# Preparation of 3,3-Bis(phosphoryl)cyclopropenes

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**Synopsis.** The reaction of 1,2-diphenyl- and 1-methyl-2-phenyl-3,3-dichloro- or dibromocyclopropenes with trialkyl phosphites, dialkyl phenylphosphonites, and alkyl diphenylphosphinites afforded cyclopropenes with 3,3-diorganophosphorous substituents in moderate yields via double Arbuzov type reactions.

In a continuation of our studies on the chemistry of cyclopropenium salts and cyclopropenes possessing heteroatom substituents[1] we have tried to prepare cyclopropenium salts with organophosphorus substituents. The reaction of 1-ethoxy-2,3-diphenylcyclopropenium tetrafluoroborate with diethyl phospite or triethylphosphite provided no good results, yielding the original diphenylcyclopropenone. The reaction with dihalocyclopropene, however, proved to be a new easy route to cyclopropenes substituted with 3,3-diorganophspophorous substituents. The dialkoxyphosphinyl derivatives of the general structure, P–$CH_2$–P or P–CHR–P, have attracted considerable attention because of their biological activities,[2] chelation to metals,[3] and roles as synthetic tools.[4]

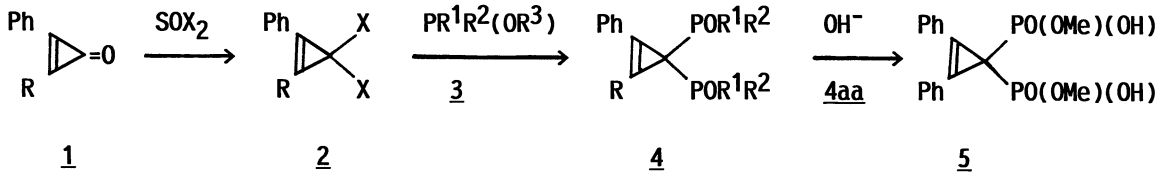
The reactions of cyclopropenones (**1**) with thionyl halides afford 3,3-dihalocyclopropenes (**2**) in good yield.[5] Since **2** are unstable to moisture they were used without isolation.

A mixture of 3,3-dichloro-1,2-diphenylcyclopropene (**2aa**) and trimethyl phosphite (**3a**, mole ratio 1 : 1.1) in dichloromethane at 40 °C for 1 d gave 3,3-bis(dimethoxyphosphinyl)-1,2-diphenylcyclopropene (**4aa**) in 37% yield. The use of a mole ratio of 1 : 2.2 afforded **4aa** in 68% yield. The structure of **4aa** was assigned from IR, $^1H$, $^{13}C$, $^{31}P$ NMR, and mass spectroscopic studies and chemical transformation. The cyclopropene **4aa** was stable under acidic conditions in a stirring mixture of $HClO_4$–$CH_2Cl_2$ at room temperature for 2 h. In contrast, upon heating at 50 °C with sodium hydroxide in methanol for 4 h **4aa** provided **5** in 88% yield, indicating the presence of a cyclopropene ring (Scheme 1). A similar treatment of **2** at 40 °C with 2.2 times excess moles of **3** yielded cyclopropenes with 3,3-diorganophosphorous substituents **4** in moderate yields, as listed in Table 1. No 1 : 1 addition product could be isolated. The yields of **4** decreased in the order OMe>OEt>$OPr^{-i}$ with the substituent of phosphorous esters.

It has been shown that the reaction of 1,1-dibromocyclopropanes with trialkyl phosphite at 90 °C in the

Table 1. Reaction of **2** with **3** at 40 °C in $CH_2Cl_2$

| Reaction | | Time/h | Product (Yield/%) |
|---|---|---|---|
| **2aa** | **3a** | 24 | **4aa** (68) |
| | **3b** | | **4ab** (48) |
| | **3c** | | **4ac** (19) |
| | **3d** | | **4ad** (46) |
| | **3e** | | **4ae** (35) |
| | **3f** | 48 | **4af** (48) |
| | **3g** | | **4af** (34) |
| **2ab** | **3a** | 24 | **4aa** (17) |
| | **3b** | | **4ab** (15) |
| **2ba** | **3a** | | **4ba** (31) |




1 2 4 5

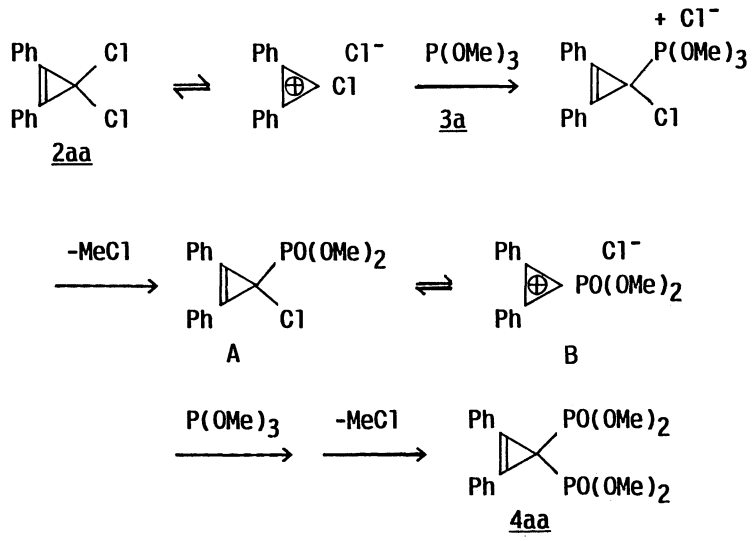
| 1 | R |
|---|---|
| a | Ph |
| b | Me |

| 2 | R | X |
|---|---|---|
| aa | Ph | Cl |
| ab | Ph | Br |
| ba | Me | Cl |

| 3 | $R^1$ | $R^2$ | $R^3$ |
|---|---|---|---|
| a | OMe | OMe | Me |
| b | OEt | OEt | Et |
| c | $OPr^{-i}$ | $OPr^{-i}$ | $Pr^{-i}$ |
| d | Ph | OMe | Me |
| e | Ph | OEt | Et |
| f | Ph | Ph | Me |
| g | Ph | Ph | Et |

| 4 | R | $R^1$ | $R^2$ |
|---|---|---|---|
| aa | Ph | OMe | OMe |
| ab | Ph | OEt | OEt |
| ac | Ph | $OPr^{-i}$ | $OPr^{-i}$ |
| ad | Ph | Ph | OMe |
| ae | Ph | Ph | OEt |
| af | Ph | Ph | Ph |
| ba | Me | OMe | OMe |

Scheme 1.




Scheme 2.

presence of triethylamine and water provides cyclopropylphosphonates via reductive phosphonation with dialkyl phosphonates.[6]

Considering the results, we obtained a plausible mechanism for the generation of a representative compound **4aa**, as shown in Scheme 2. Although the isolation of 3-chloro-3-dimethoxylphosphinyl-1,2-diphenylcyclopropene **A**, a mono-Arbuzov reaction product,[7] failed, the intermediacy of mono-adduct **A** was clear from the final product **4**. The reaction of the possible intermediate cyclopropenium salt **B** with **3a** would yield two types of substitution products. One isomer **4** was obtained as stable crystals (Table 1). The formation of another isomer might be prevented by the bulky phenyl group inhibiting substitution onto C-2 with **3** or the subsequent Arbuzov reaction to collapse to the starting reagents. The high activity of the halocyclopropenes was attributed to their aromatic nature.

## Experimental

**General.** The melting points were uncorrected. The $^1$H NMR spectra were recorded on a Hitachi R-24B (60 MHz) and $^{13}$C and $^{31}$P NMR spectra on a JEOL JNM FX-90Q (22.40 MHz). NMR spectra were recorded in $CDCl_3$, unless otherwise stated, using TMS ($^1$H and $^{13}$C) as an inner or $H_3PO_4$ ($^{31}$P) as an external standard. The IR spectra were obtained on a JEOL JIR 100.

**The Reaction of 3,3-Dichloro-1,2-diphenylcyclopropene (2aa) with Trimethyl Phosphite (3a).** A mixture of 1,2-diphenylcyclopropenone (**1a**) (0.50 g 2.4 mmol) and thionyl chloride (40 mmol) was heated at 40 °C for 2 h; excess of thionyl chloride was removed in vacuo to afford orange crystals of **2aa**. A solution of **2aa** and **3a** (5.3 mmol) in dichloromethane (10 ml) was heated at 40 °C for 24 h. The reaction mixture was condensed in vacuo to dryness, and the obtained crystals washed with petroleum ether; recrystallization from benzene–petroleum ether afforded **4aa** in 68% yield.

**4aa:** Mp 127—129 °C; IR (KBr) 1860, 1240, and 1030 cm$^{-1}$; $^1$H NMR $\delta$=3.72 (dd, $J_{POCH}$=5.4 and 5.4 Hz, 12H, 4$CH_3$) and 7.2—8.1 (m, 10H, 2Ph); $^{13}$C NMR $\delta$=23.3 (C-3), 53.0 ($CH_3$), 104.9, 125.6, 128.8(d), 129.8(d), and 130.1(d); $^{31}$P NMR $\delta$=25.26; MS (*m*/*z*) 408 ($M^+$). Found: C, 55.85; H, 5.36%. Calcd for $C_{19}H_{22}O_6P_2$: C, 55.88; H, 5.43%.

**2ab** was prepared from **1a** (2.4 mmol) and thionyl bromide (2.9 mmol) in dichloromethane (5 ml) at room temperature for 10 min. Chlorination of **1b** (2.4 mmol) with thionyl chloride (2.4 mmol) was performed at 0 °C for 5 min in dichloromethane (5 ml) to yield **2ba**.

A similar treatment of **2** with **3** yielded **4** in moderate yields, as summarized in Table 1. The physical properties of the products are as follows:

**4ab:** Mp 99—102 °C; IR (KBr) 1860, 1240, and 1020 cm$^{-1}$; $^1$H NMR $\delta$=1.20 (t, *J*=7.2 Hz, 12H, 4$CH_3$), 3.8—4.4 (m, 8H, 4$CH_2$), and 7.2—8.1 (m, 10H, 2Ph); $^{13}$C NMR $\delta$=16.3 ($CH_3$), 24.3 (C-3), 62.2 ($CH_2$), 105.4, 126.0, 128.7(d), 129.6(d), and 130.2(d); $^{31}$P NMR $\delta$=22.93; MS (*m*/*z*) 464 ($M^+$). Found: C, 59.43; 6.54%. Calcd for $C_{23}H_{30}O_6P_2$: C, 59.48; H, 6.51%.

**4ac:** Mp 80—81 °C; IR (KBr) 1840, 1220, and 980 cm$^{-1}$; $^1$H NMR $\delta$=1.20 (dd, *J*=6.0 and 6.0 Hz, 24H, 8$CH_3$), 4.3—5.0 (m, 4H, 4CH), and 7.2—8.1 (m, 10H, 2Ph); $^{13}$C NMR $\delta$=25.9 ($CH_3$), 26.3 ($CH_3$), 27.6 (C-3), 72.8(CH), 107.9, 128.4, 130.6(d), 131.4(d), and 132.3(d); $^{31}$P NMR $\delta$=21.47; MS (*m*/*z*) 520 ($M^+$). Found: C, 62.18; H, 7.43%. Calcd for $C_{27}H_{38}O_6P_2$: C, 62.29; H, 7.35%.

**4ad:** Mp 154—157 °C; IR (KBr) 1820, 1220, and 1020 cm$^{-1}$; $^1$H NMR $\delta$=3.5—3.9 (m, 6H, 2$CH_3$) and 6.9—7.9 (m, 20H, 4Ph); $^{13}$C NMR $\delta$=30.7 (C-3), 51.7 ($CH_3$), 105.6(d), 125.9(s), 127.6(d), 127.9(d), 128.4(d), 129.5(d), 129.9(d), 131.7(s), and 132.2(d); $^{31}$P NMR $\delta$=42.10; MS (*m*/*z*) 500 ($M^+$). Found: C, 69.65; H, 4.98%. Calcd for $C_{29}H_{26}O_4P_2$: C, 69.59; H, 5.23%.

**4ae:** Mp 95—97 °C; IR (KBr) 1830, 1230, and 1030 cm$^{-1}$; $^1$H NMR $\delta$=1.0—1.5 (m, 6H, 2$CH_3$), 3.7—4.5 (m, 4H, 2$CH_2$), and 6.9—8.9 (m, 20H. 4Ph); $^{13}$C NMR $\delta$=16.4 ($CH_3$), 18.3 (C-3), 61.2 ($CH_2$), 106.1 (s), 125.9(d), 127.6(d), 128.3(d), 129.4(d), 130.0(d), 130.2(d), 131.7(s), and 132.5(d); $^{31}$P NMR $\delta$=9.88; MS (*m*/*z*) 528 ($M^+$). Found: C, 70.21; H, 5.82%. Calcd for $C_{31}H_{30}O_4P_2$: C, 70.44; H, 5.72%.

**4af:** Mp 184—185 °C; IR (KBr) 1190 cm$^{-1}$; $^1$H NMR $\delta$=6.8—8.1 (m); $^{13}$C NMR $\delta$=36.6(C-3). 108.3(s), 126.5, 127.2, 127.5, 127.8, 128.3, 129.5, 129.8, 131.0, 131.7, 131.9. 132.1, and 133.8; $^{31}$P NMR $\delta$=33.68; MS (*m*/*z*) 592 ($M^+$). Found: C, 79.13; H, 5.01%. Calcd for $C_{39}H_{30}O_2P_2$: C, 79.04; H, 5.10%.

**4ba:** Mp 83—85 °C; IR (KBr) 1885, 1240, and 1020 cm$^{-1}$; $^1$H NMR $\delta$=2.45 (s, 3H, $CH_3$), 3.6—4.0 (m, 12H, 4$CH_3$), and 7.2—7.8 (m, 5H, Ph); $^{13}$C NMR $\delta$=11.8 ($CH_3$), 23.7 (C-3), 54.0 ($OCH_3$), 103.8(s), 105.1, 126.5, 130.0(d), 130.6(d), and 131.0(d);

MS ($m/z$) 348 ($M^+$). Found: C, 48.41; H, 6.13%. Calcd for $C_{14}H_{22}O_6P_2$: C, 48.28; H, 6.36%.

**Hydrolysis of 4aa.** A solution of **4aa** (0.5 mmol) in ethanol (15 ml) containing 2.5 mmols of sodium hydroxide was heated at 50 °C for 5 h. The reaction mixture was quenched to ice water and acidified with hydrochloric acid. Precipitated crystals were collected and recrystallized from ethanol to yied **5** in 88% yield.

**5**: Mp 239—242 °C; IR (KBr) 2650, 1210, and 1040 $cm^{-1}$; $^1H$ NMR ($CDCl_3$+$CF_3CO_2H$, 10:1) $\delta$=3.79 (dd, $J$=5.4 Hz, $2CH_3$) and 7.2—8.0 (m, 10H, 2Ph); $^{13}C$ NMR ($CDCl_3$+$CF_3CO_2H$, 10:1) $\delta$=23.2 (C-3), 53.6 ($CH_3$), 94.1, 124.1(s), 129.2(d), 130.1(d), and 130.9(d); $^{31}P$ NMR ($CDCl_3$+$CF_3CO_2H$, 10:1) $\delta$=26.86; MS ($m/z$) 380 ($M^+$). Found: C, 53.31; H, 4.51%. Calcd for $C_{17}H_{18}O_6P_2$: C, 53.69; H, 4.77%.

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