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Synthesis and Properties of Phosphabetaine Structures: III.[1] Phosphabetaines Derived from Tertiary Phosphines and α,β-Unsaturated Carboxylic Acids. Synthesis, Structure, and Chemical Properties

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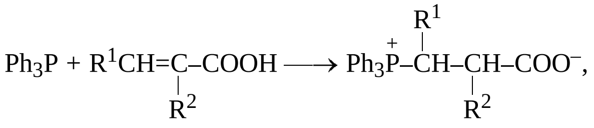
Abstract—Methods of synthesis of acylate phosphabetaines by reactions of triphenylphosphine with methacrylic, cinnamic, and *p*-methoxycinnamic acids are developed. The phosphabetaine form is proposed to exist in equilibrium with the σ^5-oxaphospholane form. The features of methylation of the phosphabetaines are discussed.

Earlier [1, 2] we developed a method of synthesis of phosphabetaine **I** (R^1, R^2 = H) by reaction of triphenylphosphine with acrylic acid and showed that a necessary condition for stabilization of the acylate phosphabetaine is the presence in its crystal lattice of a proton donor (water, chloroform, excess acrylic acid, etc.)

In the present work, with the aim to extend the range of α,β-unsaturated carboxylic acids capable of forming acylate phosphabeines, we reacted triphenylphosphine with methacrylic, cinnamic, and methoxycinnamic acids.



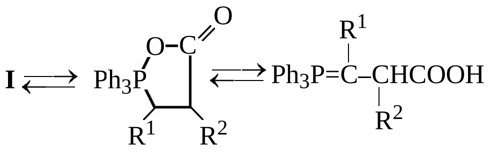
$$\mathrm{Ph_3P + R^1CH{=}\underset{R^2}{C}{-}COOH \longrightarrow Ph_3\overset{+}{P}{-}\overset{R^1}{C}H{-}\underset{R^2}{C}H{-}COO^-},$$

I

R^1 = H, Ph, *p*-$\mathrm{MeOC_6H_4}$; R^2 = H, Me.

Therewith, we supposed that aryl or methyl substituents R^1 and R^2 in the "acylate" moiety of phosphabetaines **I** would both stabilize the zwitter-ionic structure of betaines **I** and favor their isomerization into σ^5-phosphacyclanes **II**. It is well known that the latter are stabilized by ring substituents [3].

Moreover, our quantum-chemical calculations of the energy of formation of the dipolar **I** and cyclic **II** forms showed that in the gas phase the cyclic form is thermodynamically preferred [4].



II **III**

We also did not rule out formation of form **III**, in view of the published data [5, 6], according to which σ^5-oxaphospholanes can be considered latent ylides capable of entering the Wittig reaction.

The reactions of triphenylphosphines with methacrylic, cinnamic, and *p*-methoxycinnamic acids in chloroform smoothly occur at room temperature, and, according to ^{31}P NMR data, give rise to phosphonium compounds: The signal of triphenylphosphine completely disappears and signals characteristic of phosphabetaines ((δ_P 22–25 ppm) appear. The IR spectra show well-defined carboxylate absorption bands at 1600 $\mathrm{cm^{-1}}$. The product of the reaction of triphenylphosphine with methacrylic acid, betaine **I** (R^1 = H, R^2 = Me), was isolated as crystals. Moreover, the ^{31}P NMR spectra of the products of the reactions of triphenylphosphine with cinnamic and *p*-methoxycinnamic acids detect, along with betaines and in comparable quantities, phosphorane derivatives at δ_P –20.0 and –16.20 ppm, respectively. This result strongly suggest formation of phosphoranes **II**, which we did not observed earlier in the reaction of tri-

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[1] For communication II, see [1].

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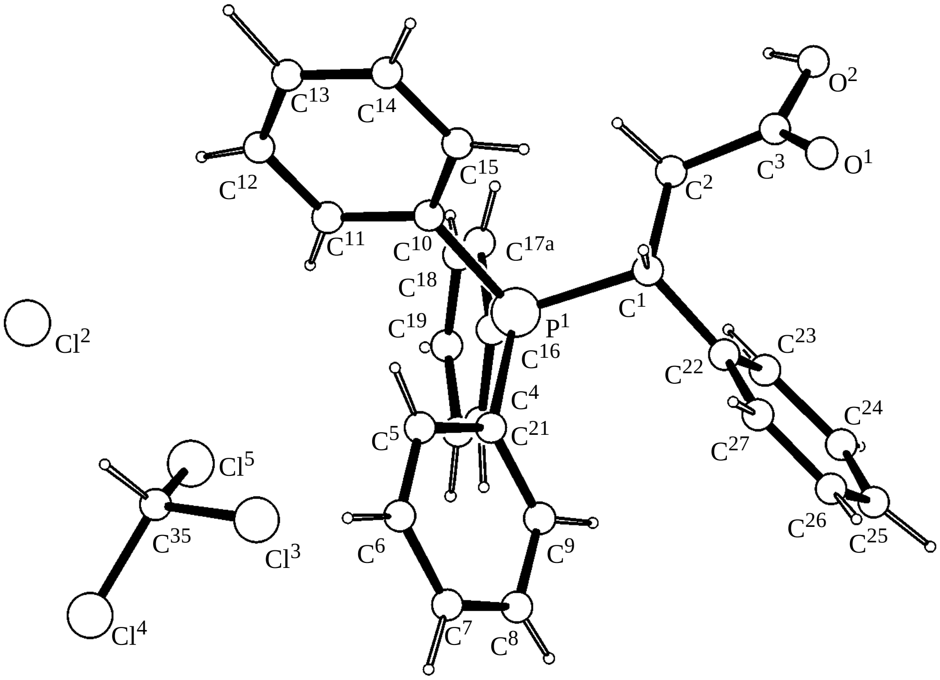
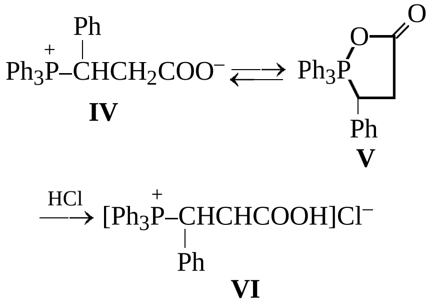


Fig. 1. Molecular structure of (2-carboxy-1-phenylethyl)triphenylphosphonium chloride (**VI**).

phenylphosphine with acrylic acid [1, 2]. Further evidence for phosphorane formation in the reactions studied is provided by the fact that treatment of the reaction mixture containing a cynnamic acid–derived betaine and its phosphorane isomer with hydrochloric acid gives rise to (2-carboxy-1-phenylethyl)triphenylphosphonium chloride (**VI**) as a single product. Thus, the signal in the phosphorane region can firmly be assigned to σ^5-phosphacyclane **V**.



$$Ph_3\overset{+}{P}{-}\overset{Ph}{C}HCH_2COO^- \rightleftarrows$$

IV

V

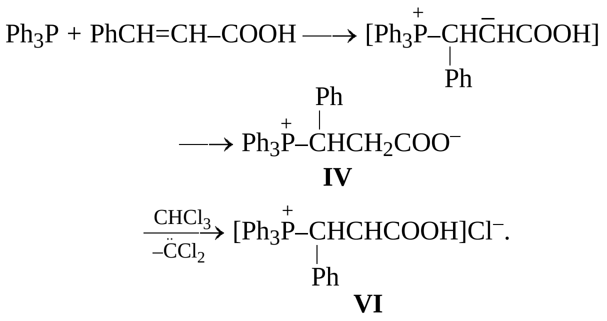
$$\xrightarrow{HCl} [Ph_3\overset{+}{P}{-}\underset{Ph}{C}HCHCOOH]Cl^-$$

VI

It is interesting that salt **VI** was isolated after prolonged standing of a dilute chloroform solution of betaine **IV**. We could grow relatively stable and well-formed crystals satisfactory for X-ray diffraction analysis.

According to X-ray diffraction data, compound **VI** is actually a phosphonium salt formed by HCl addition to phosphabetaine **VI** (Fig. 1).

Since thoroughly purified starting materials and solvents contained no hydrogen chloride, it remains to suggest that phosphabetaine **IV** formed by the reaction of triphenylphosphine with cinnamic acid has, for the sake of stabilization, to decompose chloroform to hydrogen chloride and dichlorocarbene. Note that chloroform is also present in the crystal of phosphonium salt **VI** (Fig. 1).



$$Ph_3P + PhCH{=}CH{-}COOH \longrightarrow [Ph_3\overset{+}{P}{-}\underset{Ph}{C}H\overset{-}{C}HCOOH]$$

$$\longrightarrow Ph_3\overset{+}{P}{-}\overset{Ph}{C}HCH_2COO^-$$

IV

$$\xrightarrow[-\ddot{C}Cl_2]{CHCl_3} [Ph_3\overset{+}{P}{-}\underset{Ph}{C}HCHCOOH]Cl^-.$$

VI

The asymmetric part of the unit cell contains one independent ion part of [(2-carboxy-1-phenylethyl)triphenylphosphonium chloride (**VI**)] and one solvation chloroform molecule. The phosphorus atom has a usual, distorted tetrahedral coordination, and its bond lengths and angles (Table 1) are values characteristic of phosphonium salts [7]. These results nicely agree with those we obtained earlier with betaine **I** (R = H) [2]. The bond lengths and angles in the benzene rings, too, are normal values (Table 1). The conformation of the $P^1C^1C^2C^3$ fragment is *transoid* [torsion angle $\varphi(P^1C^1C^2C^3)$ 174.1(3)°] and that of the $C^1C^2C^3O^2$

Table 1. Bond lengths (*d*, Å) and bond (ω, deg) and torsion angles (φ, deg) in structure **VI**

Bond	*d*	Bond	*d*	Bond	*d*	Bond	*d*
Cl^3–C^{35}	1.723(7)	C^8–C^9	1.389(6)	O^2–H^2	0.85(5)	C^{17}–C^{18}	1.369(8)
Cl^4–C^{35}	1.693(7)	C^{10}–C^{11}	1.401(6)	C^1–C^2	1.521(6)	C^{18}–C^{19}	1.338(8)
Cl^5–C^{35}	1.647(8)	C^{10}–C^{15}	1.384(6)	C^1–C^{22}	1.515(7)	C^{19}–C^{20}	1.359(7)
P^1–C^1	1.837(4)	C^{11}–C^{12}	1.372(8)	C^2–C^3	1.504(6)	C^4–C^5	1.399(7)
P^1–C^4	1.788(4)	C^{12}–C^{13}	1.365(8)	C^6–C^7	1.363(8)	C^4–C^9	1.389(6)
P^1–C^{10}	1.799(5)	C^{13}–C^{14}	1.378(7)	C^7–C^8	1.362(8)	C^5–C^6	1.362(6)
P^1–C^{16}	1.791(5)	C^{14}–C^{15}	1.390(7)	C^{20}–C^{21}	1.389(7)	C^{22}–C^{23}	1.379(8)
O^1–C^3	1.214(5)	C^{16}–C^{17}	1.390(6)	C^{22}–C^{27}	1.394(6)	C^{25}–C^{26}	1.338(9)
O^2–C^3	1.304(5)	C^{16}–C^{21}	1.363(6)	C^{23}–C^{24}	1.404(9)	C^{26}–C^{27}	1.382(8)
				C^{24}–C^{25}	1.331(8)		
Bond angle	**ω**	**Bond angle**	**ω**	**Bond angle**	**ω**	**Bond angle**	**ω**
$C^1P^1C^4$	109.9(2)	$C^4C^5C^6$	120.0(5)	$O^2C^3C^2$	117.3(4)	$C^{22}C^{23}C^{24}$	118.3(5)
$C^1P^1C^{10}$	108.9(2)	$C^5C^6C^7$	121.0(5)	$P^1C^4C^5$	119.8(3)	$C^{23}C^{24}C^{25}$	122.3(6)
$C^1P^1C^{16}$	111.1(2)	$C^6C^7C^8$	120.1(4)	$P^1C^4C^9$	121.3(4)	$C^{24}C^{25}C^{26}$	119.3(6)
$C^4P^1C^{10}$	108.3(2)	$C^7C^8C^9$	120.5(5)	$C^5C^4C^9$	118.9(4)	$C^{25}C^{26}C^{27}$	121.9(5)
$C^4P^1C^{16}$	111.0(2)	$C^4C^9C^8$	119.5(5)	$P^1C^{16}C^{17}$	118.3(3)	$C^{22}C^{27}C^{26}$	119.2(5)
$C^{10}P^1C^{16}$	107.5(2)	$P^1C^{10}C^{11}$	118.4(3)	$P^1C^{16}C^{21}$	123.5(3)	$C^{13}C^{14}C^{15}$	119.8(5)
$C^3O^2H^2$	106.(3)	$P^1C^{10}C^{15}$	122.4(3)	$C^{17}C^{16}C^{21}$	118.1(4)	$C^{10}C^{15}C^{14}$	120.3(4)
$P^1C^1C^2$	111.5(3)	$C^{11}C^{10}C^{15}$	119.2(4)	$C^{16}C^{17}C^{18}$	119.1(5)	$C^{12}C^{13}C^{14}$	119.9(5)
$P^1C^1C^{22}$	111.9(3)	$C^{10}C^{11}C^{12}$	119.5(4)	$C^{17}C^{18}C^{19}$	122.9(5)	$Cl^4C^{35}Cl^5$	109.9(4)
$C^2C^1C^{22}$	113.6(4)	$C^{11}C^{12}C^{13}$	121.3(5)	$C^{18}C^{19}C^{20}$	118.6(5)	$Cl^4C^{35}H^{35}$	99.(3)
$C^1C^2C^3$	112.7(4)	$C^{16}C^{21}C^{20}$	120.9(4)	$C^{19}C^{20}C^{21}$	120.2(5)	$Cl^5C^{35}H^{35}$	124.(3)
$O^1C^3O^2$	120.1(4)	$C^1C^{22}C^{23}$	121.3(4)	$Cl^3C^{35}Cl^4$	109.9(4)	$Cl^3C^{35}Cl^5$	113.3(4)
$O^1C^3C^2$	122.6(4)	$C^{23}C^{22}C^{27}$	119.0(5)	$Cl^3C^{35}H^{35}$	100.(4)		
Torsion angle	**φ**	**Torsion angle**	**φ**	**Torsion angle**	**φ**	**Torsion angle**	**φ**
$C^4P^1C^1C^2$	–179.8(3)	$C^{22}C^1C^2C^3$	–58.4(5)	$C^{16}P^1C^4C^9$	55.9(4)	$P^1C^{16}C^{17^a}C^{18}$	–178.5(4)
$C^4P^1C^1C^{22}$	51.8(4)	$P^1C^1C^{22}C^{23}$	88.1(5)	$C^1P^1C^{10}C^{11}$	161.8(3)	$P^1C^{16}C^{21}C^{20}$	177.1(4)
$C^{10}P^1C^1C^2$	–61.3(4)	$P^1C^1C^{22}C^{27}$	–94.6(5)	$C^1P^1C^{10}C^{15}$	–21.4(4)	$C^1C^{22}C^{23}C^{24}$	175.3(5)
$C^{10}P^1C^1C^{22}$	170.3(3)	$C^2C^1C^{22}C^{23}$	–39.2(6)	$C^4P^1C^{10}C^{11}$	–78.7(4)	$C^1C^{22}C^{27}C^{26}$	–177.6(5)
$C^{16}P^1C^1C^2$	56.9(4)	$C^2C^1C^{22}C^{27}$	138.1(4)	$C^4P^1C^{10}C^{15}$	98.1(4)	$C^4P^1C^{16}C^{21}$	–14.6(5)
$C^{16}P^1C^1C^{22}$	–71.5(4)	$C^1C^2C^3O^1$	–19.2(6)	$C^{16}P^1C^{10}C^{11}$	41.3(4)	$C^{10}P^1C^{16}C^{17}$	44.3(4)
$C^1P^1C^4C^5$	113.9(4)	$C^1C^2C^3O^2$	162.8(4)	$C^{16}P^1C^{10}C^{15}$	–141.9(4)	$C^{10}P^1C^{16}C^{21}$	–132.9(4)
$C^1P^1C^4C^9$	–67.5(4)	$P^1C^4C^5C^6$	178.7(4)	$C^1P^1C^{16}C^{17}$	–74.8(4)	$H^2O^2C^3O^1$	–178(4)
$C^{10}P^1C^4C^5$	–4.9(4)	$P^1C^4C^9C^8$	–178.6(4)	$C^1P^1C^{16}C^{21}$	108.1(4)	$H^2O^2C^3C^2$	0.5(4)
$C^{10}P^1C^4C^9$	173.7(4)	$P^1C^{10}C^{11}C^{12}$	176.9(4)	$C^4P^1C^{16}C^{17}$	162.5(4)	$P^1C^1C^2C^3$	174.1(3)
$C^{16}P^1C^4C^5$	–122.7(4)	$P^1C^{10}C^{15}C^{14}$	–177.5(4)				

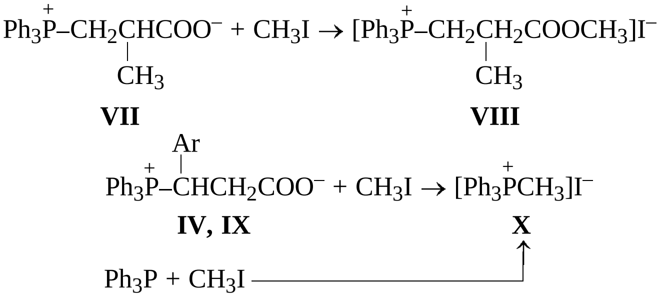
fragment is close to *eclipsed* [φ –19.2(6)°], which is, too, nicely consistent with what have been found in betaine **I** (R = H). It is interesting to note that the $P^1C^1C^2C^3$ fragment in similar phosphonium has an *orthogonal* conformation [2]. The fact that the carbonyl fragment preserves its conformation may be associated with intra- and intermolecular interactions in the crystal. As already mentioned, betaine structures are stabilized by H bonding with proton donors, which distinguish them from phosphonium salts [1, 2, 4]. However, in the crystal of compound **VI** we found a solvation molecule of chloroform, which takes part in intermolecular interactions like C–H···Cl (Fig. 2). The tendency of HCl molecule to exist in crystal as an ion pair and the ability of chloride anion to H-bond formation is well known [8]. In the crystal of compound **VI**, the intermolecular H bond C^{35}–$H^{35}\cdots Cl^2$ has the following parameters: $d(C^{35}–H^{35})$

1.05(7), $d(H^{35}\cdots Cl^2)$ 2.38(7), $d(C^{35}\cdots Cl^2)$ 3.384(7) Å, and $\Gamma C^{35}H^{35}Cl^2$ 159(5)°. Moreover, we found a classical H bond between the cation and anion: $O^2{-}H^2\cdots Cl^{2'}$ $[x, -1 + y, z]$ $d(O^2{-}H^2)$ 0.86(5), $d(H^2\cdots Cl^2)$ 2.12(5), $d(O^2\cdots Cl^2)$ 2.970(4) Å, and $\angle O^2H^2Cl^2$ 171(5)°.

Thus, we obtained evidence to show that betain **IV** undergoes facile hydrochlorination and that σ^5-oxaphospholane **V** can convert to phosphonium chloride **VI**. At the same time, it should be stressed that all our attempts to isolate and identify cyclic phosphoranes from the reaction mixtures failed. Some assumptions as to the reasons for this failure we will present later. We also failed to react betaine **IV** with benzaldehyde and thus cannot postulate the betain–phosphorane–phosphorus ylide equilibrium.

Interesting and unexpected results were obtained in alkylation of the newly synthesized betaines with methyl iodide.

Whereas phosphabetaine **VII** obtained from triphenylphosphine and methacrylic acid reacts with methyl iodide by a scheme we established earlier [1, 2] with the acrylate derivative, giving methyl ester **VIII**, the reactions of phosphabetaines **IV** and **IX** synthesized from cinnamic acids with methyl iodide involve P–C bond cleavage and result in formation of methyltriphenylphosphonium iodide. The structure of the latter was proved by ^1H and ^{31}P NMR and IR spectroscopy and by independent synthesis.



$$\mathrm{Ph_3\overset{+}{P}{-}CH_2\underset{CH_3}{C}HCOO^- + CH_3I \rightarrow [Ph_3\overset{+}{P}{-}CH_2\underset{CH_3}{C}H_2COOCH_3]I^-}$$

VII **VIII**

$$\mathrm{Ph_3\overset{+}{P}{-}\overset{Ar}{C}HCH_2COO^- + CH_3I \rightarrow [Ph_3\overset{+}{P}CH_3]I^-}$$

IV, IX **X**

$$\mathrm{Ph_3P + CH_3I \rightarrow X}$$

Ar = Ph (**IV**), *p*-MeOC_6H_4 (**IX**).

Aiming at extending the range of phosphabetaines obtained by phosphine addition to α,β-unsaturated carboxylic acids, we turned to aliphatic tertiary phosphines. However, contrary to expectations, tributylphosphine proved less rather than more reactive than triphenylphosphine toward unsaturated carboxylic acids. We could only isolate and firmly identify the adduct of tributylphosphine with acrylic acid (compound **XI**) and its alkylation product **XII** as oily liquids not crystallizing upon prolonged standing.

Such a different reactivity of aromatic and aliphatic phosphines is difficult to understand. One of the possible reasons may lie in the fact that aryl substituents better stabilize the phosphonium center than alkyls.

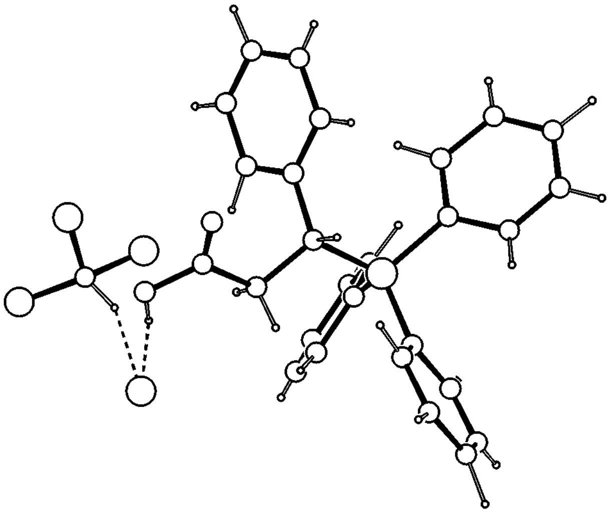
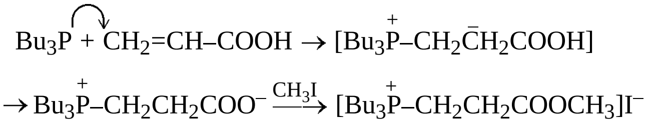


Fig. 2. Intermolecular interactions in the crystal of phosphonium chloride **VI**.



$$\mathrm{Bu_3P + CH_2{=}CH{-}COOH \rightarrow [Bu_3\overset{+}{P}{-}CH_2\overset{-}{C}H_2COOH]}$$

$$\mathrm{\rightarrow Bu_3\overset{+}{P}{-}CH_2CH_2COO^- \xrightarrow{CH_3I} [Bu_3\overset{+}{P}{-}CH_2CH_2COOCH_3]I^-}$$

XI **XII**

EXPERIMENTAL

The IR spectra were obtained on a Specord M-80 spectrometer in the range 700–3600 cm^{-1} in thin films and mineral oil between KBr plates. The ^1H and ^{31}P NMR spectra were obtained in $CDCl_3$ on a Varian Unity-300 spectrometer at 300 MHz (^1H), internal reference HMDS, and at 121.64 MHz (^{31}P), external reference H_3PO_4.

X-ray diffraction study. Crystals of compound **VI**, $[C_{27}H_{24}O_2P_1]^+Cl^{-}\cdot CNCl_3$, triclinic. At 20°C, a 9.869(1), b 9.999(2), c 14.258(2) Å; α 81.45(1), β 85.446(9), γ 82.11(1)°; V 1375.6(4) Å^3, Z 2, d_{calc} 1.37 g/cm^3, space group P-1. The unit cell parameters and the intensities of 5920 reflections, 3005 of which had $I \geq 3\sigma$, were measured on an Enraf–Nonius CAD-4 automatic four-circle diffractometer (λMoK_α radiation, graphite monochromator, ω/2θ scanning, $\theta \leq 29°$). No intensity decay of three reference reflections was observed during measurements. Absorption was not included (μMo 5.1 sm^{-1}). The structure was solved by the direct method by the SIR program [9] and refined first isotropically and then anisotropically.

Table 2. Atomic coordinates in structure **I**, equivalent isotropic thermal parameters of non-hydrogen atoms $B = 4/3\sum_{i=1}^{3}\sum_{j=1}^{3}(a_i a_j)B(i,j)$ (Å^2) and isotropic thermal parameters of hydrogen atoms B_{iso} (Å^2)

Atom	*x*	*y*	*z*	*B*	Atom	*x*	*y*	*z*	*B*
Cl^2	–0.4578(1)	0.2503(1)	–0.2428(1)	4.75(3)	C^{24}	–0.1621(6)	–0.0540(6)	0.1954(4)	6.4(1)
Cl^3	–0.1263(2)	0.3606(2)	–0.1449(2)	9.22(6)	C^{25}	–0.2843(5)	–0.0169(6)	0.2371(5)	6.2(2)
Cl^4	–0.1951(3)	0.1487(3)	–0.0056(2)	18.1(1)	C^{26}	–0.2917(5)	0.0506(6)	0.3120(4)	5.5(1)
Cl^5	–0.3355(4)	0.4040(3)	–0.0022(3)	22.2(1)	C^{27}	–0.1756(5)	0.0779(5)	0.3500(4)	4.1(1)
P^1	0.1410(1)	0.2252(1)	0.29625(8)	2.60(2)	C^{35}	–0.2568(7)	0.2963(7)	–0.0719(5)	7.1(2)
O^1	0.0557(3)	–0.1894(3)	0.4602(2)	4.40(8)	H^1	0.060(3)	0.082(3)	0.423(3)	2.5(8)
O^2	0.2294(3)	–0.2290(3)	0.3873(3)	4.50(8)	H^2	0.294(5)	–0.276(5)	0.347(4)	7(1)
C^1	0.0810(4)	0.0635(4)	0.3503(3)	3.0(1)	H^5	0.075(3)	0.454(3)	0.394(3)	2.5(8)
C^2	0.1956(4)	–0.0550(4)	0.3504(4)	3.5(1)	H^6	–0.087(4)	0.643(4)	0.386(3)	5(1)
C^3	0.1536(5)	–0.1862(4)	0.4031(3)	3.2(1)	H^7	–0.278(5)	0.659(5)	0.301(4)	8(1)
C^4	0.0033(4)	0.3614(4)	0.2981(3)	2.73(9)	H^8	–0.280(4)	0.479(4)	0.217(3)	4(1)
C^5	0.0089(5)	0.4644(5)	0.3538(3)	3.5(1)	H^9	–0.119(3)	0.297(3)	0.203(2)	2.5(8)
C^6	–0.0945(5)	0.5698(5)	0.3540(4)	4.7(1)	H^{11}	0.351(4)	0.391(4)	0.260(3)	3.5(9)
C^7	–0.2041(5)	0.5775(5)	0.3000(4)	4.8(1)	H^{12}	0.508(5)	0.443(5)	0.337(3)	6(1)
C^8	–0.2122(5)	0.4783(5)	0.2455(4)	4.5(1)	H^{13}	0.569(6)	0.351(6)	0.508(4)	9(2)
C^9	–0.1087(4)	0.3692(5)	0.2436(3)	3.6(1)	H^{14}	0.401(3)	0.190(3)	0.569(2)	2.2(8)
C^{10}	0.2744(4)	0.2600(4)	0.3647(3)	2.79(9)	H^{15}	0.225(4)	0.146(4)	0.484(3)	4(1)
C^{11}	0.3615(5)	0.3545(5)	0.3227(4)	3.8(1)	H^{17}	0.377(4)	0.091(4)	0.210(3)	5(1)
C^{12}	0.4598(5)	0.3878(5)	0.3749(4)	4.8(1)	H^{18}	0.541(4)	0.893(4)	0.929(3)	3.5(9)
C^{13}	0.4758(5)	0.3290(5)	0.4667(4)	4.7(1)	H^{19}	0.382(4)	0.205(4)	–0.050(3)	5(1)
C^{14}	0.3906(5)	0.2363(5)	0.5093(4)	4.4(1)	H^{20}	0.165(4)	0.320(4)	–0.040(3)	5(1)
C^{15}	0.2893(5)	0.2020(5)	0.4582(3)	3.5(1)	H^{21}	0.061(5)	0.339(5)	0.101(4)	7(1)
C^{16}	0.2125(4)	0.2150(4)	0.1777(3)	3.1(1)	H^{23}	0.061(5)	–0.040(5)	0.189(4)	8(1)
C^{17}	0.3417(5)	0.1420(6)	0.1656(4)	4.6(1)	H^{24}	–0.140(5)	–0.096(5)	0.142(3)	6(1)
C^{18}	0.3993(6)	0.1358(7)	0.0755(4)	6.3(2)	H^{25}	–0.365(5)	–0.046(5)	0.218(4)	7(1)
C^{19}	0.3387(5)	0.2008(6)	–0.0021(3)	4.9(1)	H^{26}	–0.371(4)	0.067(4)	0.348(3)	6(1)
C^{20}	0.2128(6)	0.2733(6)	0.0087(4)	5.2(1)	H^{27}	–0.182(4)	0.118(4)	0.407(3)	4(1)
C^{21}	0.1496(5)	0.2798(5)	0.0988(3)	4.2(1)	H^{35}	–0.306(6)	0.256(6)	–0.122(5)	11(2)
C^{22}	–0.0472(4)	0.0392(4)	0.3069(3)	3.3(1)	H^{221}	0.221(4)	–0.067(4)	0.278(3)	5(1)
C^{23}	–0.0396(6)	–0.0257(5)	0.2276(4)	5.0(1)	H^{222}	0.271(4)	0.972(4)	0.381(3)	5(1)

Hydrogen atoms were revealed by difference synthesis and refined isotropically in the final stage. The final divergence factors were R 0.046 and R_W 0.082, on 1996 reflections with $F^2 \geq 3\sigma$.

All calculations were performed on AlphaStation 200 using the MolEN program package [10]. Molecular drawings and analysis of intermolecular contacts were perfomed using the PLATON program [8]. The atomic coordinates are listed in Table 2.

Synthesis and alkylation of 3-(triphenylphosphonio)propanoate (**I**) have been described in [1].

Reaction of triphenylphosphine with methacrylic acid. A solution of 0.81 g methacrylic acid in 5 ml of chloroform was added dropwise with stirring to a solution of 2.4 g of triphenylphosphine in 7 ml of chloroform. The reaction mixture was left to stand for 1 week at room temperature, and the solvent was then removed in a vacuum. The residue was treated with absolute diethyl ether, the precipitate that formed was filtered off, washed with diethyl ether, and dried in a vacuum to obtain compound **VII** as colorless crystals, mp 175–182°C. IR spectrum: ν(CO) 1605 cm^{-1}. ^{31}P NMR spectrum: δ_P 18.2 ppm.

Betaine **VII** was alkylated with methyl iodide according to the procedure in [1] to obtain phosphonium salt **VIII**, mp 115°C. IR spectrum: ν(CO) 1700 cm^{-1}. ^{31}P NMR spectrum: δ_P 22.4 ppm.

Reaction of triphenylphosphine with cinnamic acid. Cinnamic acid, 2.12 g, was thoroughly mixed with a solution of 3.47 g of triphenylphosphine in 5 ml of chloroform, and the mixture was left to stand for 1 week at room temperature, treated with 1 ml with diethyl ether, and then left to stand for 1 week at 10°C. Well-formed crystals dropped, which, according to X-day diffraction data, phosphonium salt **VI** containing one solvation chloroform molecule, mp 68°C. IR spectrum: ν(CO) 1705 cm^{-1}. ^{31}P NMR spectrum: δ_P 18 ppm.

The reaction of triphenylphosphine with *p*-methoxycinnamic acid was performed in a similar way.

Methyltriphenylphosphonium iodide (X). *a.* A solution of 1.12 g of cinnamic acid in 5 ml of chloroform was added with stirring to a solution of 1.97 g of triphenylphosphine in 5 ml of chloroform. The reaction mixture was left to stand for 1 day, and the solvent was removed in a vacuum. According to spectral data, the reaction product was betaine **IV**. Without isolation, it was treated with 1.07 g, and the resulting mixture was left to stand for an additional 1 day, after which the solvent was removed in a vacuum, and the residue was treated with diethyl ether. The precipitate that formed was filtered off, washed with diethyl ether, and dried in a vacuum to isolate compound **X** as yellow crystals, mp 190–195°C. ^{31}P NMR specrum: δ_P 52.8 ppm. The ^1H NMR spectrum showed a doublet of methyl protons at δ 3.14 ppm (J^2_{PH} 7.08 Hz).

b. A solution of methyl iodide, 1.16 g, was added to a solution of 2.1 g of triphenylphosphine in 7 ml of chloroform. The reaction mixture was left to stand for 1 day and treated as described in experiment *a* to obtain a compound coincident in melting point and NMR and IR spectra with that obtained in experiment *a*.

Reaction of tributylphosphine with acrylic acid. Acrylic acid, 0.41 g, was added dropwise with stirring to a solution of 1.12 g of tributylphosphine in 5 ml of chloroform. Strong heat release was observed. The reaction mixture was left to stand for 1 day, and the solvent was removed in a vacuum to obtain betaine **XI** as an oily substance, n_D^{20} 1.4751. IR spectrum: ν(CO) 1600 cm^{-1}. ^{31}P NMR spectrum: δ_P 23 ppm.

Compound **XI** was alkylated by the above-described procedure to give phosphonium salt **XII** as a tarry substance. IR spectrum: ν(CO) 1730 cm^{-1}. ^{31}P NMR spectrum: δ_P 23.4 ppm.

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