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SOME REACTIONS OF ARSONIUM YLIDES INVOLVING TRANSYLIDATION

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Summary

Methylenetriphenylarsenane, a nonstabilized arsonium ylide, has been shown to undergo transylidation on treatment with acyl halides to give carbonyl stabilized acylmethylenetriphenylarsenanes.

Introduction

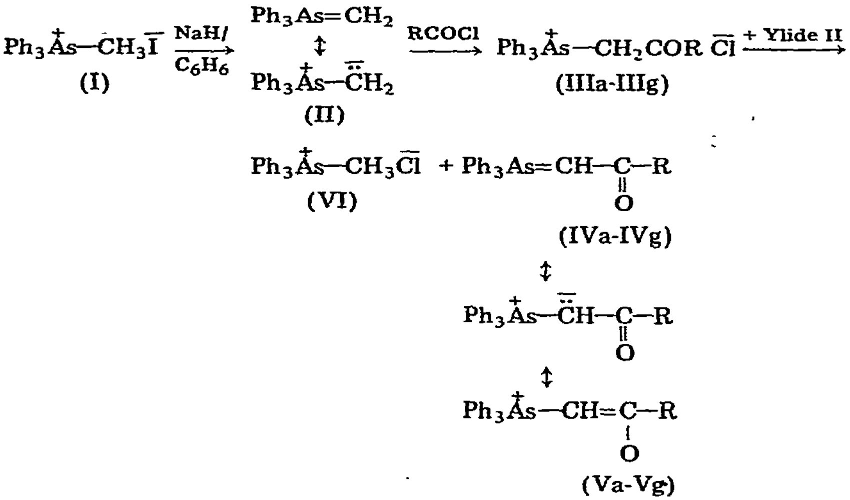
The transylidation of phosphonium ylides is of considerable importance in preparative organic chemistry [1], but the transylidation reactions of arsonium ylides have not previously been reported.

Following our studies of the reactions of arsonium ylides [2-4], we have now investigated some transylidation reactions of methylenetriphenylarsenane (II), a non-stabilized arsonium ylide.

Results and discussion

Heating a mixture of triphenylarsine and methyl iodide gave methyltriphenylarsonium iodide (I) in good yield. Treatment of I with sodium hydride in benzene at room temperature produced an intense yellow colour due to formation of the ylide II. Two moles of the ylide II on reaction with acyl chlorides (1 mole) underwent transylidation to give carbonyl-stabilized acylmethylenetriphenylarsenanes (IVa-IVg) and arsonium salt (VI), as illustrated in Scheme 1. The transylidation is a two step process. In the first step the ylide II undergoes *C*-acylation to form acylated arsonium salts (IIIa-IIIg). Because of the influence of the carbonyl group these salts are sufficiently acidic to react with a second mole of strongly basic ylide II to undergo transylidation, in the second step, affording acylated arsonium ylides (IVa-IVg) and the conjugate acid, methyltriphenylarsonium chloride (VI). A similar pattern of acylation and transylidation has been reported for analogous phosphonium [5] and sulfonium ylides [6].

SCHEME 1



(IV, Va: R = CH_3; b: R = C_6H_5; c: R = p-$OCH_3C_6H_4$; d: R = p-$CH_3C_6H_4$; e: R = p-BrC_6H_4; f: R = p-$NO_2C_6H_4$; g: R = 2,5-$(NO_2)_2C_6H_3$)

All the acylmethylenetriphenylarsenanes (IVa-IVg) prepared (Table 1) showed considerable stability when exposed to the atmosphere at room temperature. The structures of these ylides were confirmed by IR spectra and by the melting points in the case of known ylides. IR spectra (KBr) (Table 1) of the ylides (IVa-IVg) showed a strong carbonyl absorption in the range 1490-1530 cm^{-1}, indicating a significant contribution of the enolate structure (Va-Vg), which accounts for the stability of these ylides.

TABLE 1

STRUCTURE AND PHYSICAL PROPERTIES OF ACYLMETHYLENETRIPHENYLARSENANES $Ph_3As{=}CHCOR$ (IVa-IVg)

Ylide	R	Recryst. solvent	Yield (%)	M.p. (°C)	IR spectra (KBr) $\nu(C{=}O)$ (cm^{-1})
IVa	CH_3	$CHCl_3$/hexane (1/4)	65	160-161[a]	1500
IVb	C_6H_5	C_6H_6-hexane (1/4)	70	165-167[b]	1515
IVc	p-$OCH_3C_6H_4$	$CHCl_3$-hexane (1/4)	60	142-143[c]	1500
IVd	p-$CH_3C_6H_4$	$CHCl_3$/EtOAc (1/4)	75	150[d]	1490
IVe	p-BrC_6H_4	$CHCl_3$/hexane (1/4)	70	155-157[e]	1500
IVf	p-$NO_2C_6H_4$	$CHCl_3$/petroleum ether (40-60°C)	50	100-101[f]	1525
IVg	2,5-$(NO_2)_2$-C_6H_3	$CHCl_3$/hexane (1/4)	40	136-137[g]	1550

[a] Lit. [7] 165-166°C. [b] Lit. [8] 167-169°C. [c] Lit. [8] 145-146°C. [d] Lit. [8] 150-151°C. [e] Lit. [8] 155-156°C. [f] Lit. [8] 110-112°C. [g] New ylide.

Experimental

Melting points were determined on a Gallenkamp apparatus and are uncorrected. IR spectra (KBr) were recorded on a Perkin–Elmer Infracord instrument. The purity of the products was checked by TLC. Unless otherwise stated all the reactions were carried out under nitrogen.

Preparation of methyltriphenylarsonium iodide (I)

A mixture of triphenylarsine (12.2 g, 0.04 mole) and an excess of methyl iodide (50 g) was boiled under reflux for one week under nitrogen. The mixture was then kept at room temperature for three days and ether was added to precipitate 10.6 g (60%) of methyltriphenylarsonium iodide (I). The salt I was twice recrystallized from chloroform/ether (1/4) to give brown-yellow crystals, m.p. 170-172°C (Lit. [9] 174-175°C).

Preparation of acylmethylenetriphenylarsenanes (IVa-IVg) by transylidation reactions

The acyl halide (0.01 mole) was added to a stirred suspension of methylenetriphenylarsenane (II), prepared from 8.8 g (0.02 mole) of I and 0.48 g (0.02 mole) of sodium hydride in 120 ml of anhydrous benzene. The mixture was kept at room temperature under nitrogen for 3 days, then filtered to remove residual methyltriphenylarsonium halide (IV) and sodium hydride. The filtrate evaporated under reduced pressure to leave an oil, which was crystallized from the appropriate solvent (Table 1) to give the acylmethylenetriphenylarsenane.

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