

STUDIES OF APPLICATIONS OF ORGANOELEMENT COMPOUNDS OF GROUPS V AND VI IN ORGANIC SYNTHESSES

XLVI *. SYNTHESIS, REACTIVITY AND CRYSTAL STRUCTURE OF TRIFLUOROACETYLMETHYLENETRIPHENYLARSORANE

YANCHANG SHEN*, ZHAOCHANG FAN and WEIMING QIU

Shanghai Institute of Organic Chemistry, Academia Sinica, 345 Lingling Lu, Shanghai (China)

(Received July 21st, 1986)

Summary

The in situ reaction of methylenetriphenylarsorane with ethyl trifluoroacetate gave trifluoroacetylmethylenetriphenylarsorane (**1**). Compound **1** was found to be very stable and did not react with aldehydes, but upon reaction with trifluoroacetic anhydride, bis(trifluoroacetyl)methylenetriphenylarsorane (**2**) was formed. The crystal structure of **1** has been determined, and the bond order is 1.62 which accounts for its lower reactivity.

Introduction

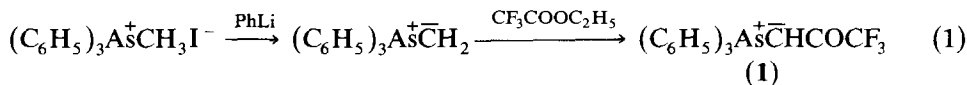
Arsonium ylides bearing an electron-withdrawing substituent at the alkylidene moiety have been found to be more reactive than the corresponding phosphonium ylides and to be able to react with aldehydes as well as ketones in moderate to excellent yields [1]. As far as the fluorinated arsonium ylides are concerned, only a few reports appeared in the literature. Burton et al. [2] reported the synthesis of perfluorocyclobutylidenetri-*n*-butylarsorane which was very stable and unable to react with aldehydes, but no structural evidence about its lower reactivity was given. Here we report the synthesis, reactivity and crystal structure of trifluoroacetylmethylenetriphenylarsorane.

Results and discussion

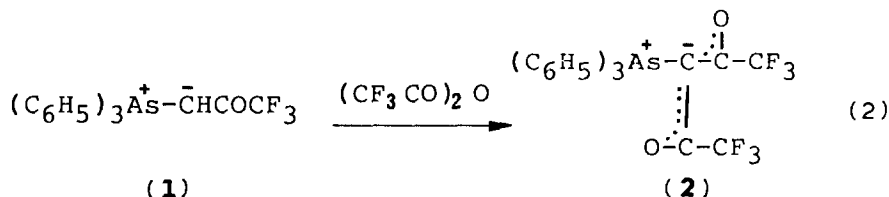
The in situ reaction of methylenetriphenylarsorane generated from methyltriphenylarsonium iodide and phenyllithium with ethyl trifluoroacetate gave trifluoro-

* For part XLV see ref. 6.

acetylmethylenetriphenylarsorane (1) in 62% yield (eq. 1).



Attempts to prepare trifluoroacetylmethylenetriphenylarsorane by reaction of methylenetriphenylarsorane with trifluoroacetyl chloride were unsuccessful. This fluorinated arsorane was found to be very stable and did not react with aldehydes under conditions similar to those for the reaction of benzoylmethylenetriphenylarsorane with aldehydes [3]. However, it did react with trifluoroacetic anhydride to give bis(trifluoroacetyl)methylenetriphenylarsorane (2) in 79% yield (eq. 2).



The difference in chemical behavior of trifluoroacetylmethylenetriphenylarsorane and benzoylmethylenetriphenylarsorane can be elucidated on the basis of their crystal structures. The crystal structure of benzoylmethylenearsorane has been reported previously [4] and that of trifluoroacetylmethylenetriphenylarsorane is shown in Fig. 1. There are four molecules in a unit cell ($Z = 4$), and the structure shows disorder. The trifluoromethyl group takes two alternative sets of positions with equal probability, which are related by a rotation of about 60° around C(20)–C(21) as shown in Table 1. Some selected bond lengths and angles of the title compound are listed in Table 2.

As to the structure of arsonium ylides, there are two probable canonical forms 3 and 4 (eq. 3), 3 is referred as "Ylene" and 4 as "Ylide".

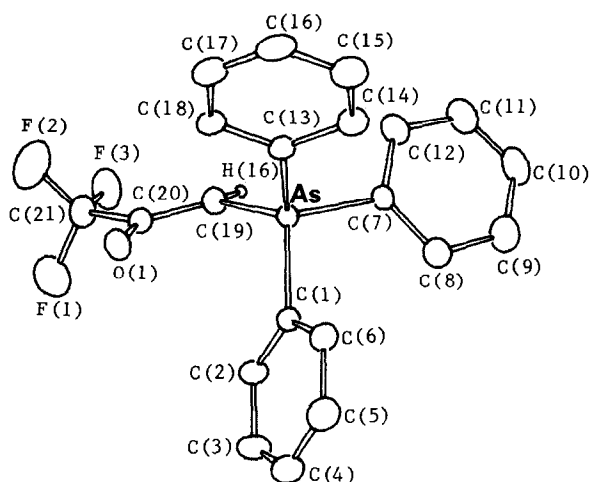


Fig. 1. Crystal structure of trifluoroacetylmethylenetriphenylarsorane.

TABLE 1
BOND ANGLES (°) OF TWO TRIFLUOROMETHYL GROUPS

F(1)–C(21)–F'(2)	63(2)	F'(2)–C(21)–F(3)	48(2)
F(3)–C(21)–F'(1)	58(1)	F'(1)–C(21)–F(2)	52(1)
F(2)–C(21)–F'(3)	54(1)	F'(3)–C(21)–F(1)	58(1)

TABLE 2
SOME SELECTED BOND LENGTHS (Å) AND ANGLES (°)

As–C(1)	1.931(7)	C(19)–C(20)	1.43(1)	C(21)–F'(1)	1.34(2)
As–C(7)	1.910(7)	C(20)–C(21)	1.54(1)	C(21)–F'(2)	1.38(4)
As–C(13)	1.919(7)	C(20)–O	1.22(1)	C(21)–F'(3)	1.32(2)
As–C(19)	1.855(8)	C(21)–F(1)	1.33(2)	C(19)–H(16)	1.19(8)
		C(21)–F(2)	1.31(2)		
		C(21)–F(3)	1.30(2)		
C(1)–As–C(7)	107.7(3)	As–C(19)–C(20)	118.2(6)		
C(1)–As–C(13)	107.9(3)	C(19)–C(20)–C(21)	113.2(7)		
C(1)–As–C(19)	112.4(3)	C(19)–C(20)–O	129.3(8)		
C(7)–As–C(13)	106.1(3)	C(21)–C(20)–O	117.6(8)		
C(7)–As–C(19)	107.8(3)	As–C(19)–H(16)	112(4)		
C(13)–As–C(19)	114.5(3)	C(20)–C(19)–H(16)	133(4)		

As shown in Table 2, the bond length of As–C(19) (ylidic carbon) is 1.855 Å which corresponds to the bond order of 1.62 derived by the linear interpolation procedure in which the bond lengths of As–C and As=C were taken as 1.982 and 1.777 Å respectively, as given by Pauling [5]. However, in the benzoylmethylenetriphenylarsorane the bond length of As–C(19) is 1.87 Å [5], corresponding to a bond order of 1.55. It could be concluded that “Ylene” makes a greater contribution to the two structures of trifluoroacetylmethylenetriphenylarsorane than that of benzoylmethylenetriphenylarsorane. This accounts for the lower reactivity of the title compound.

Experimental

Preparation of trifluoroacetylmethylenetriphenylarsorane (1)

A solution of methylenetriphenylarsorane generated from methyltriphenylarsonium iodide (4.5 g, 10 mmol) and phenyllithium (10 mmol) in absolute ether (50 ml) was stirred at -70°C under nitrogen while an ether solution of ethyl trifluoroacetate (1.7 g, 12 mmol) was slowly added. After stirring at -70°C for 1 h, the mixture was gradually brought to 25°C , stirred for an additional 2 h, and then treated with 2% hydrobromic acid (20 ml). The precipitate that formed, was filtered, dissolved in water and treated with sodium carbonate solution. The precipitate was recrystallized from benzene/petroleum ether ($30\text{--}60^{\circ}\text{C}$) to give pure trifluoroacetylmethylenetriphenylarsorane; yield: 2.6 g (62%); m.p. $213\text{--}214^{\circ}\text{C}$.

Analysis. Found: C, 60.62; H, 3.80; F, 13.73. $\text{C}_{21}\text{H}_{16}\text{AsF}_3\text{O}$ calcd.: C, 60.59; H, 3.87; F, 13.69%. Selected IR data (KCl): $1590(\text{s}), 1570(\text{s})\text{ cm}^{-1}$. ^1H NMR (CDCl_3/TMS): 4.49(s,1H); 7.40–7.80(m,15H) ppm. ^{19}F NMR (CDCl_3/TFA): $-3.7(\text{s})\text{ ppm}$. MS m/e : 416 (M^+), 347 ($M^+ - \text{CF}_3$).

Reaction of trifluoroacetylmethylenetriphenylarsorane (1) with benzaldehyde

A solution of trifluoroacetylmethylenetriphenylarsorane (0.1 g, 0.24 mmol) and benzaldehyde (40 mg, 0.47 mmol) in absolute benzene (1 ml) was heated at 60 °C for 2 h under nitrogen (the same conditions as the reaction of benzoylmethylenetriphenylarsorane with benzaldehyde [4]). After chromatography of the reaction mixture on silica gel only the starting material was recovered.

Reaction of trifluoroacetylmethylenetriphenylarsorane (1) with trifluoroacetic anhydride

Trifluoroacetylmethylenetriphenylarsorane (**1**; 2.0 g, 4.8 mmol) and absolute toluene (30 ml) were placed in a flask with a dry ice/ethanol-cooled condenser. The mixture was stirred at room temperature while a toluene solution (5 ml) of trifluoroacetic anhydride (0.6 g, 2.86 mmol) was slowly added. After addition, the reaction mixture was stirred at room temperature for 2 h. Then the solvent was evaporated and the residue was eluted from the column on silica gel with 5/1 petroleum ether (30–60 °C)/ethyl acetate to give a solid which recrystallized from methanol to afford pure bis(trifluoroacetyl)methylenetriphenylarsorane (**2**); yield: 1.0 g (79%); m.p. 143–144 °C.

TABLE 3

FINAL ATOMIC COORDINATES ($\times 10^4$) AND THERMAL PARAMETERS

Atom	x	y	z	B_{eq}
As	2441(1)	1036(1)	547(0)	3.6(0)
C(1)	3831(6)	1523(7)	1148(4)	4.1(3)
C(2)	4786(7)	626(9)	1161(5)	5.9(4)
C(3)	5779(7)	998(12)	1600(6)	7.9(6)
C(4)	5789(8)	2177(11)	2007(5)	7.2(5)
C(5)	4813(9)	3044(10)	1986(5)	7.4(5)
C(6)	3812(7)	2740(8)	1569(5)	5.6(4)
C(7)	2542(6)	2033(7)	-390(4)	4.3(3)
C(8)	3495(8)	2916(10)	-527(5)	6.5(5)
C(9)	3474(10)	3677(12)	-1201(6)	8.7(6)
C(10)	2584(10)	3491(10)	-1737(5)	7.9(6)
C(11)	1691(10)	2608(11)	-1592(5)	8.5(6)
C(12)	1643(9)	1841(10)	-927(5)	6.9(5)
C(13)	1038(6)	1726(8)	1063(4)	4.5(3)
C(14)	644(8)	3067(9)	890(6)	6.7(5)
C(15)	-337(9)	3580(11)	1291(7)	8.6(6)
C(16)	-929(7)	2788(11)	1822(6)	7.8(6)
C(17)	-566(7)	1507(11)	1946(5)	7.1(5)
C(18)	426(7)	937(9)	1580(4)	5.7(4)
C(19)	2390(7)	-841(7)	317(4)	5.1(4)
C(20)	2454(7)	-1701(7)	977(4)	4.9(4)
C(21)	2470(9)	-3257(9)	789(6)	7.8(6)
O	2496(5)	-1368(6)	1645(3)	5.9(3)
F(1)	3481(12)	-3783(11)	1072(7)	12.3(8)
F(2)	1535(13)	-3829(12)	1114(8)	14.3(9)
F(3)	2439(11)	-3606(8)	74(5)	9.4(6)
F'(1)	1453(17)	-3693(15)	459(11)	12.5(12)
F'(2)	3371(22)	-3594(20)	279(20)	21.2(22)
F'(3)	2485(18)	-3990(13)	1426(9)	10.7(10)
H(16)	2550(70)	-1040(80)	-330(40)	4.9(20)

Analysis. Found: C, 53.57; H, 2.92; F, 22.86. $C_{23}H_{15}AsF_6O_2$ calcd.: C, 53.93; H, 2.95; F, 22.25%. Selected IR data (KCl): 1660(s), 1580(s) cm^{-1} . 1H NMR ($CDCl_3/TMS$): 7.36–7.80(m) ppm. ^{19}F NMR ($CDCl_3/TFA$): –5.6(s) ppm. MS m/e : 512 (M^+), 443 ($M^+ - CF_3$).

X-ray data collection

The crystals of trifluoroacetylmethylenetriphenylarsorane were grown from 9/1 methanol/water.

The oscillation and Weissenberg photographs showed that the crystals belong to the monoclinic system with space group $P2_1/c$. The unit cell parameters are: a 11.108(3), b 9.635(2), c 17.564(4) Å, β 89.82(2)°. V_c 1879.8(7) Å³, Z = 4, D_c 1.47 $g\ cm^{-3}$.

The X-ray diffraction intensity data were collected on a RASA-IIS four-circle diffractometer with graphite-monochromatized $Mo-K_\alpha$ radiation (λ 0.70926 Å) and 3337 independent reflections in the range of $3^\circ \leq 2\theta \leq 50^\circ$ were measured. Of these, 2583 reflections with $|F_0| > 3\sigma(|F_0|)$ were considered observed and used for structure resolution and refinement.

Structure resolution and refinement

The structure was resolved by heavy-atom Patterson and Fourier synthesis techniques. After the arsenic atom had been located, the position of all non-hydrogen atoms were revealed by subsequent Fourier synthesis. The crystal structure was refined by the block-diagonal matrix least-squares techniques with isotropic thermal parameters. Further refinements with anisotropic thermal parameters were carried out to a final R index of 0.059. The final atomic coordinates and thermal parameters are listed in Table 3.

Acknowledgement

Thanks are due to the Science Fund of Academia Sinica for financial support.

References

- 1 Y.-Z. Huang and Y.-C. Shen, *Adv. Organomet. Chem.*, 20 (1982) 115.
- 2 D.J. Burton and P.D. Vander Valk, *J. Fluorine Chem.*, 18 (1982) 413.
- 3 W.-Y. Ting, H.-S. Cheng, W.-Y. Shen and Y.-T. Huang, *Bull. Nat. Sci. Univ., Chem. Chem. Eng. Sect.*, (1965) 540.
- 4 M.-C. Shao, X.-L. Jin, Y.-Q. Tang, Q.-C. Huang and Y.-Z. Huang, *Tetrahedron Lett.*, 23 (1982) 5343.
- 5 L. Pauling, *The Nature of the Chemical Bond*, Cornell University, Ithaca, 1960, p. 224.
- 6 Y.-C. Shen and J.-H. Zheng, *J. Fluorine Chem.*, in press.