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STUDIES ON YLIDES: CARBONYL OLEFINATION WITH (*p*-NITROBENZYLIDENE)TRIPHENYLARSENANE*

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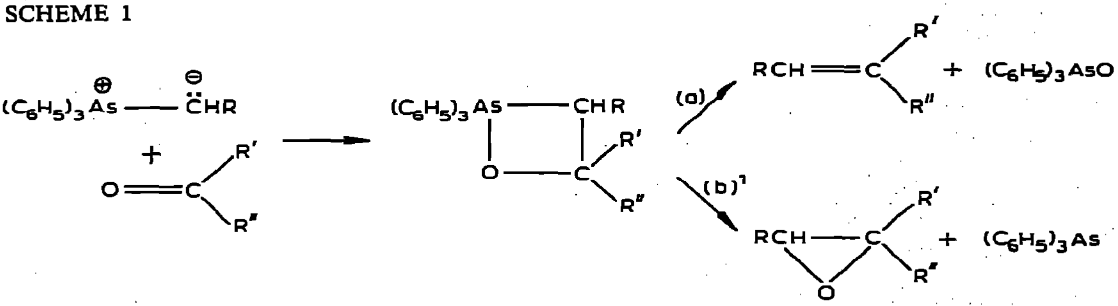
SUMMARY

(*p*-Nitrobenzylidene)triphenylarsenane, a semistabilized arsonium ylide has been prepared and reacted with carbonyl compounds to yield olefins as opposed to epoxidation products. Treatment of the ylide with a ranged acyl halides gave new disubstituted arsonium ylides. IR and NMR spectral data for the resulting products are reported.

INTRODUCTION

Arsonium ylides, have been reported to yield either olefins or epoxides in reactions with carbonyl compounds (Scheme 1).

SCHEME 1



Stabilized ylides [R = –C(O)R]^{2,3} follow path (a) yielding olefins, whereas, non-stabilized ylides (R = H, CH_3)^{4,5} follow path (b), giving epoxides almost exclusively or rearrangement products. However, the behaviour of the semistabilized arsonium ylides (*e.g.* R = C_6H_4X-*p*) towards carbonyl compounds is somewhat ambivalent; thus benzylidenetriphenylarsenane^6 and (*p*-nitrobenzylidene)triphenylarsenane^2 follow both paths (a) and (b) yielding approximately equimolar amounts of

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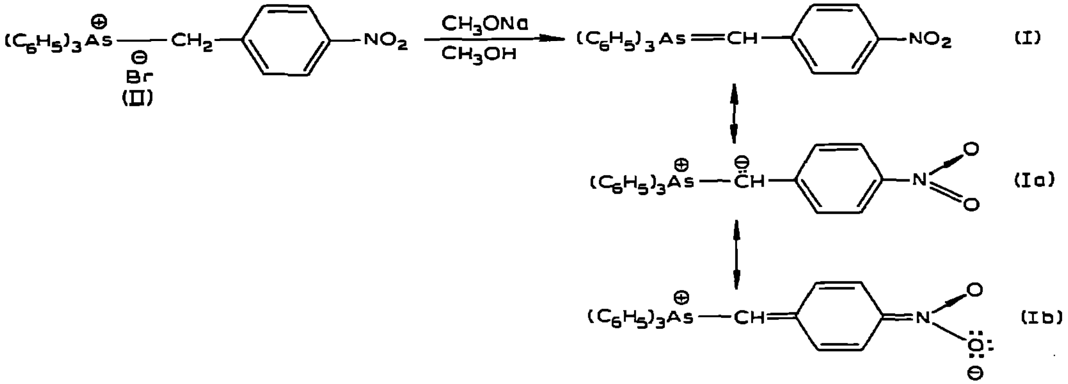
olefin and epoxide. Recently Trippett *et al.*[7] showed that semistabilized *p*-substituted benzylidenetriphenylarsonium ylides could react either by path (a) or by path (b), giving only olefins or epoxides.

We have studied the reactions of (*p*-nitrobenzylidene)triphenylarsenane (I), a semistabilized arsonium ylide, with a variety of carbonyl substrates in order to ascertain the exact path of carbonyl olefination and its stereochemical nature.

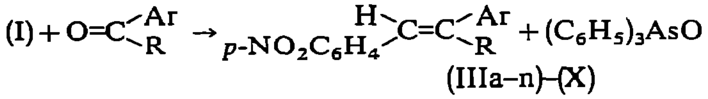
RESULTS AND DISCUSSION

Heating a mixture of triphenylarsine and *p*-nitrobenzyl bromide at the reflux temperature gave (*p*-nitrobenzyl)triphenylarsonium bromide (II) in 80% yield.

SCHEME 2



SCHEME 3



$$\mathrm{(I)} + \mathrm{O{=}C}{<}^{\mathrm{Ar}}_{\mathrm{R}} \rightarrow p\text{-}\mathrm{NO_2C_6H_4}{>}^{\mathrm{H}}\mathrm{C{=}C}{<}^{\mathrm{Ar}}_{\mathrm{R}} + (\mathrm{C_6H_5})_3\mathrm{AsO}$$

(IIIa–n)–(X)

(III) a: Ar$=C_6H_5$, R$=$H
b: Ar$=4\text{-}NO_2C_6H_4$, R$=$H
c: Ar$=3\text{-}NO_2C_6H_4$, R$=$H
d: Ar$=2\text{-}NO_2C_6H_4$, R$=$H

e: Ar$=4\text{-}ClC_6H_4$, R$=$H
f: Ar$=2\text{-}ClC_6H_4$, R$=$H
g: Ar$=4\text{-}CH_3C_6H_4$, R$=$H
h: Ar$=3\text{-}CH_3C_6H_4$, R$=$H
i: Ar$=4\text{-}CH_3OC_6H_4$, R$=$H
j: Ar$=3\text{-}CH_3OC_6H_4$, R$=$H
k: Ar$=2\text{-}CH_3OC_6H_4$, R$=$H
l: Ar$=3,4\text{-}(CH_3O)_2C_6H_3$, R$=$H
m: Ar$=3,4\text{-}(CH_3O)_2\text{-}6\text{-}BrC_6H_2$, R$=$H
n: Ar$=3,4\text{-}(OCH_2O)C_6H_3$, R$=$H

(IV), Ar$=$2-furyl, R$=$H
(V), Ar$=$2-pyridyl, R$=$H
(VI), Ar$= -CH{=}CHC_6H_5$, R$=$H
(VII), Ar$= -C_6H_4CH{=}CHC_6H_4NO_2\text{-}4$; R$=$H

(VIII), Ar$=$R$=$9-fluorenyl
(IX), Ar$=C_6H_5$, R$=C_6H_5$
(X), Ar$=1\text{-}C_{10}H_7$, R$=CH_3$

Treatment of (II) with sodamide in benzene or sodium methoxide in methanol, generated an intense red colour due to ylide (I) (Scheme 2).

The reaction of (I) with various mono- and di-substituted benzaldehydes (Scheme 3), carried out at room temperature, gave 60–90% yields of *trans-p*-nitrostilbenes (IIIa–n). Similarly the reaction of (I) with 2-furfural and picolinealdehyde gave *trans*-2-(*p*-nitrostyryl)furan (IV) and -pyridine (V), respectively. Ylide (I) also reacted smoothly with cinnamaldehyde and terephthaldehyde to give *trans,trans*-1-(*p*-nitrophenyl)-4-phenyl-1,3-butadiene (VI) and 1,4-bis(*p*-nitrostyryl)benzene (VII).

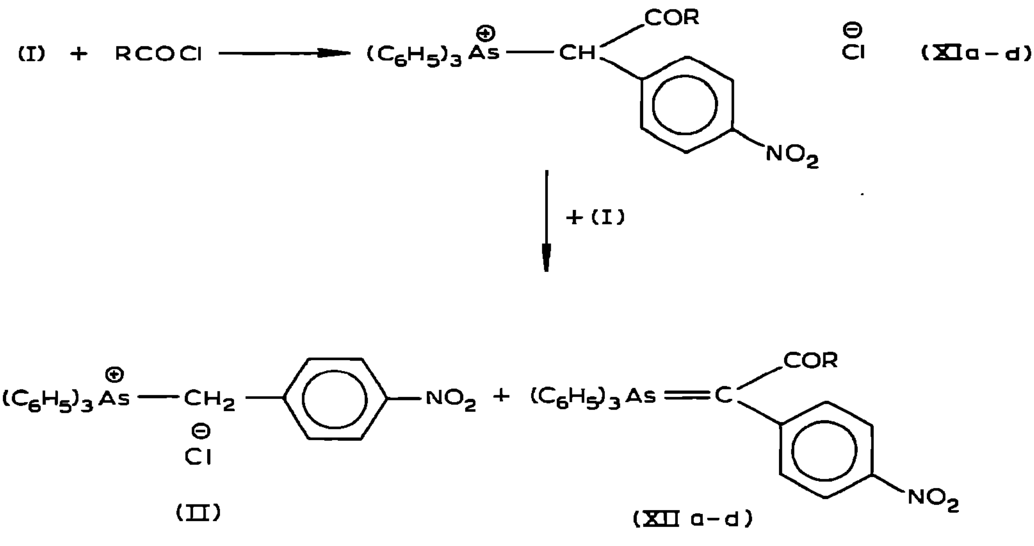
The reactions of (I) with ketones were interesting. The ylide failed to react with acetophenone but reacted energetically with 9-fluorenone, benzophenone and 1-acetonaphthone in benzene solution at the reflux temperature to give α-substituted stilbenes, (VIII)–(X).

Towards carbonyl compounds, the ylide (I) favours 100% olefination (path a) as opposed to epoxidation, probably because of the strongly electron-withdrawing effect of *p*-nitro group. The exclusive formation of olefins and non-availability of epoxides are in accord with behaviour of the analogous phosphonium ylide[8] and with the observations of Trippett *et al.*[7].

The di- and tri-substituted olefins (III)–(X) (Table 1) were obtained almost exclusively *trans*-isomers. Similar exclusive *trans*-olefination has also been reported for the analogous phosphonium ylide[9].

The IR spectra of the olefins showed absorptions at 1600–1585 cm^{-1} [ν(C=C)]

SCHEME 4



(XI), (XII) a : R = CH_3

b : R = C_6H_5

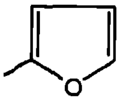
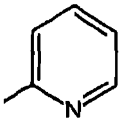
c : R = 4-$NO_2C_6H_4$

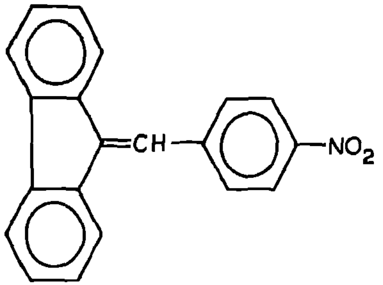
d : R = 2,5-$(NO_2)_2C_6H_3$

(*continued on p. 252*)

TABLE 1

Trans-DI- AND TRI-SUBSTITUTED OLEFINS (III)–(X)

Compound	*Ar*	*R*	*Yield* (%)	*Recryst. solvent*	*M.p.* (°C)	*Empirical formula*	*Analysis found (calcd.) (%)*	
							C	*H*
(IIIa)	C_6H_5	H	80	EtOH	155–57[a]	$C_{14}H_{11}NO_2$	74.65 (74.66)	4.88 (4.88)
(IIIb)	$4\text{-}NO_2C_6H_4$	H	94	AcOH	288–90[b]	$C_{14}H_{10}N_2O_4$	62.60 (62.66)	3.69 (3.70)
(IIIc)	$3\text{-}NO_2C_6H_4$	H	90	AcOH	218–21[c]	$C_{14}H_{10}N_2O_4$	62.63 (62.66)	3.71 (3.70)
(IIId)	$2\text{-}NO_2C_6H_4$	H	93	EtOH (80%)	145–48[d]	$C_{14}H_{10}N_2O_4$	62.64 (62.66)	3.70 (3.70)
(IIIe)	$4\text{-}ClC_6H_4$	H	85	AcOH	188–90[e]	$C_{14}H_{10}NO_2Cl$	64.72 (64.74)	3.43 (3.46)
(IIIf)	$2\text{-}ClC_6H_4$	H	82	EtOH/H_2O (1/1)	120–22[f]	$C_{14}H_{10}NO_2Cl$	64.73 (64.74)	3.44 (3.46)
(IIIg)	$4\text{-}CH_3C_6H_4$	H	75	AcOH	145–47[g]	$C_{15}H_{13}NO_2$	75.30 (75.31)	5.43 (5.42)
(IIIh)	$3\text{-}CH_3C_6H_4$	H	72	$CHCl_3$/EtOH (1/2)	108–10[h]	$C_{15}H_{13}NO_2$	75.28 (75.31)	5.42 (5.43)
(IIIi)	$4\text{-}CH_3OC_6H_4$	H	76	AcOH	132–34[i]	$C_{15}H_{13}NO_3$	70.54 (70.58)	5.08 (5.09)
(IIIj)	$3\text{-}CH_3OC_6H_4$	H	72	EtOH	86–87[j]	$C_{15}H_{13}NO_3$	70.57 (70.58)	5.00 (5.09)
(IIIk)	$2\text{-}CH_3OC_6H_4$	H	70	EtOH (80%)	120–22[k]	$C_{15}H_{13}NO_3$	70.56 (70.58)	5.05 (5.09)
(IIIl)	$3,4\text{-}(CH_3O)_2C_6H_3$	H	65	EtOH/H_2O(1/1)	133–34[l]	$C_{16}H_{15}NO_4$	67.35 (67.36)	5.25 (5.26)
(IIIm)	$3,4\text{-}(CH_3O)_2\text{-}6\text{-}BrC_6H_2$	H	75	AcOH	110–15[m]	$C_{16}H_{14}NO_4Br$	52.75 (52.77)	4.34 (4.34)
(IIIn)	$3,4\text{-}(OCH_2O)C_6H_3$	H	70	Benzene/petroleum ether (60–80) (1/1)	191–94[n]	$C_{15}H_{11}NO_4$	66.88 (66.89)	4.01 (4.09)
(IV)		H	65	EtOH	128–29[o]	$C_{12}H_9NO_3$	66.99 (66.99)	4.00 (4.09)
(V)		H	68	Benzene/Hexane (1/3)	130–31[p]	$C_{13}H_{10}N_2O_2$	68.88 (68.87)	4.43 (4.42)

(VI)	$-CH{=}CHC_6H_5$	H	60	Benzene/Cyclohexane (1/2)	180–81[q]	$C_{16}H_{13}NO_2$	71.74 (71.76)	4.30 (4.32)
(VII)	$-C_6H_4CH{=}CHC_6H_4NO_2$-4	H	65	Xylene	285–87[r]	$C_{22}H_{16}N_2O_4$	71.74 (71.76)	4.30 (4.32)
(VIII)			53	EtOH	163–65[s]	$C_{20}H_{13}NO_2$	80.27 (80.28)	4.34 (4.34)
(IX)	C_6H_5	C_6H_5	55	Benzene/petroleum ether (60–80)(1/2)	145–46[t]	$C_{20}H_{15}NO_2$	80.27 (80.28)	4.34 (4.34)
(X)	1-$C_{10}H_7$	CH_3	25	$CHCl_3$/Hexane (1/2)	118–20[u]	$C_{19}H_{15}NO_2$	78.85 (78.89)	5.20 (5.19)

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[a] Lit.[12] 157. [b] Lit.[13] 282. [c] Lit.[14] 220–222. [d] Lit.[15] 143. [e] Lit.[16] 186. [f] Lit.[15] 124–125. [g] Lit.[17] 150. [h] Lit.[18] 108–109. [i] Lit.[19] 133. [j] Lit.[17] 87. [k] Lit.[17] 122. [l] Lit.[20] 133 [m] Unreported. [n] Lit.[21] 194. [o] Lit.[22] 130–31. [p] Lit.[16] 133–133.5. [q] Lit.[23] 181–182. [r] Lit.[24] 286–290. [s] Lit.[25] 167–168. [t] Lit.[26] 148. [u] Unreported.

TABLE 2

CHEMICAL SHIFTS OF *trans*-DI- AND TRI-SUBSTITUTED OLEFINS

Compound	*Aromatic protons* δ *(ppm)*	*Olefinic protons* δ *(ppm)*	*Other groups* δ *(ppm)*
(IIIa)	7.62–8.23	7.18	
(IIIb)	7.67–8.25	7.30	
(IIId)	7.64–8.40	7.20	
(IIIe)	7.80–8.50	7.47	
(IIIf)	7.62–8.40	7.20	
(IIIg)	7.52–8.58	7.30	2.38 (CH_3)
(IIIh)	7.80–8.58	7.41	2.62 (CH_3)
(IIIj)	7.60–8.38	7.20	3.87 (OCH_3)
(IIIl)	7.30–8.40	7.12	4.03 (OCH_3)
(IIIm)	7.65–8.45	7.40	4.05 (OCH_3)
(IIIn)	7.35–7.95	7.26	6.10 (O_2CH_2)
(IV)	7.70–8.20	7.45	
(VI)	7.20–7.81	6.90	
(VII)	7.30–7.80	6.82	
(VIII)	7.25–7.91	6.64	
(X)	7.72–8.20	7.61	2.88 (CH_3)

and at 970–954 cm^{-1}; the latter are associated with out-of-plane deformations of hydrogen attached to the *trans*-olefinic system[10]. The NMR spectra (Table 2) exhibited olefinic protons in the range δ 7.20–7.47 and aromatic protons at δ 7.30–8.50. A characteristic absorption of α-methyl protons was also observed in α-methyl-substituted olefin (X) at δ 2.88.

Acylation of (I) was also investigated. Reaction of (I) with acetyl chloride, benzoyl chloride, *p*-nitrobenzoyl chloride and 2,5-dinitrobenzoyl chloride yielded four new, disubstituted, carbonyl-stabilized arsonium ylides (XIIa–d), presumably via initial *C*-acylation followed by proton abstraction from the corresponding arsonium salts (XIa–d) (Scheme 4).

EXPERIMENTAL

Melting points were determined on a GallenKamp apparatus and are uncorrected. IR spectra were recorded on a Perkin–Elmer infracord instrument. NMR spectra were recorded ($CDCl_3$ solutions) on a Varian A-60 spectrometer using TMS as a standard. All the products were separated and purified by column chromatography using alumina. Purity was checked by TLC.

Preparation of (p-nitrobenzyl)triphenylarsonium bromide (II)

A solution of triphenylarsine (12.2 g, 0.04 mole) and *p*-nitrobenzyl bromide, (9.1 g, 0.044 mole) in benzene (60 ml) was boiled under reflux for 4 h. Excess of solvent was evaporated on a steam bath and petroleum ether (60–80°) was added to precipitate 16.5 g (80%) of (*p*-nitrobenzyl)triphenylarsonium bromide (II). The salt (II) was twice recrystallized from chloroform/benzene (1/2) to give white microcrystals, m.p. 150–151° (Lit.[11] 151–152°). (Found: C, 57.45; H, 4.00. $C_{25}H_{21}AsBrNO_2$ calcd.: C, 57.47; H, 4.02%.)

Reaction of ylide (I) with aromatic aldehydes

To a suspension of ylide (I), prepared from 2.0 g (4 mmol) of salt (II) and sodium methoxide (4 mmol) in methanol (100 ml), was added, in an atmosphere of nitrogen, 4 mmol of aromatic aldehyde. The mixture was stirred at room temperature for 6 h. The resulting yellow solid was collected, washed with water, dried and purified by crystallizations from the appropriate solvent to yield the *trans*-disubstituted olefin (IIIa–n)–(VII) (Table 1).

Reaction of ylide (I) with ketones

To a suspension of (I), prepared from 2.0 g (4 mmol) of (II) and sodamide (0.19 g, 5 mmol) in anhydrous benzene (120 ml) under nitrogen was added 4 mmol of ketone, and the mixture was stirred at 60° for 10 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 the *trans*-tri-substituted olefin (VIII)–(X) (Table 1).

Acylation of ylide (I)

To a stirred solution of (II) (5.2 g, 10 mmol) in anhydrous benzene (100 ml) was added 0.39 g (10 mmol) of sodamide, followed by acyl chloride (5 mmol). After stirring at room temperature for 3 days, the reaction mixture was filtered to remove residual salt (II) and sodamide. The filtrate was concentrated by evaporation to give an oil, which was crystallized from a suitable solvent to give the disubstituted carbonyl-stabilized arsonium ylide. In this way were prepared: [(*p*-nitrophenyl)acetylmethylene]triphenylarsenane (XIIa) obtained as yellow crystals (n-hexane), yield 0.7 g (30%), m.p. 280–285°, IR spectrum (KBr) 1570 cm^{-1} [ν(C=O)] (Found: C, 67.18; H, 4.55. $C_{27}H_{22}AsNO_3$ calcd.: C, 67.20; H, 4.55%.); [(*p*-nitrophenyl)benzoylmethylene]triphenylarsenane (XIIb) as pale yellow needles (chloroform/n-hexane (1/4), yield 0.9 g (35%), m.p. 180–185°, IR spectrum (KBr) 1520 cm^{-1} [ν(C=O)] (Found: C, 70.43; H, 4.39. $C_{32}H_{24}AsNO_3$ calcd.: C, 70.47; H, 4.40%.); [(*p*-nitrophenyl)(4-nitrobenzoyl)methylene]triphenylarsenane (XIIc) as yellow microcrystals (n-hexane), yield 0.5 g (20%), IR spectrum (KBr) 1515 cm^{-1} [ν(C=O)] (Found: C, 65.00; H, 3.87. $C_{37}H_{23}AsN_2O_5$ calcd.: C, 65.09; H, 3.89%.); [(*p*-nitrophenyl)(2,5-dinitrobenzoyl)methylene]triphenylarsenane (XIId) as yellow prisms (benzene/n-hexane (1/4)), yield 0.5 g (18%), m.p. 268–270°, IR spectrum (KBr) 1512 cm^{-1} [ν(C=O)]. (Found: C, 60.46; H, 3.63. $C_{32}H_{22}AsN_3O_7$ calcd.: C, 60.47; H, 3.62%.)

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