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STUDIES ON YLIDES
EXCLUSIVE FORMATION OF OLEFINS FROM CARBONYL COMPOUNDS ON TREATMENT WITH *para*-BROMO- AND *para*-IODO-BENZYLIDENETRIPHENYLARSENANES

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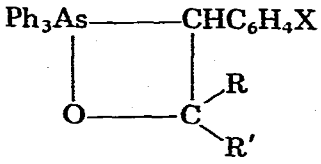
Summary

Two new semistabilized arsonium ylides, *para*-bromo- and *para*-iodo-benzylidenetriphenylarsenane, have been formed, and treated with a range of carbonyl compounds to yield exclusively *trans*-olefins. In no case was an epoxide obtained.

Introduction

Interest in the dual behaviour of arsonium ylides towards carbonyl compounds was initiated by the observations of Trippett and Walker [1] that the cyclic I, formed from the reaction of *para* substituted benzylidenetriphenylarsenanes with carbonyl compounds, leads to olefins when the benzylidene *para* substituent is highly electron-withdrawing but otherwise to epoxides. This prompted us to investigate the reaction more fully. We also continue our studies [2,3] of the factors which control the direction of breakdown of I, by studying the reactions of two new, semistabilized arsonium ylides, *p*-bromo- (IIa) and *p*-iodo-benzylidenetriphenylarsenane (IIb), with a series of carbonyl compounds, in order to determine the influence of *p*-halo substituents. (II, X = Cl). We were expecting the formation of epoxides, as reported [1] for *para*-chlorobenzylidenetriphenylarsenane but observed different products.



(I)

Results and discussion

The reaction of triphenylarsine with *p*-bromo- and *p*-iodo-benzyl bromide in refluxing benzene gave *p*-bromobenzyltriphenylarsonium bromide (IIIa) and *p*-iodobenzyltriphenylarsonium bromide (IIIb) in good yields. Treatment of these salts (IIIa and IIIb) with suitable base generated an intense yellow and pale yellow colour due to formation of ylides IIa and IIb respectively (Scheme 1) Sodamide in benzene was a suitable base for the dehydrohalogenation of IIIa but failed in the case of IIIb. The deprotonation of the salt IIIb was effected by sodium hydride in tetrahydrofuran (THF).

SCHEME 1

$$\mathrm{Ph_3As^+{-}CH_2C_6H_4X\text{-}}p\ \mathrm{Br^-} \xrightarrow{\text{base}} \begin{array}{c} \mathrm{Ph_3As{=}CHC_6H_4X\text{-}}p \\ \updownarrow \\ \mathrm{Ph_3As^+{-}\bar{C}HC_6H_4X\text{-}}p \end{array}$$

(IIIa) $X = Br$;
(IIIb) $X = I$

(IIa) $X = Br$;
(IIb) $X = I$

$$\downarrow \mathrm{ArCHO}$$

$$\mathrm{Ph_3AsO + ArCH{=}CHC_6H_4X\text{-}}p$$

(IVa-VI)

(IVa) $Ar = C_6H_5$; $X = Br$;
(IVb) $Ar = 4\text{-}ClC_6H_4$; $X = Br$;
(Va) $Ar = C_6H_5$; $X = I$;
(Vb) $Ar = 3\text{-}NO_2C_6H_4$; $X = I$;
(Vc) $Ar = 4\text{-}ClC_6H_4$; $X = I$;
(Vd) $Ar = 2,4\text{-}(Cl)_2C_6H_3$; $X = I$;
(Ve) $Ar = 4\text{-}CH_3C_6H_4$; $X = I$;
(Vf) $Ar = 4\text{-}CH_3OC_6H_4$; $X = I$;
(Vg) $Ar = 3\text{-}CH_3OC_6H_4$; $X = I$;
(Vh) $Ar = 3,4\text{-}(CH_3O)_2C_6H_3$; $X = I$;
(Vi) $Ar = 3,4\text{-}(OCH_2O)C_6H_3$; $X = I$;
(VI) $Ar = 4\text{-}IC_6H_4CH{=}CHC_6H_4$; $X = I$

The reaction of IIa with benzaldehyde and *p*-chlorobenzaldehyde, at room temperature gave good yields of *trans-p*-bromostilbenes (IVa and IVb) (Scheme 1). Similarly the ylide IIb reacted smoothly with a range of mono- and di-substituted benzaldehydes in THF at room temperature to give 55-75% yields of *trans-p*-iodostilbenes Va-Vi. The reaction of IIb with terephthaldehyde at room temperature gave *trans-trans*-1,4-bis(*p*-iodostyryl)benzene (VI).

In reactions of both the ylides IIa and IIb with carbonyl compounds the formation of olefin products rather than epoxides is favoured; this contrasts with the results observed for *p*-chlorobenzylidenetriphenylarsenane [1] which gives epoxides. The exclusive formation of olefins from ylides IIa and IIb cannot

TABLE 1

trans-DIARYL SUBSTITUTED OLEFINS IVa-VI $ArCH=CHC_6H_4X$-*p*

Compound	Ar	X	Yield (%)	Recrystallization solvent	M.p. (°C)	Emperical formula	Analysis found (calcd.) (%)	
							C	H
IVa	C_6H_5	Br	50	$CHCl_3$/ Hexane	132-133[a]	$C_{14}H_{11}Br$	64.84 (64.86)	4.22 (4.24)
IVb	4-ClC_6H_4	Br	55	EtOH	227-228	$C_{14}H_{10}BrCl$	57.23 (57.24)	3.47 (3.47)
Va	C_6H_5	I	55	EtOH (80%)	148-150[b]	$C_{14}H_{11}I$	54.88 (54.90)	3.55 (3.59)
Vb	3-$NO_2C_6H_4$	I	75	AcOH	120-122	$C_{14}H_{10}INO_2$	47.85 (47.46)	2.80 (2.84)
Vc	4-ClC_6H_4	I	65	EtOH	199-200	$C_{14}H_{10}ClI$	49.32 (49.33)	2.94 (2.93)
Vd	2,4-$(Cl)_2C_6H_3$	I	70	EtOH (90%)	119-120	$C_{14}H_9Cl_2I$	44.78 (44.80)	2.41 (2.40)
Ve	4-$CH_3C_6H_4$	I	62	$CHCl_3$/ Hexane	210-212	$C_{15}H_{13}I$	56.22 (56.25)	4.04 (4.06)
Vf	4-$CH_3OC_6H_4$	I	64	C_6H_6/ Hexane	214-215	$C_{15}H_{13}IO$	53.55 (53.57)	3.86 (3.86)
Vg	3-$CH_3OC_6H_4$	I	60	C_6H_6/ Hexane	88-89	$C_{15}H_{13}IO$	53.55 (53.57)	3.86 (3.86)
Vh	3,4-$(CH_3O)_2C_6H_3$	I	60	EtOH	134-135	$C_{16}H_{15}IO_2$	52.43 (52.45)	4.06 (4.09)
Vi	3,4-$(OCH_2O)C_6H_3$	I	68	$CHCl_3$/ Hexane	155	$C_{15}H_{11}IO_2$	51.40 (51.43)	3.12 (3.14)
VI	4-$IC_6H_4CH=CHC_6H_4$	I	55	Toluene	255-257	$C_{22}H_{16}I_2$	49.42 (49.43)	2.98 (2.99)

[a] Lit [6] 135°C. [b] Lit. [7] 152°C.

be explained at present, but it appears that along with the influence of substituents on the ylide carbanion there may be effects of solvent and base on the course of decomposition of I.

The reactivity of IIb towards carbonyl compounds appears to be greater than that of IIa, and it gives olefins Va-Vi in better yields.

All the diaryl substituted ethylenes IVa-VI (Table 1), most of them new, were obtained almost exclusively as the *trans* isomers. The spectral data were also consistent with that expected for *trans* stereoisomers [4].

The IR spectra (Table 2) of the olefins showed absorptions at 1625-1585 cm^{-1} [ν(C=C)] and 981-925 cm^{-1}; the latter absorptions are associated with out-of-plane deformations of hydrogen in the *trans* olefinic system [5]. The NMR spectra (Table 2) exhibited olefinic protons in the range of δ 6.80-7.47 and aromatic multiplet ranging from δ 6.95-8.38 ppm.

Experimental

Melting points were determined on a Gallenkamp apparatus, and are uncorrected. IR spectra were recorded on a Perkin—Elmer infrared instrument.

TABLE 2

IR AND NMR SPECTRA OF *trans*-DIARYL SUBSTITUTED OLEFINS

Compound	IR data (KBr), (cm^{-1})		NMR data (CDCl$_3$)[a]		
	ν(C=C)	Out-of-plane deformations of H in a *trans*-olefinic system	δ (ppm)	No. protons	Assignment
IVa	1600	925	7.15-7.68, m	9H	Aromatic
			7.08, q	2H	Olefinic
IVb	1590	925	7.22-7.70, m	8H	Aromatic
			7.08, s	2H	Olefinic
Va	1585	975	7.10-7.80, m	9H	Aromatic
			6.82, q	2H	Olefinic
Vb	1600	978	7.82-8.38, m	8H	Aromatic
			7.47, q	2H	Olefinic
Vc	1590	970	7.30-7.86, m	8H	Aromatic
			7.10, q	2H	Olefinic
Vd	1585	968	7.38-7.94, m	7H	Aromatic
			7.32, q	2H	Olefinic
Ve	1625	978			
Vf	1590	972	7.02-7.80, m	8H	Aromatic
			6.80, q	2H	Olefinic
			3.80, s	3H	OCH$_3$
Vg	1600	970	6.95-7.83, m	8H	Aromatic
			6.80, q	2H	Olefinic
			3.80, s	3H	OCH$_3$
Vh			7.30-8.40, m	7H	Aromatic
			7.12, q	2H	Olefinic
			4.03, s	6H	OCH$_3$
Vi	1620	970	7.29-7.84, m	7H	Aromatic
			6.80, q	2H	Olefinic
			6.08, s	2H	—OCH$_2$O—
VI	1605	981			

[a] m = multiplet, s = singlet, q = quartet.

NMR spectra were recorded (CDCl$_3$ solutions) on a Varian A-60 spectrometer using TMS as an internal standard. All the products were purified by column chromatography using alumina. Purity was checked by TLC.

Preparation of p-bromobenzyltriphenylarsonium bromide (IIIa)

A solution of 12.24 g (0.04 mol) of triphenylarsine and 10 g (0.04 mol) of *p*-bromobenzyl bromide in 60 ml of anhydrous benzene was heated under reflux on a steam bath for 6 h. The resulting solid was collected, washed with benzene, and crystallized three times from a mixture of chloroform/benzene (1/4) to give brown crystals of *p*-bromobenzyltriphenylarsonium bromide (IIIa), m.p. 182-184°C, yield 15.6 g (70%). (Found: C, 53.92; H, 3.75. $C_{25}H_{21}AsBr_2$ calcd.: C, 53.95; H, 3.77%.)

Preparation of p-iodobenzyltriphenylarsonium bromide (IIIb)

A mixture of triphenylarsine (12.24 g, 0.04 mol) and *p*-iodobenzyl bromide (11.08 g, 0.04 mol) in 60 ml of benzene was boiled under reflux for 2 days. The excess of solvent was removed on a steam bath and petroleum ether (60-80°)

was added to precipitate 18.8 g (80%) of *p*-iodobenzyltriphenylarsonium bromide (IIIb). This was recrystallized twice from chloroform/ethyl acetate (1/4) to give pale yellow microcrystals, m.p. 158°C. NMR spectrum ($CDCl_3$): δ 6.89-7.89 (19H, aromatic, m) and δ 5.54 (2H, methylene, s). (Found: C, 49.73; H, 3.44. $C_{25}H_{21}AsBrI$ calcd.: C, 49.75; H, 3.46%.)

Reaction of ylide IIa with aromatic aldehydes

To a suspension of ylide IIa, prepared from 3.33 g (0.006 mol) of salt IIIa and 0.23 g (0.006 mol) of sodamide in 50 ml of anhydrous benzene, 0.006 mol of aromatic aldehyde was added under nitrogen. The mixture was stirred at room temperature for 20 h. The residue containing triphenylarsine oxide and unreacted sodamide was removed by filtration, and the filtrate was concentrated on a steam bath under reduced pressure. The resulting oily mass was extracted with benzene and chromatographed to give diaryl substituted olefins IVa and IVb (Table 1), which were further purified by crystallization.

Reaction of ylide IIb with aromatic aldehydes

To a pale yellow suspension of ylide IIb, generated from 2.41 g (0.004 mol) of salt IIIb and 0.004 mol of 50% sodium hydride in 50 ml of tetrahydrofuran, 0.004 mol of the aromatic aldehyde was added under nitrogen. The mixture was stirred at room temperature for 48 h. The solvent was then evaporated off, the residue was taken up in benzene, and the filtered solution and the filtrate chromatographed. Elution with benzene/petroleum ether (1/1), in general, afforded the *trans*-diaryl substituted olefin Va-Vi (Table 1).

Reaction of ylide IIb with terephthaldehyde

To a stirred solution of ylide IIb prepared from 4.82 g (0.008 mol) of IIIb and 1.0 g (50% slurry) of sodium hydride in 100 ml of tetrahydrofuran, was added 0.53 g (0.004 mol) of terephthaldehyde. The mixture was heated under reflux for 24 h under nitrogen and the procedure described above was followed. Elution with benzene/petroleum ether (2/1) gave *trans-trans*-1,4-bis(*p*-iodostyryl)benzene (VI) (Table 1). It was further purified by crystallization from toluene to give green-yellow needles.

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