Stereochemistry of Some Organic Derivatives of Group VB Elements. Part VII.[1] Crystal and Molecular Structure of Triphenyl-(2-acetyl-3,4,5-triphenylcyclopenta-2,4-dienyl)arsonium Perchlorate

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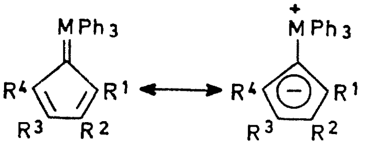
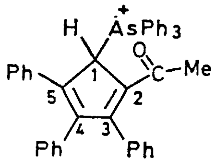
The crystal structure of the title compound has been determined by three-dimensional *X*-ray methods. It is formed by protonation of the parent arsonium cyclopentadienylide at the 1-position of the cyclopentadienyl ring. There is thus no delocalisation between the arsonium moiety and the cyclopentadiene system. The environment at arsenic is slightly distorted tetrahedral [$As^+ \cdots O(Ac)$ 3·100(11) Å]; As^+–C(sp^3) is 1·963 ± 0·013 Å, and mean As^+≡C(Ph) 1·908 ± 0·007 Å.

The perchlorate ion is held in the crystal by a C–H ··· O hydrogen bond (H ··· O 2·2 Å) between a perchlorate oxygen and the acidic five-membered ring proton. Crystals are monoclinic, space group $P2_1/c$ with $Z = 4$ in a cell of dimensions a = 11·939(1), b = 18·337(2), c = 17·570(2) Å, β = 105·85(2)°. The structure was solved from diffractometer data by the heavy-atom method and refined by least-squares calculations to R 0·066 for 1558 observed reflexions.

RECENTLY there has been considerable interest in the electrophilic substitution reactions of triphenyl-phosphonium and -arsonium cyclopentadienides [2–5], (I), which also readily form perchlorate salts.[4,5] We report here the structure of triphenyl-(2-acetyl-3,4,5-triphenylcyclopenta-2,4-dienyl)arsonium perchlorate, (II),[6] which was investigated in order to establish the site of protonation of the parent ylide (I; R^1 = Ac; $R^2 = R^3 = R^4$ = Ph),[7] and to provide details of the bonding pattern in the protonated system.



(I)



(II)

EXPERIMENTAL

Crystal Data.—$C_{43}H_{34}AsClO_5$, M = 741·1, Monoclinic, a = 11·939(1), b = 18·337(2), c = 17·570(2) Å, β = 104·85(2)°, U = 3718 Å^3, D_m not measured, Z = 4, D_c = 1·32, $F(000)$ = 1528. Space group $P2_1/c$ (C^5_{2h}, No. 14) from systematic absences: $h0l$ l odd, and $0k0$ k odd. Cu-K_α X-radiation, λ = 1·5418 Å; μ(Cu-K_α) = 23·7 cm^{-1}.

Crystallographic Measurements.—Preliminary space-group data were obtained from precession and Weissenberg photographs. Accurate cell dimensions were obtained from least-squares refinement of diffractometer setting angles of 12 reflexions. The crystal chosen for the data collection was a prism bounded by the planes {110}, {1$\bar{1}$0}, {001} and with dimensions *ca.* 0·08 × 0·07 × 0·19 mm. Intensity data were collected to a $\theta_{max.}$ 45° on a Hilger and Watts Y 290 computer-controlled diffractometer. The θ—2θ scan technique was used with a symmetric scan of 0·8°, consisting of 80 steps of 0·01° of 0·75 s. Stationary-crystal–stationary-counter background counts of 15 s were measured at each end of the integrated scan. The maximum variation in intensity of 3 standard reflexions (*ca.* 3000 counts s^{-1}) monitored regularly throughout data collection was <1·5%. Each intensity was corrected for background. Of 2656 independent reflexions 1558 had $I > 3\sigma(I)$ {where $\sigma(I)$ = [scan + 4 × (sum of background counts) + (0·05 intensity)^2]$^{1/2}$} and were considered observed. Data were corrected for Lorentz and polarization factors, but not for absorption or extinction.

Structure Solution and Refinement.—The co-ordinates of the As atom were obtained from a three-dimensional Patterson distribution. One cycle of refinement of F [with $\sigma(F) = 0{\cdot}5\sigma(F^2)/F$], in which the scale factor was varied, yielded R 0·47 and the weighted factor, R' 0·55 {$R' = [\Sigma w(F_o - F_c)^2/\Sigma wF_o{}^2]^{1/2}$}. Atomic scattering factors for carbon, oxygen, chlorine, and arsenic were taken from ref. 8. Only observed reflexions were included in the least-squares calculations and the function minimized was R' (above). Absolute weights [based on $\sigma(F_o)$] were used throughout refinement. An initial electron-density distribution based on phases derived from the As atom yielded the positions of the Cl and 17 light atoms. Successive difference maps yielded chemically sensible positions for all non-hydrogen atoms. The structure was then refined by full-matrix least-squares calculations, with the phenyl groups included as rigid bodies [C–C (aromatic) 1·397 Å; C–C–C 120°], and with isotropic thermal parameters for all atoms, to R 0·082. Refinement continued with the non-group atoms permitted to vibrate anisotropically, and with the group atoms given individual isotropic thermal parameters. Refinement converged at R 0·066 and R' 0·072. On the last cycles the maximum shift in any positional parameter was <0·50. Final positional parameters are listed in Table 1.

A difference map calculated using the F_c values from the parameters listed in Table 1 contained a number of small peaks, the highest being 0·4 eÅ^{-3}. Many of these peaks appeared in positions corresponding to phenyl hydrogen atoms, however no attempt was made to include these in any calculations. One of the highest peaks appeared in a chemically reasonable position for the hydrogen atom bound to C(1) and is shown in Figure 2 in the position found from the difference map.

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[1] Part VI, G. Ferguson and F. C. March, *J.C.S. Dalton*, 1975, 1291.

[2] B. H. Freeman and D. Lloyd, *J. Chem. Soc.* (*C*), 1971, 3165; Z. Yoshida, S. Yoneda, Y. Murata, and H. Hashimoto, *Tetrahedron Letters*, 1971, 1523.

[3] D. Lloyd and M. I. C. Singer, *Chem. and Ind.*, 1971, 786.

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[6] D. Lloyd and M. I. C. Singer, *J. Chem. Soc.* (*C*), 1971, 2941.

[7] G. Ferguson and D. F. Rendle, *J.C.S. Dalton*, 1975, 1284.

[8] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1965.

The final error in an observation of unit weight, calculated over all observed data, was 2·19 and ranged from 1·8 to 2·6 over 10 ranges of intensity in a non-systematic way, indicating that while the relative weighting of the data is adequate, the absolute weighting scheme is not as good as one might hope. One reason for this relatively high value is the incomplete refinement. A lower R could no doubt be obtained if the phenyl group atoms were refined individually (as evidenced for instance, by the rather large σ values for some parameters of some of the group atoms listed in Table 1), however, the greatly increased computing effort involved did not seem warranted. Final values for the structure amplitudes, thermal parameters, and details of planes are listed in Supplementary Publication No. 21307 (8 pp., 2 microfiche).* Final agreement factors for all 2656 data are R 0·119 and R' 0·086.

Table 1

Final atomic parameters

(*a*) Fractional co-ordinates of non-group atoms

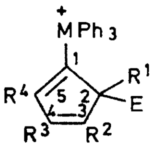
Atom	*x*/*a*	*y*/*b*	*z*/*c*
As	0·14522(15)	0·13401(8)	0·09085(10)
Cl	0·3057(5)	0·3532(3)	0·2927(3)
C(1)	0·2382(13)	0·2205(7)	0·1318(8)
C(2)	0·2017(15)	0·2858(8)	0·0793(9)
C(3)	0·2878(16)	0·3087(8)	0·0483(8)
C(4)	0·3911(13)	0·2628(9)	0·0792(9)
C(5)	0·3638(13)	0·2118(8)	0·1274(8)
C(6)	0·0856(17)	0·3179(10)	0·0726(9)
C(7)	0·0457(14)	0·3920(8)	0·0390(10)
O(1)	0·0173(9)	0·2796(6)	0·0999(6)
O(2)	0·3237(10)	0·3950(6)	0·3625(7)
O(3)	0·2257(14)	0·3903(7)	0·2327(8)
O(4)	0·4086(12)	0·3414(8)	0·2721(7)
O(5)	0·2594(10)	0·2838(6)	0·3053(6)
H(Cl)	0·2448	0·2238	0·1930

(*b*) Group atoms

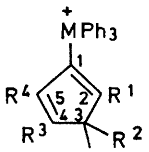
Atom	*x*/*a*	*y*/*b*	*z*/*c*	B_{iso}
C(11)	0·2903(8)	0·3746(5)	−0·0002(5)	4·4(3)
C(12)	0·3469(11)	0·4375(7)	0·0347(4)	8·2(5)
C(13)	0·3478(20)	0·5000(6)	−0·0107(6)	9·7(5)
C(14)	0·2922(23)	0·4995(5)	−0·0910(5)	7·5(4)
C(15)	0·2356(15)	0·4366(5)	−0·1259(3)	7·4(4)
C(16)	0·2347(8)	0·3741(4)	−0·0805(6)	6·1(4)
C(21)	0·5026(7)	0·2761(5)	0·0602(6)	4·7(3)
C(22)	0·6023(10)	0·2904(9)	0·1202(4)	6·7(4)
C(23)	0·7095(9)	0·2969(19)	0·1025(6)	7·1(4)
C(24)	0·7170(8)	0·2890(23)	0·0249(7)	6·7(4)
C(25)	0·6173(9)	0·2747(15)	−0·0351(4)	6·7(4)
C(26)	0·5102(7)	0·2683(6)	−0·0174(5)	5·3(4)
C(31)	0·4442(7)	0·1598(4)	0·1787(5)	4·3(3)
C(32)	0·5257(12)	0·1216(8)	0·1497(4)	4·9(3)
C(33)	0·6004(22)	0·0722(15)	0·1981(8)	6·2(4)
C(34)	0·5936(26)	0·0609(17)	0·2755(8)	6·4(4)
C(35)	0·5120(19)	0·0992(11)	0·3044(6)	6·5(4)
C(36)	0·4373(9)	0·1486(5)	0·2560(6)	5·0(3)
C(41)	0·0450(8)	0·1542(5)	−0·0100(4)	4·6(3)
C(42)	−0·0749(8)	0·1494(6)	−0·0210(5)	5·4(4)
C(43)	−0·1491(6)	0·1641(10)	−0·0949(6)	6·7(4)
C(44)	−0·1035(8)	0·1837(10)	−0·1577(5)	6·9(4)
C(45)	0·0164(9)	0·1885(6)	−0·1467(5)	6·1(4)
C(46)	0·0906(6)	0·1738(5)	−0·0728(6)	4·9(3)
C(51)	0·2402(7)	0·0517(4)	0·0841(6)	4·6(3)
C(52)	0·2638(16)	0·0340(9)	0·0124(5)	5·8(4)
C(53)	0·342(5)	−0·022(3)	0·0089(9)	6·6(4)
C(54)	0·396(7)	−0·060(4)	0·0772(13)	6·5(4)
C(55)	0·373(5)	−0·043(3)	0·1488(10)	6·0(4)
C(56)	0·2946(21)	0·0135(12)	0·1523(5)	5·2(4)
C(61)	0·0522(7)	0·1037(6)	0·1589(5)	4·7(3)
C(62)	0·0139(10)	0·0314(5)	0·1546(5)	5·8(4)
C(63)	−0·0540(12)	0·0074(5)	0·2036(7)	7·3(4)
C(64)	−0·0837(11)	0·0556(7)	0·2569(6)	7·0(4)
C(65)	−0·0454(8)	0·1278(6)	0·2611(5)	7·3(4)
C(66)	0·0226(8)	0·1519(4)	0·2122(6)	6·1(4)

RESULTS AND DISCUSSION

Previous work [2-4] on electrophilic substitution of phosphonium and arsonium cyclopentadienides has shown that substitution takes place, if possible, preferentially at the 2- or 5-positions of the cyclopentadienyl ring, or otherwise at the 3- or 4-positions [see (III) and (IV) for arbitrary numbering]. This has been rationalized [3] in terms of the structures of the transition states for these substitution reactions, which were assumed to be closely related to the σ complexes (III) and (IV) involved in the reaction paths; (III) should have greater stability than (IV) since the former involves a linear conjugated system and (IV) a cross-conjugated system. The protonation of cyclopentadienides has usually followed a similar pattern,[4,5] and no previous example is known of electrophilic attack at the 1-position, excepting of course Wittig-type reactions of the ylides. However in the case of (I), R^1 = Ac, $R^2 = R^3 = R^4$ = Ph, our results establish that protonation has occurred at the 1-position to yield the cation (II).



(III)



(IV)

The crystal structure consists of discrete cations and perchlorate anions (Figure 1). The structure of the protonated cation is shown in Figure 2 and details of the molecular geometry in Table 2. The cyclopentadiene ring is planar and C–C distances around the ring are as expected for sp^3—sp^2 bonds [C(1)–C(5) and C(1)–C(2)], sp^2—sp^2 single bonds [C(3)–C(4) and all ring–side-chain distances], and double bonds [C(3)–C(2), C(4)–C(5)]. Conjugation can thus occur between the double bonds C(4)=C(5), C(2)=C(3), and C(6)=O(1). Ideally, for such conjugation to occur the plane of the acetyl group should be coplanar with that of the ring. The angle found is 13·8°, however, which is unlikely to decrease the potential for overlap between orbitals of atoms C(6) and C(2) significantly. In the parent ylide, where considerable conjugation between the acetyl group and the cyclopentadienyl ring is known to occur, the angle between the corresponding planes is 5·3°. Configuration (V), which would result from substitution at the 2-position, does not allow conjugation between the ring and the acetyl side-chain. Configuration (VI), which would permit conjugation, apparently is less energetically favourable than (II), possibly because the site of the arsonium group in the case of (VI) results in a measure of cross-conjugation, which is absent in (II). The phenyl groups at the 3-, 4-, and 5-positions do not appear to be involved in conjugation with the cyclopentadiene ring to any great

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

extent since the angles between the phenyl ring planes and the five-membered ring vary from 40·3 to 118·6°.

The exocyclic angles around the five-membered ring vary from 119·2 to 129·8° so as to minimize the C(7) ··· C(11) (3·12 Å), C(11) ··· C(21) (3·07 Å), and C(21) ··· C(31) (3·18 Å) interactions. Thus the angles C(2)=C(3)–C(11), C(3)=C(2)–C(6), C(4)=C(5)–C(31), and C(5)=C(4)–C(21) (Figure 1) are 5—7° greater than angles C(3)–C(4)–C(21) and C(4)–C(3)–C(11). If this had not been the case, and the exocyclic angles had been all equal, the double bonds at C(2)=C(3) and C(4)=C(5) would have resulted in extremely unfavourable short contacts between C(7) ··· C(11) and C(21) ··· C(31).

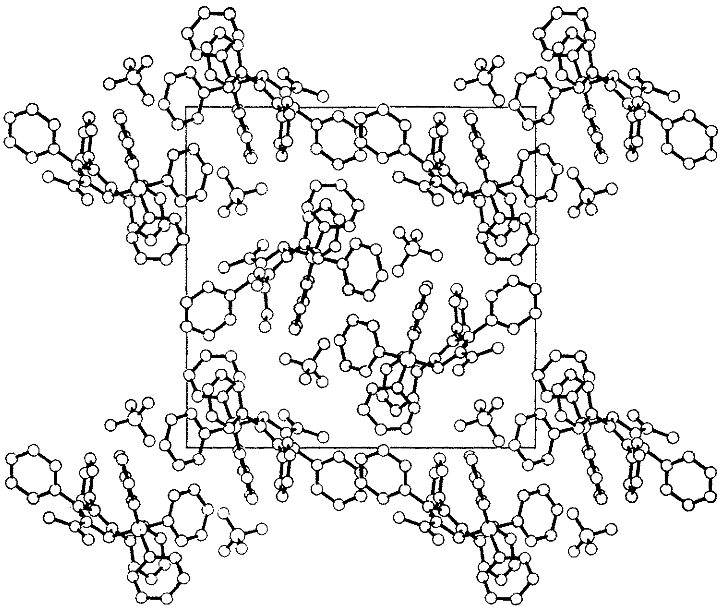


FIGURE 1 The crystal structure as viewed along the *a**-axis. Origin of cell is at bottom left, with *b* horizontal, and *c* vertical

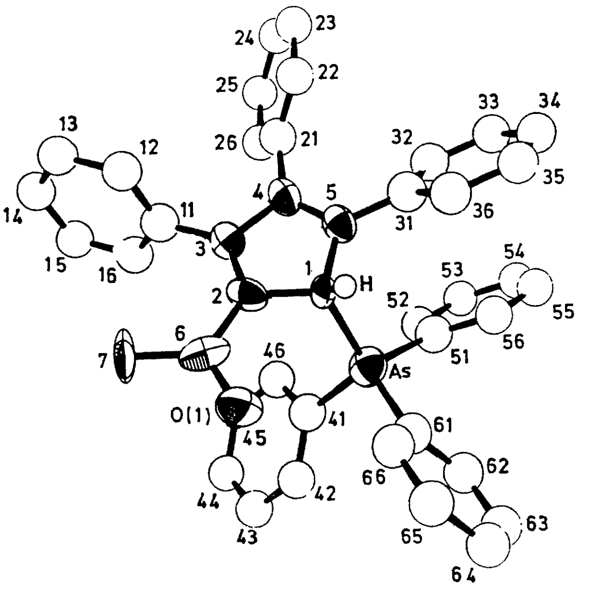
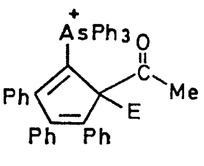
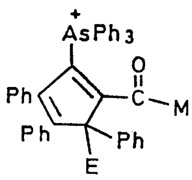


FIGURE 2 The protonated cation showing the crystallographic numbering scheme (atoms with numbers only are carbon); thermal ellipsoids are drawn at 50% probability

Co-ordination about arsenic is a slightly distorted tetrahedron (see Table 2) with C–As–C angles 105—112°. The co-ordination environment about arsenic in the parent ylide [7] is intermediate between that of a regular tetrahedron and trigonal bipyramid because of a close contact between the oxygen atom of the acetyl group and the arsenic atom [2·770(3) Å]. This interaction was attributed to a large contribution to the ground electronic state from a canonical form which placed a formal negative charge on the oxygen atom. Such a canonical form is not possible with the protonated species but the corresponding As$^+$ ··· O distance [3·100(11) Å] is significantly less than the normal van der Waals contact distance (3·4 Å).[9] The As$^+$–C(Ph) distances [mean 1·908(9) Å] are as expected and the orientations of the phenyl rings bound to arsenic appear to be determined by intramolecular packing effects. As$^+$–C(1) [1·963(13) Å] Is not significantly different from the sums of the relevant single-bond covalent radii (1·98 Å),[9] and contrasts with



(V)



(VI)

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[9] L. Pauling, 'The Nature of the Chemical Bond,' Cornell University Press, Ithaca, New York, 1948.

1·881(4) Å in the parent ylide. The structure of the perchlorate anion is close to a regular tetrahedron with O–Cl–O angles 107·8(8)—111·3(8)° and mean Cl–O distance (uncorrected) 1·407(10) Å. Shortest interion distances, listed in Table 2, all correspond to van der Waals contacts except that between O(5) and the five-membered ring C–H moiety which appears to be a C–H · · · O hydrogen bond with O · · · H 2·22, H–C 1·06, C · · · O 3·21 Å, Cl–O · · · H 105, and C–H · · · O 154°. The proton involved is the most acidic in the molecule and the geometry details are entirely in accord with those found for such hydrogen bonds in other systems.[10-12]

TABLE 2

Interatomic distances (Å) and angles (°)

(*a*) In the cation

(i) Distances (σ C–C 0·018, C–O 0·016, As–C 0·013 Å)

C(1)–C(2)	1·507	C(4)–C(21)	1·474
C(1)–C(5)	1·530	C(5)–C(31)	1·483
C(1)–As	1·963	C(6)–C(7)	1·509
C(2)–C(3)	1·348	C(6)–O(1)	1·261
C(2)–C(6)	1·483	C(41)–As	1·904
C(3)–C(4)	1·478	C(51)–As	1·910
C(3)–C(11)	1·483	C(61)–As	1·909
C(4)–C(5)	1·355		

(ii) Angles (mean σ C–As–C 0·4, As–C–C 0·8, C–C–C 1·1°)

As–C(41)–C(46)	120·3	C(5)–C(31)–C(36)	119·8
As–C(41)–C(42)	119·7	C(5)–C(31)–C(32)	120·2
As–C(51)–C(56)	119·8	C(5)–C(1)–C(2)	100·6
As–C(51)–C(52)	120·0	C(1)–C(2)–C(3)	111·4
As–C(61)–C(66)	121·5	C(1)–C(2)–C(6)	118·8
As–C(61)–C(62)	118·5	C(3)–C(2)–C(6)	129·6
As–C(1)–C(2)	111·7	C(2)–C(3)–C(11)	128·0
As–C(1)–C(5)	111·5	C(2)–C(3)–C(4)	108·9
C(1)–As–C(41)	110·2	C(11)–C(3)–C(4)	122·6
C(1)–As–C(51)	111·8	C(3)–C(4)–C(5)	108·2
C(1)–As–C(61)	111·7	C(3)–C(4)–C(21)	122·6
C(41)–As–C(51)	109·8	C(21)–C(4)–C(5)	129·2
C(41)–As–C(61)	108·1	C(4)–C(5)–C(31)	127·0
C(51)–As–C(61)	105·0	C(1)–C(5)–C(31)	121·7
C(3)–C(11)–C(16)	120·1	C(1)–C(5)–C(4)	110·8
C(3)–C(11)–C(12)	119·9	C(2)–C(6)–C(7)	125·7
C(4)–C(21)–C(26)	119·5	O–C(6)–C(7)	118·7
C(4)–C(21)–C(22)	120·3	O–C(6)–C(2)	115·5

(*b*) Perchlorate anion

(i) Distances (mean σ 0·014 Å)

Cl–O(2)	1·414	Cl–O(4)	1·384
Cl–O(3)	1·404	Cl–O(5)	1·427

(ii) Angles (mean σ 0·8°)

O(2)–Cl–O(3)	108·2	O(3)–Cl–O(4)	111·0
O(2)–Cl–O(4)	111·3	O(3)–Cl–O(5)	109·4
O(2)–Cl–O(5)	109·1	O(4)–Cl–O(5)	107·8

(*c*) Some intramolecular non-bonded contacts

O(1) · · · As	3·100(11)	O(1) · · · C(41)	3·07(1)
O(1) · · · C(66)	3·05(1)		

TABLE 2 (*Continued*)

(*d*) Interion contacts

O(2) · · · C(52^{I})	3·18	O(4) · · · C(55^{II})	3·38
O(2) · · · C(54^{II})	3·34	O(4) · · · C(5)	3·42
O(2) · · · C(53^{I})	3·44	O(5) · · · C(1)	3·21
O(3) · · · C(6)	3·17	O(5) · · · C(45^{I})	3·26
O(3) · · · C(2)	3·26	O(5) · · · C(46^{I})	3·39
O(3) · · · C(63^{III})	3·35		

Roman numeral superscripts refer to the following equivalent positions:

I $x, \frac{1}{2} - y, \frac{1}{2} + z$ III $-x, \frac{1}{2} + y, \frac{1}{2} - z$
II $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$

We thank the National Research Council of Canada for Operating and Computing Grants (to G. F.). Calculations were carried out on the University IBM 370/155 computer with local modifications of '*X*-Ray '72'.[13] Diagrams were prepared with the aid of ORTEP.[14]

[4/2220 *Received*, 28*th October*, 1974]

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