = 3/7, 3H), 3.08, 3.18 (2d, $J = 11$ Hz, cis/trans, 3H), 2.50, 2.49 (2s, cis/trans, 3H), 2.32 (s, 3H), 2.25 (q, $J = 6.6$ Hz, 1H), 1.52 (d, $J = 6.6$ Hz, trans, 0.7×3H), 1.46 (d, $J = 6.6$ Hz, cis, 0.3×3H). m/z: 353 (M^+, 1.51), 317 (5.10), 281 (11.74), 228 (2.64), 191 (100.00), 155 (7.31), 105 (2.30). IR (film): 2958, 1616, 1451, 1281, 1041, 1002, 854, 493 cm^{-1}. Anal. cacld. For $C_{14}H_{19}Cl_2O_4P$: C, 47.62; H, 5.42. Found: C, 47.78; H, 5.57.

3f: ^{1}H NMR (300 MHz) δ: 7.58 (m, 2H), 7.40 (m, 3H), 4.00 (m, 2H), 3.73~3.80 (m, 2H), 2.51 (q, $J = 6.5$ Hz, 1H), 1.33 (d, $J = 6.5$ Hz, 3H), 0.98 (m, 6H). m/z: 353 (M$^+$, 4.41), 317 (6.58), 281 (7.73), 263 (1.86), 200 (2.24), 163 (100.00), 155 (23.28), 77 (23.13). IR (film): 2986, 1450, 1275, 1034, 886, 702, 512 cm^{-1}. Anal. cacld. For $C_{14}H_{19}Cl_2O_4P$: C, 47.61; H, 5.42. cacld: C, 47.60; H, 5.49.

3g: ^{1}H NMR (400 MHz) δ: 7.45 (d, $J = 7.4$ Hz, 2H), 7.22 (d, $J = 7.4$ Hz, 2H), 4.00 (m, 2H), 3.70 (m, 1H), 3.51 (m, 1H), 3.15 (s, 3H), 2.22 (q, $J = 6.6$ Hz, 1H), 1.49 (d, $J = 6.6$ Hz, 3H), 1.28 (m, 3H), 1.01 (m, 3H). m/z: 367 (M$^+$, 7.50), 3.31 (7.51), 295 (5.04), 277 (1.48), 214 (3.87), 177 (100.00), 155 (38.12), 91 (22.30). IR (film): 2985, 1454, 1275, 1034, 1002, 886, 729, 539 cm^{-1}. Anal. cacld. For $C_{15}H_{21}Cl_2O_4P$: C, 49.06; H, 5.76. Found: C, 49.05; H, 5.86.

3h: ^{1}H NMR (400 MHz) δ: 7.45 (d, $J = 7.4$ Hz, 2H), 6.86 (d, $J = 7.4$ Hz, 2H), 3.94 (m, 2H), 3.74 (s, 3H), 3.64 (m, 1H), 3.49 (m, 1H), 2.11 (q, $J = 6.6$ Hz, 1H), 1.42 (d, $J = 6.6$ Hz, 3H), 1.17 (t, $J = 7.0$ Hz, 3H), 0.95 (t, $J = 7.0$ Hz, 3H). m/z: 383 (M$^+$, 6.65), 374 (17.55), 311 (2.75), 230 (1.11), 193 (100.00), 155 (11.52), 135 (1.42). IR (film): 2985, 1612, 1517, 1254, 1033, 1000, 886, 519 cm^{-1}. Anal. cacld. For $C_{15}H_{21}Cl_2O_5P$: C, 47.01; H, 5.53. Found: C, 46.98; H, 6.05.

3i: ^{1}H NMR (400 MHz) δ: 7.41 (d, $J = 8.5$ Hz, 2H), 7.28 (d, $J = 8.5$ Hz, 2H), 3.92 (m, 2H), 3.64 (m, 1H), 3.51 (m, 1H), 2.11 (q, $J = 6.5$ Hz, 1H), 1.39 (d, $J = 6.5$ Hz, 3H), 1.14 (t, $J = 4.3$ Hz, 3H), 0.93 (t, $J, = 4.3$ Hz, 3H). m/z: 387 (M$^+$, 31.51), 351 (14.81), 315 (14.95), 297 (1.19), 234 (2.07), 197 (100.00), 155 (29.50). IR (film): 2986, 1599, 1494, 1274, 1033, 1004, 885, 514 cm^{-1}. Anal. cacld. For $C_{14}H_{18}Cl_3O_4P$: C, 43.53; H, 4.65. cacld.: C, 43.36; H, 4.86.

3j: ^{1}H NMR (400 MHz) δ: 6.98~7.28 (m, 3H), 4.07 (m, 2H), 3.54 (m, 1H), 3.24 (m, 1H), 2.49, 2.48 (2s, cis/trans, 3H), 2.32 (s, 3H), 2.24 (q, $J = 6.6$ Hz, 1H), 1.51 (d, $J = 6.6$ Hz, trans, 0.7 × 3H), 1.45 (d, $J = 6.6$ Hz, cis, 0.3 × 3H), 1.30 (t, $J = 7.1$ Hz, 3H), 0.91 (t, $J = 7.1$ Hz, 3H). m/z: 381 (M$^+$, 1.73), 345 (3.30), 329 (9.01), 228 (2.37), 191 (100.00), 155 (17.07), 105 (4.29). IR (film): 2984, 1616, 1452, 1274, 1033, 999, 882, 501 cm^{-1}. Anal. cacld. For: $C_{16}H_{23}Cl_2O_4P$: C, 50.41; H, 6.08, cacld.: C, 49.77; H, 6.37.

3k: ^{1}H NMR (400 MHz) δ: 4.11 (m, 4H), 2.35–2.10 (m, 4H), 1.51–1.65 (m, 2H), 1.32 (t, 3H). m/z: 315 (M$^+$ – 1, 1062), 281 (6.67), 233 (100), 205 (29.82), 177 (29.80), 155 (17.35), 127 (23.24), 99 (42.39). IR (film): 2984, 1589, 1473, 1270, 1063, 1040. Anal. cacld. For: $C_{11}H_{19}C_{12}O_4P$: C, 41.64; H, 5.99. Cacld: C, 41.59; H, 5.99.

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