to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990*b*). Software used to prepare material for publication: *SHELXL*93.

The authors would like to thank the Malaysian Government and Universiti Sains Malaysia for research grant R & D No. 123-3417-2201, and State Science and Technology Commission and National Nature Science Foundation of China for a major key research project.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1198). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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α-Phenylselenomethoxycarbonylmethyl(triphenyl)arsorane

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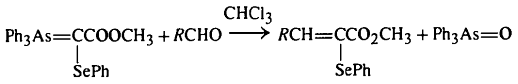
(*Received 27 March 1995; accepted 13 June 1995*)

Abstract

The crystal structure of α-phenylselenomethoxycarbonylmethyl(triphenyl)arsorane, $[Ph_3AsC(COOCH_3)SePh]$, has been determined by X-ray diffraction. The compound is a stable α-organoselenoarsonium ylide. Delocalization of electronic density appears to be restricted from atoms O(1) to Se including the As atom. The As—C(1) and Se—C(1) bonds have double-bond characteristics.

Comment

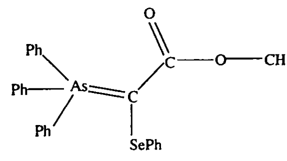
As the Wittig reaction played an important role in olefination, a number of relevant investigations have been performed. Although α-selenophosphonium ylides have been synthesized, α-seleno-substituted phosphonium ylides containing an α-electron-attracting group cannot undergo a Wittig reaction (Petragnani, Rodrigues & Comasseto, 1976; Braga, Comasseto & Petragnani, 1984). Considering that the reactivity of arsonium ylides is higher than that of corresponding phosphonium ylide, we recently synthesized α-phenylselenomethoxycarbonylmethyltriphenylarsorane, which is the first example of an α-seleno-substituted arsonium ylide. Moreover, we found that the compound had sufficient activity to undergo a Wittig-type reaction and so developed the first method of stereoselective synthesis of (*Z*)-α-phenylseleno-α,β-unsaturated esters (Huang, Huang & Huang, 1995).



$$Ph_3As{=}\underset{\displaystyle SePh}{\underset{|}{C}}COOCH_3 + RCHO \xrightarrow{CHCl_3} RCH{=}\underset{\displaystyle SePh}{\underset{|}{C}}CO_2CH_3 + Ph_3As{=}O$$

$R = C_6H_5$-, 4-ClC_6H_4-, 4-$CH_3C_6H_4$-, 4-$NO_2C_6H_4$-, $(CH_3)_2CHCH_2$-, CH_3CHCH-

The molecular structures of arsonium ylides have been studied previously (Shao, Jin, Tang, Huang & Huang, 1982; Fan & Shen, 1984; Ferguson & Rendle, 1975, 1976; Hu, Shi, Huang, Dong & Huang, 1989). To our knowledge, however, no information on the structure of an α-selenoarsonium(phosphonium) ylide has been reported. The present investigation was undertaken in order to characterize the stability and reactivity of the title compound, (I).



(I)

Fig. 1 is an *ORTEP* (Johnson, 1965) diagram of the molecule $[Ph_3AsC(COOCH_3)SePh]$. As can be seen, the geometry at the As atom is a distorted tetrahedron. There are two kinds of As—C bond: As—C(Ph) has a mean length of 1.931 (9) Å and As—C(1) a mean length of 1.824 (9) Å. The former is in good agreement with the reported value [1.932 (6) Å] for 1-acetyl-2,3,4-triphenyl-5-(triphenylarsonio)cyclopentadienide (Ferguson & Rendle, 1975). The latter is approximately equal to the mean length of the As—C_{sp^2} single bond (1.897 Å;

Palenik, 1972) and double bond (1.78 Å; Pauling, 1960), but is shorter than those (1.86–1.89 Å) reported for comparable bonds in the arsonium ylide (Fan & Shen, 1984; Ferguson & Rendle, 1975). This indicates that the As—C(1) bond has some double-bond characteristics. Although the Se—C(Ph) bond length [1.954 (9) Å] agrees with the sum of the normal covalent radii (Se 1.17, C 0.77 Å), the length [1.873 (9) Å] of Se—C(1) is much shorter than the sum of the radii and the bond length [1.977 (12) Å] of $Se(CH_3)_2$ (Wells, 1962). The short bond length of Se—C(1) also displays striking characteristics of a multiple bond, which would be the formation of d–$p\pi$ bond between the Se and C(1) atoms. Also, the carbonyl distance [1.227 (11) Å] and the C(1)—C(2) bond length [1.437 (15) Å] are longer than that (1.17 Å) reported for $[Ph_3AsC(COOCH_3)C_2F_5]$ (Fan & Shen, 1984) and much shorter than the C—C single-bond distance. These phenomena show that delocalization of electron density occurs in the conjugated system starting from O(1) to Se and including As. The fact that As, C(1), Se, C(2) and O(1) reside in a perfect plane with a maximum deviation of 0.018 Å for C(2), and that C(1) is sp^2 rather than sp^3, provide further evidence for this theory.

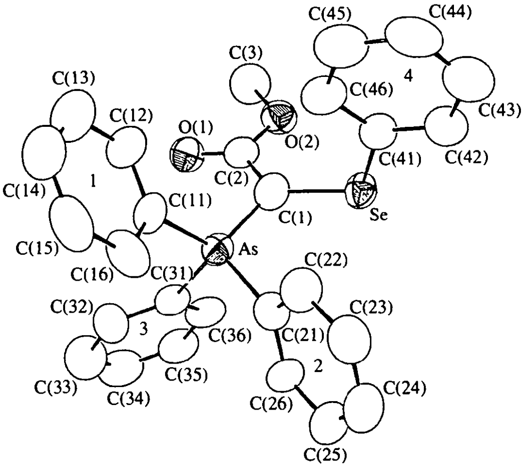


Fig. 1. The molecular structure and the numbering scheme for the complex. Displacement ellipsoids are shown at the 50% probability level.

When an ylide has an electron-withdrawing group capable of effectively participating in conjugation at the methylene moiety, its stability increases. The phenylselenyl group, as an electron-withdrawing group linking with C(1), takes part in delocalization resulting in a shorter As—C(1) bond in comparison with the values of other arsonium ylide (Fan & Shen, 1984), and increases the stability of the compound. Nevertheless, overlap of the p orbitals of C and $4d$ orbitals of As in the compound is less effective than that of the p orbitals of C and $3d$ orbitals of P in selenophosphoranes. Thus, the title compound can undergo a Wittig reaction while selenophosphoranes can not.

In the compound, all phenyl rings from (1) to (4) and the COOC group are individually planar and rotate around the As—C(Ph), C(2)—C(1) and Se—C(1) bonds, respectively, so as to minimize intra- and intermolecular interactions. As a result, the following angles were observed: rings (1) and (2) 59.6 (4), (1) and (3) 101.3 (3), (2) and (3) 78.4 (4), plane COOC and ring (1) 57.9 (3), plane COOC and (4) 81.4°. The As···O(1) distance [2.921 (5) Å] is considerably less than the sum of the appropriate van der Waals radii (3.40 Å). Crystal packing involves a pair of centrosymmetrical molecules in the unit cell.

Experimental

Freshly prepared $[Ph_3AsC(COOCH_3)SePh]$, according to the literature method (Huang, Huang & Huang, 1985), was dissolved in 4.2 ml of a mixed solution of ethyl acetate and chloroform (6:1 v/v). After filtering, the solution was left and evaporated slowly at room temperature. After a few days, single crystals suitable for X-ray analysis were obtained.

Crystal data

$C_{27}H_{23}AsO_2Se$
$M_r = 533.36$
Triclinic
$P\bar{1}$
$a = 9.840\,(2)$ Å
$b = 10.379\,(4)$ Å
$c = 13.804\,(3)$ Å
$\alpha = 111.50\,(2)°$
$\beta = 105.40\,(2)°$
$\gamma = 102.12\,(2)°$
$V = 1188.0\,(7)$ Å^3
$Z = 2$
$D_x = 1.493$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10$–$14°$
$\mu = 2.96$ mm^{-1}
$T = 293$ K
Prism
0.4 × 0.2 × 0.13 mm
Pale yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical, ψ scans (North, Phillips & Mathews, 1968)
$T_{min} = 0.947$, $T_{max} = 0.999$
4459 measured reflections
3927 independent reflections
2101 observed reflections $[I > 3\sigma(I)]$

$R_{int} = 0.032$
$\theta_{max} = 25°$
$h = 0 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = -16 \rightarrow 16$
3 standard reflections monitored every 200 reflections intensity decay: 17.1%

Refinement

Refinement on F
$R = 0.048$
$wR = 0.054$
$S = 1.973$

$(\Delta/\sigma)_{max} = 0.01$
$\Delta\rho_{max} = 0.875$ e Å^{-3}
$\Delta\rho_{min} = -0.533$ e Å^{-3}
Extinction correction: none

2101 reflections
280 parameters
H atoms refined isotropically
Unit weights applied

Atomic scattering factors
from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Se	0.3597 (1)	0.3272 (1)	0.73651 (7)	4.11 (2)
As	0.5471 (1)	0.6752 (1)	0.84447 (7)	3.57 (2)
O(1)	0.7595 (7)	0.5658 (7)	0.7544 (5)	4.8 (2)
O(2)	0.6417 (7)	0.3209 (7)	0.6826 (5)	4.9 (2)
C(1)	0.525 (1)	0.4828 (9)	0.7645 (7)	4.2 (2)
C(2)	0.650 (1)	0.463 (1)	0.7332 (7)	3.9 (2)
C(3)	0.767 (1)	0.299 (1)	0.654 (1)	6.8 (4)
C(11)	0.534 (1)	0.7925 (9)	0.7618 (7)	4.1 (2)
C(12)	0.585 (1)	0.761 (1)	0.6745 (8)	5.5 (3)
C(13)	0.572 (1)	0.843 (1)	0.6143 (9)	7.0 (4)
C(14)	0.511 (1)	0.950 (1)	0.6396 (8)	6.6 (3)
C(15)	0.457 (1)	0.978 (1)	0.7255 (9)	6.7 (3)
C(16)	0.471 (1)	0.898 (1)	0.7873 (8)	5.4 (3)
C(21)	0.3827 (9)	0.6749 (8)	0.8928 (7)	3.7 (2)
C(22)	0.242 (1)	0.641 (1)	0.8173 (8)	4.9 (3)
C(23)	0.121 (1)	0.637 (1)	0.8511 (9)	5.6 (3)
C(24)	0.142 (1)	0.665 (1)	0.9606 (9)	6.4 (3)
C(25)	0.283 (1)	0.700 (1)	1.0367 (8)	5.9 (3)
C(26)	0.403 (1)	0.704 (1)	1.0039 (7)	4.6 (3)
C(31)	0.730 (1)	0.783 (1)	0.9772 (7)	3.9 (2)
C(32)	0.802 (1)	0.931 (1)	1.0166 (8)	5.5 (3)
C(33)	0.931 (1)	1.002 (1)	1.114 (1)	7.2 (4)
C(34)	0.984 (1)	0.927 (1)	1.1708 (9)	6.9 (4)
C(35)	0.909 (1)	0.779 (1)	1.1322 (8)	5.6 (3)
C(36)	0.780 (1)	0.707 (1)	1.0338 (7)	4.5 (3)
C(41)	0.2072 (9)	0.299 (1)	0.5995 (7)	4.0 (2)
C(42)	0.070 (1)	0.200 (1)	0.5647 (8)	5.4 (3)
C(43)	−0.047 (1)	0.176 (1)	0.4697 (9)	7.0 (4)
C(44)	−0.018 (1)	0.252 (1)	0.4100 (9)	6.9 (4)
C(45)	0.119 (1)	0.353 (1)	0.4455 (9)	7.1 (4)
C(46)	0.237 (1)	0.379 (1)	0.5423 (8)	5.5 (3)

Table 2. *Selected geometric parameters* (Å, °)

Se—C(1)	1.873 (9)	As—C(31)	1.936 (7)
Se—C(41)	1.954 (9)	O(1)—C(2)	1.227 (11)
As—C(1)	1.824 (9)	O(2)—C(2)	1.355 (9)
As—C(11)	1.951 (11)	O(2)—C(3)	1.426 (9)
As—C(21)	1.906 (10)	C(1)—C(2)	1.437 (15)
C(1)—Se—C(41)	104.3 (3)	O(2)—C(2)—C(1)	114.7 (7)
C(1)—As—C(11)	116.5 (3)	As—C(11)—C(12)	118.7 (6)
C(1)—As—C(21)	106.8 (3)	As—C(11)—C(16)	119.9 (7)
C(1)—As—C(31)	113.5 (3)	C(12)—C(11)—C(16)	121.4 (7)
C(11)—As—C(21)	104.4 (4)	As—C(21)—C(22)	120.1 (6)
C(11)—As—C(31)	107.3 (3)	As—C(21)—C(26)	120.4 (6)
C(21)—As—C(31)	107.7 (3)	As—C(31)—C(32)	121.2 (6)
Se—C(1)—As	122.0 (4)	As—C(31)—C(36)	117.1 (6)
Se—C(1)—C(2)	123.9 (6)	Se—C(41)—C(42)	116.8 (6)
As—C(1)—C(2)	113.9 (6)	Se—C(41)—C(46)	121.7 (6)
O(1)—C(2)—O(2)	121.9 (8)	C(2)—O(2)—C(3)	115.5 (6)
O(1)—C(2)—C(1)	123.3 (7)		

Table 3. *Contact distances* (Å)

Se· · ·O(2)	3.064 (5)	As· · ·O(1)	2.921 (5)

The cell was not reduced. The orientation matrix $\bar{1}00/0\bar{1}0/111$ generates a reduced cell with a = 9.840, b = 10.379, c = 13.231 Å, β = 107.58, γ = 102.12°. The data were corrected for Lorentz and polarization effects based on the intensity measurement. During data collection, the crystal slightly decomposed due to exposure to the X-ray, causing a 17% decrease in the intensity. The structure was solved by direct methods. All non-H atoms were located through difference Fourier synthesis and refined by full-matrix least-squares methods, including anisotropic temperature factors. The majority of the H atoms were located by the same method and a few H atoms connected to the phenyl rings were located by calculation. All H atoms were refined with an isotropic displacement parameter in the final run. Program used throughout the analysis: *Enraf–Nonius SDP-Plus Structure Determination Package* (Frenz, 1985).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Data reduction: *SDP* (B. A. Frenz & Associates Inc., 1985). Program(s) used to solve structure: *SDP*, *MULTAN*80 (Main *et al.*, 1980). Program(s) used to refine structure: *SDP*. Molecular graphics: *SDP*, *PLUTO* (Motherwell & Clegg, 1978).

This work was supported by the Natural Science Foundation of China.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1054). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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