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STUDIES ON YLIDES: GENERATION AND REACTIONS OF NEW 2-NAPHTHYLMETHYLENETRIPHENYLARSENANES

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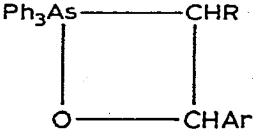
Summary

Two new semistabilized arsonium ylides have been generated and treated with carbonyl compounds. In reaction with carbonyl compounds, the carbanionic centres of both the ylides attack the carbonyl carbon to form similar cyclic intermediates. These intermediates, however, decompose to give different reaction products. The structures of the products are indicated by IR and NMR spectroscopy.

Introduction

Recently studies of the structural factors which influence the course of olefination or epoxidation of cyclic transitional intermediate I in reactions of semistabilized arsonium ylides with carbonyl compounds have been reported [1—4]. We now describe studies on the interesting behaviour of 2-naphthylmethylenetriphenylarsenanes, a new series of arsonium ylides, towards carbonyl compounds.



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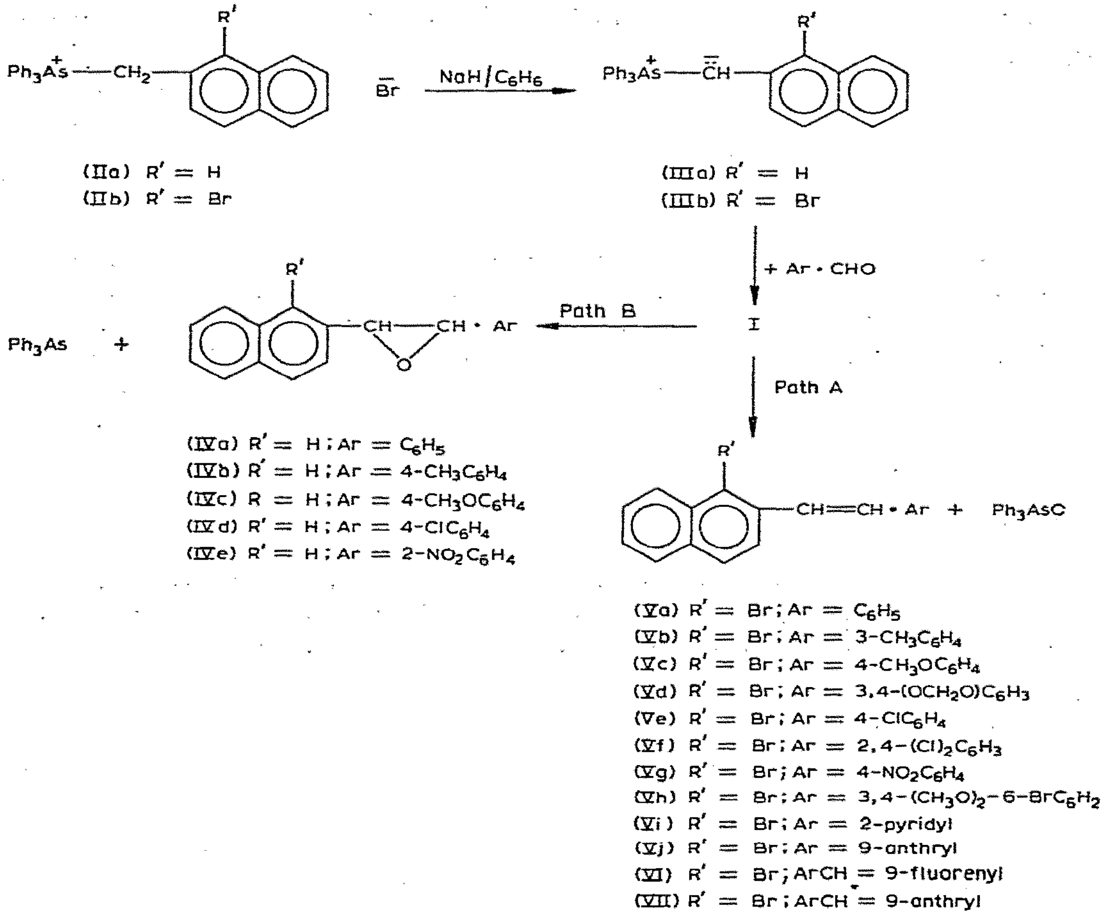
Results and discussion

Treatment of triphenylarsine with 2-bromomethylnapthalene and 1-bromo-2-bromomethylnaphthalene at elevated temperatures afforded 2-naphthylmethyltriphenylarsonium bromide (IIa) and 1-bromo-2-naphthylmethyltriphenylarsonium bromide (IIb) in good yields. Transient intense yellow colorations indicated the generation of 2-naphthylmethylenetriphenylarsenane (IIIa) and 1-bromo-2-naphthylmethylenetriphenylarsenane (IIIb), which results from proton abstraction from their respective salts (IIa and IIb) with sodium hydride in benzene (Scheme 1). The structural identity of the new arsonium ylides (IIIa, IIIb)

SCHEME 1



(IIa) $R' = H$
(IIb) $R' = Br$

(IIIa) $R' = H$
(IIIb) $R' = Br$

(IVa) $R' = H$; $Ar = C_6H_5$
(IVb) $R' = H$; $Ar = 4\text{-}CH_3C_6H_4$
(IVc) $R = H$; $Ar = 4\text{-}CH_3OC_6H_4$
(IVd) $R' = H$; $Ar = 4\text{-}ClC_6H_4$
(IVe) $R' = H$; $Ar = 2\text{-}NO_2C_6H_4$

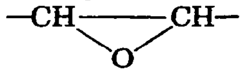
(Va) $R' = Br$; $Ar = C_6H_5$
(Vb) $R' = Br$; $Ar = 3\text{-}CH_3C_6H_4$
(Vc) $R' = Br$; $Ar = 4\text{-}CH_3OC_6H_4$
(Vd) $R' = Br$; $Ar = 3,4\text{-}(OCH_2O)C_6H_3$
(Ve) $R' = Br$; $Ar = 4\text{-}ClC_6H_4$
(Vf) $R' = Br$; $Ar = 2,4\text{-}(Cl)_2C_6H_3$
(Vg) $R' = Br$; $Ar = 4\text{-}NO_2C_6H_4$
(Vh) $R' = Br$; $Ar = 3,4\text{-}(CH_3O)_2\text{-}6\text{-}BrC_6H_2$
(Vi) $R' = Br$; Ar = 2-pyridyl
(Vj) $R' = Br$; Ar = 9-anthryl
(VI) $R' = Br$; ArCH = 9-fluorenyl
(VII) $R' = Br$; ArCH = 9-anthryl

was confirmed by NMR spectra of their corresponding salts (IIa, IIb) and by their chemical reactions.

The ylide IIIb followed a similar course of reaction (Path A) towards carbonyl compounds as reported for the analogous 2-naphthylmethylenetriphenylphosphonium ylide [5]. However, ylide IIIa followed a different path B. Seemingly, the carbanionic centres of both ylides (IIIa, IIIb) attack the carbonyl carbon to form similar cyclic intermediates (I) which decomposed via path A or path B to give different reaction products (Scheme 1).

Thus, the ylide IIIa reacted with a range of substituted benzaldehydes at room temperature, following path B, to give epoxides (IVa—IVe) in good yields, whereas the reaction of ylide IIIb with a series of aromatic aldehydes under similar reaction conditions followed exclusively olefination (path A) affording the olefins (Va—Vj) (Scheme 1). Similarly, the reaction of ylide IIIb with 9-fluorenone and 9-anthrone was also successful at elevated temperature to give exocyclic olefins (VI and VII) in fair yields.

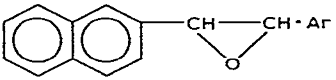
With carbonyl compounds the ylide IIIa gave epoxides exclusively but ylide IIIb gave only olefins. In no case were both olefins and epoxides isolated and in all cases only *trans*-epoxides or *trans*-olefins were detected.

All the epoxides (IVa—IVe) (Table 1) and olefins (Va—Vj, VI and VII) (Table 2) obtained in this study are new. Their structures were confirmed by IR and NMR spectral studies (Table 3). IR spectra of the ethylene epoxides showed two characteristic absorption bands near 832 and 848 cm^{-1}; the latter absorption bands are attributed to the asymmetrical ring stretching of the C—C bond due to contraction of the C—O bond. The NMR spectra of ethylene epoxide showed a characteristic absorption of epoxy protons,  at δ 3.96—4.26 ppm and an aromatic multiplet in the range of δ 6.77—8.03 ppm.

The IR spectra of *trans*-ethylenes (Va—Vj) showed absorptions at 1635—1605 (ν(C=C)) and at 987—950 cm^{-1}. The latter absorptions are associated with out-of-plane deformations of hydrogen attached to the *trans*-olefinic system [6]. The NMR spectra of ethylenes exhibited olefinic proton resonances in the range δ 6.75—7.18 ppm and aromatic multiplet resonances in the range δ 6.90—8.30, ppm. The methylene protons in the exocyclic olefin VII absorbed at δ 1.29 ppm.

TABLE 1

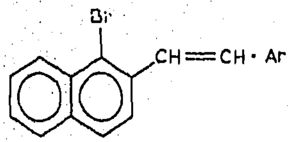
trans-DIARYL-SUBSTITUTED EPOXIDES (IVa—IVe)



Compound	Ar	Yield (%)	Recryst. solvent	M.p. (°C)	Empirical formula	Analysis Found (cald.) (%)	
						C	H
IVa	C_6H_5	90	EtOH	113—115	$C_{18}H_{14}O$	87.77 (87.79)	5.68 (5.69)
IVb	4-$CH_3C_6H_4$	80	EtOAc	110—112	$C_{19}H_{16}O$	87.67 (87.68)	5.13 (5.15)
IVc	4-$CH_3OC_6H_4$	85	$CHCl_3$/MeOH	139—140	$C_{19}H_{16}O_2$	82.62 (82.65)	5.79 (5.79)
IVd	4-ClC_6H_4	92	C_6H_6/hexane	128—130	$C_{18}H_{13}OCl$	77.01 (77.00)	4.62 (4.63)
IVe	2-$NO_2C_6H_4$	95	EtOAc	122—123	$C_{18}H_{13}NO_3$	74.22 (74.23)	4.44 (4.46)

TABLE 2

trans-DIARYL SUBSTITUTED OLEFINS (Va—Vj, VI and VII)



Compound	Ar	Yield (%)	Recryst. solvent	M.p. (°C)	Empirical formula	Analysis Found (calcd.) (%)	
						C	H
Va	C_6H_5	65	$CHCl_3$/hexane	112—115	$C_{18}H_{13}Br$	69.87 (69.90)	4.18 (4.20)
Vb	3-$CH_3C_6H_4$	62	C_6H_6/hexane	88—90	$C_{19}H_{15}Br$	70.56 (70.58)	4.63 (4.64)
Vc	4-$OCH_3C_6H_4$	60	EtOH	130—135	$C_{19}H_{15}BrO$	67.24 (67.25)	4.41 (4.42)
Vd	3,4-$(OCH_2O)_2C_6H_3$	70	EtOH	118—120	$C_{19}H_{13}BrO_2$	64.29 (64.30)	3.66 (3.67)
Ve	4-ClC_6H_4	75	EtOH	141	$C_{18}H_{12}BrCl$	62.94 (62.96)	3.51 (3.50)
Vf	2,4-$(Cl)_2C_6H_3$	70	$CHCl_3$/hexane	139—140	$C_{18}H_{11}BrCl_2$	57.13 (57.14)	2.90 (2.92)
Vg	4-$NO_2C_6H_4$	95	$CHCl_3$/hexane	158—160	$C_{18}H_{12}NO_2Br$	61.03 (61.08)	3.36 (3.38)
Vh	3,4-$(CH_3O)_2$-6-BrC_6H_2	50	EtOH/H_2O (3:1)	178—180	$C_{20}H_{16}Br_2O_2$	55.77 (55.80)	3.56 (3.57)
Vi	2-Py[a]	60	EtOH (90%)	144—146	$C_{17}H_{12}NBr$	65.79 (65.80)	3.85 (3.87)
Vj	9-Anthryl[a]	58	EtOH	166—167	$C_{26}H_{17}Br$	76.26 (76.28)	4.14 (4.16)
VI	ArCH=9-Fl	50	EtOH (90%)	102	$C_{24}H_{15}Br$	75.18 (75.19)	3.90 (3.91)
VII	ArCH=9-An	40	$CHCl_3$/hexane	108—110	$C_{25}H_{17}Br$	75.55 (75.56)	4.28 (4.28)

[a] Py = pyridyl, An = anthryl, Fl = fluorenyl.

TABLE 3

NMR SPECTRA ($CDCl_3$) OF EPOXIDES AND OLEFINS

Compound	δ (ppm)	Number of protons	Assignment
IVa	7.31—8.02, m[a]	12H	Aromatic
	4.12, q	2H	
IVb	7.00—7.95, m	11H	Aromatic
	3.97, q	2H	
	2.36, s	3H	CH_3
IVc	6.77—8.04, m	11H	Aromatic
	3.96, q	2H	
	3.82, s	3H	OCH_3
IVd	7.10—8.03, m	11H	Aromatic
	3.98, q	2H	
IVe	7.08—8.28, m	11H	Aromatic
	4.26, q	2H	
Va	7.28—8.05, m	11H	Aromatic
	6.95, q	2H	—CH=CH—
Vb	7.32—8.00, m	10H	Aromatic
	6.99, q	2H	—CH=CH—
	2.81, s	3H	CH_3
Vc	7.50—7.90, m	10H	Aromatic
	6.98, q	2H	—CH=CH—
	3.60, s	3H	$-OCH_3$
Vd	7.40—8.20, m	9H	Aromatic
	7.00, q	2H	—CH=CH—
	6.10, s	2H	$-OCH_2O-$
Vg	7.42—8.30, m	10H	Aromatic
	7.18, q	2H	—CH=CH—
Vh	7.30—8.20, m	8H	Aromatic
	6.82, q	2H	—CH=CH—
	4.05, s	6H	OCH_3
Vj	6.90—8.10, m	15H	Aromatic
	6.75, q	2H	—CH=CH—
VII	7.50—8.01, m	14H	Aromatic
	7.33, s	1H	$>C{=}CH-$
	1.29, s	2H	$>CH_2$

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

Experimental

Melting points were determined on a Gallenkamp apparatus and are uncorrected. IR spectra (KBr) were recorded on a Perkin—Elmer infracord instrument. NMR spectra were recorded ($CDCl_3$ solutions) on a Varian A60 spectrometer using TMS as an internal standard and are reported in δ (ppm) values. All products were separated and purified by column chromatography using alumina. Purity was checked by TLC.

Preparation of 2-naphthylmethyltriphenylarsonium bromide (IIa)

A mixture of triphenylarsine (12.2 g, 0.04 mol) and 2-bromomethylnaphthalene (9.6 g, 0.044 mol) was heated as a melt at 100°C for 60 h. The resulting solid was washed with ether and extracted with chloroform. The excess of solvent was evaporated under reduced pressure and n-hexane was added to precipitate 8.4 g (40%) of 2-naphthylmethyltriphenylarsonium bromide (IIa). An analytical sample of salt (IIa) was recrystallized twice from chloroform/n-hexane to give white microcrystals, m.p. 158°C. NMR spectrum ($CDCl_3$): δ (ppm) 7.42—7.84 (22H, aromatic protons, multiplet) and 5.68 (2H, methylene protons, singlet). (Found: C, 66.00; H, 4.52. $C_{29}H_{24}AsBr$ calcd.: C, 66.03; H, 4.55%).

Preparation of 1-bromo-2-naphthylmethyltriphenylarsonium bromide (IIb)

A solution of 12.2 g (0.04 mol) of triphenylarsine and 13.2 g (0.044 mol) of 1-bromo-2-bromomethylnaphthalene in 60 ml of anhydrous benzene was boiled under reflux for 6 days in an inert atmosphere of nitrogen. Excess of solvent was evaporated off on a steam bath and petroleum ether (60—80°) was added to precipitate 8 g (32%) of 1-bromo-2-naphthylmethyltriphenylarsonium bromide (IIb). The salt IIb was recrystallized three times to give grey-white microcrystals, m.p. 148-150°C. NMR spectrum ($CDCl_3$): δ (ppm) 7.41—7.92 (21H, aromatic protons, multiplet) and 5.84 (2H, methylene protons, singlet). (Found: C, 57.41; H, 3.75. $C_{29}H_{23}AsBr$ calcd.: C, 57.42; H, 3.79%).

Reaction of ylide IIIa with benzaldehydes

To an intense yellow suspension of ylide IIIa, generated from 2.1 g (0.004 mol) of salt IIa and 0.5 g (50% slurry) of sodium hydride in 60 ml of anhydrous benzene, was added, under nitrogen, 0.004 mol of substituted benzaldehyde. The mixture was stirred at room temperature for 3 days after which it was poured into water. The benzene layer was washed with water, dried and evaporated. The residue was chromatographed on neutral alumina. Elution with petroleum ether (40—60°) gave triphenylarsine, m.p. and mixed m.p. 60°C. Elution with petroleum ether (40—60°)/benzene (1:1) gave 1-aryl-2-(2-naphthyl)-1,2-ethylene epoxide (IVa—IVe) in fair to good yields. It was further purified by crystallization from appropriate solvent (Table 1).

Reaction of ylide IIIb with aromatic aldehydes

To a stirred suspension of ylide IIIb, prepared from 2.4 g (0.004 mol) of salt IIb and 0.5 g (50% slurry) of sodium hydride in 100 ml of anhydrous benzene, was added, under nitrogen, 0.004 mol of aromatic aldehyde. The reaction proceeded at room temperature for 24 h. The resulting precipitate, containing triphenylarsine oxide and unreacted sodium hydride, was removed by filtration and the filtrate was evaporated under reduced pressure. The oily product was chromatographed over neutral alumina. Elution with benzene gave *trans*-1-aryl-2-(1-bromo-2-naphthyl)ethylene (Va—Vj) in fair to good yield. It was further purified by recrystallization from an appropriate solvent (Table 2).

Reaction of ylide IIIb with exocyclic ketones

To a suspension of ylide IIIb, prepared from 2.4 g (0.004 mol) of salt IIb and

0.5 g (50% slurry) of sodium hydride in 100 ml of anhydrous benzene under nitrogen, was added 0.004 mol of exocyclic ketone. The reaction mixture was heated under reflux for 3 days. The resulting solid, containing unreacted sodium hydride and triphenylarsine oxide, was removed and the filtrate was concentrated on a steam bath under reduced pressure. The resulting oily mass was chromatographed over alumina. Elution with benzene afforded exocyclic olefin (VI and VII) in fair yield (Table 2).

Acknowledgements

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