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STUDIES ON YLIDES: EXCLUSIVE CARBONYL OLEFINATION WITH SEMISTABILIZED ARSONIUM YLIDES

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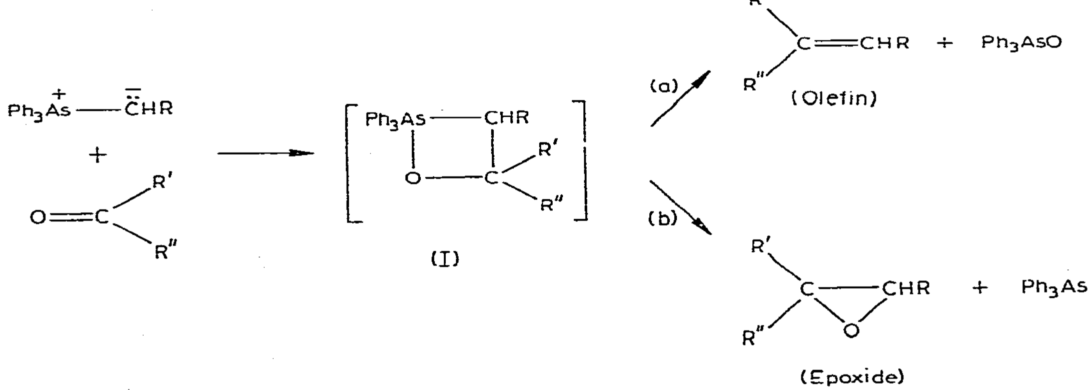
Summary

The reactions of some semistabilized arsonium ylides with 9-anthrones and 9-anthraldehyde give 9-arylidene-10-hydroanthracenes, 9-arylidene-2-chloro-10-hydroanthracenes and 1-aryl-2-(9-anthryl)ethylenes, respectively. IR and NMR spectral data of the products are reported.

Introduction

The decomposition of the cyclic transitory intermediate (I), formed by the attack of semistabilized arsonium ylide on carbonyl carbon, is of current interest to synthetic organic chemists [6—9]. Earlier reports on the reactivity of arsonium ylides towards carbonyl compounds have shown that non-stabilized ylides [1,2] give epoxides via path (b), whereas stabilized ylides [3,4] follow

SCHEME 1



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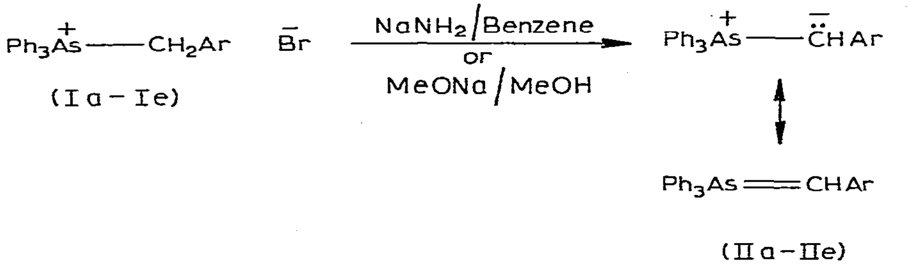
path (a), yielding olefins. However, semistabilized arsonium ylides [3,5,6] react with carbonyl compounds to give either olefin or epoxide or both in the same reaction (Scheme 1). Following our previous research [7—9], we have generated some semistabilized arsonium ylides and studied their reactions with bulky aldehydes and ketones in order to ascertain the exact path of the reaction.

Results and discussion

Quaternization of triphenylarsine with *p*-substituted benzyl bromides and 1-bromo-2-bromomethylnaphthalene at reflux temperature gave *p*-substituted benzyltriphenylarsonium bromides (Ia—Id) and 1-bromo-2-naphthylmethyltriphenylarsonium bromide (Ie) respectively in good yields. The salts (Ia—Ie) on reaction with sodamide in benzene or sodium methoxide in methanol gave *p*-substituted benzylidenetriphenylarsenanes (IIa—IId) and 1-bromo-2-naphthylmethylenetriphenylarsenane (IIe) (Scheme 2).

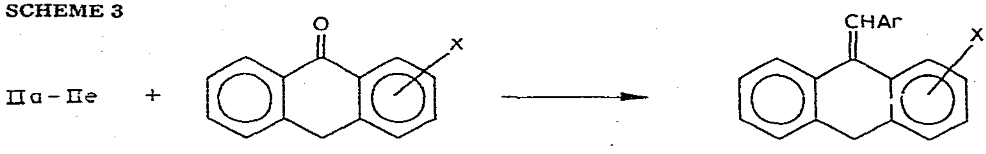
SCHEME 2



(a) Ar = 2-$NO_2C_6H_4$; (b) Ar = 3-$NO_2C_6H_4$; (c) Ar = 4-$NO_2C_6H_4$; (d) Ar = 4-I C_6H_4 ; (e) Ar = 1-Br-2-$C_{10}H_6$

The ylides (IIa—IIe) failed to react with anthrone (IIIa) and 2-chloroanthrone (IIIb) at room temperature, but the reaction was successful at reflux temperature, affording 9-arylidene-10-hydroanthracenes (IVa—IVe) and 9-arylidene-2-chloro-10-hydroanthracenes (IVf—IVj) in good yields (Scheme 3).

SCHEME 3

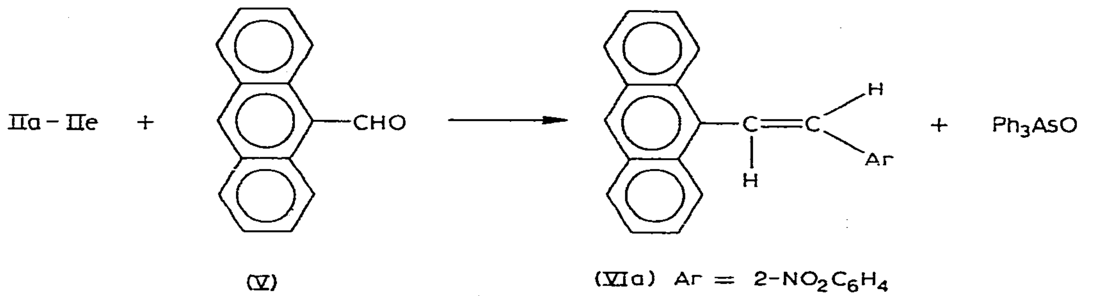


(IIIa) X = H
(IIIb) X = 2-Cl

(IVa) X = H ; Ar = 2-$NO_2C_6H_4$
(IVb) X = H ; Ar = 3-$NO_2C_6H_4$
(IVc) X = H ; Ar = 4-$NO_2C_6H_4$
(IVd) X = H ; Ar = 4-I C_6H_4
(IVe) X = H ; Ar = 1-Br-2-$C_{10}H_6$
(IVf) X = 2-Cl ; Ar = 2-$NO_2C_6H_4$
(IVg) X = 2-Cl ; Ar = 3-$NO_2C_6H_4$
(IVh) X = 2-Cl ; Ar = 4-$NO_2C_6H_4$
(IVi) X = 2-Cl ; Ar = 4-I C_6H_4
(IVj) X = 2-Cl ; Ar = 1-Br-2-$C_{10}H_6$

The reaction of ylides (IIa—IIe) with 9-anthraldehyde (V), carried out at room temperature, gave exclusively *trans*-1-aryl-2-(9-anthryl)ethylenes (VIa—VIe) in fair to good yields (Scheme 4).

SCHEME 4



(VIa) Ar = $2\text{-}NO_2C_6H_4$
(VIb) Ar = $3\text{-}NO_2C_6H_4$
(VIc) Ar = $4\text{-}NO_2C_6H_4$
(VId) Ar = $4\text{-}IC_6H_4$
(VIe) Ar = $1\text{-}Br\text{-}2\text{-}C_{10}H_6$

With carbonyl compounds, the ylides (IIa—IIe) favour the formation of olefins via path (a) as opposed to epoxidation. The reason for the exclusive formation of olefins (IVa—IVj, VIa—VIe) and the non-availability of epoxides from ylides (IIa—IIe) is probably due to the substituents attached to the ylide carbanion and the bulky nature of the carbonyl compounds (IIIa, IIIb, V), which might affect the decomposition of the cyclic transitory intermediate (I). The exclusive formation of olefins is in accord with behaviour of the analogous phosphonium ylides [10,11].

All the exocyclic olefins (IVa—IVj) and substituted ethylenes (VIa—VIe), most of which are new, were obtained almost exclusively as *trans*-isomers. The products gave satisfactory elemental analyses and the spectral data of the substituted ethylenes (VIa—VIe) were also consistent with those expected for *trans*-stereoisomers.

The IR spectra (Table 1) of exocyclic olefins (IVa—IVj) and ethylenes (VIa—VIe) show absorptions at 1610—1575 cm^{-1} (ν(C=C)) and 970—950 cm^{-1}; the latter absorptions are associated with out-of-plane deformations of hydrogen attached to the *trans*-olefinic system [12]. The NMR spectra (Table 1) for exocyclic olefins (IVa—IVj) exhibit olefinic protons in the range δ(ppm) 7.23—7.45, an aromatic multiplet in the range δ 7.40—8.60 and the CH_2 protons in the range δ 1.29—1.63. The NMR spectra of *trans*-ethylenes (VIa—VIe) show aromatic protons in the range δ 6.24—6.60.

Experimental

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

TABLE 1

SPECTRAL DATA OF ANTHRACENE DERIVATIVES IVa—IVj; VIa—VIe

Compound	NMR data ($CDCl_3$)			IR data (KBr) (cm^{-1})	
	δ (ppm) [a]	Number of protons	Assignment	C=C stretching vibrations	Out-of-plane deformations of hydrogen attached to olefinic bond
IVa				1575	966
IVb	7.40—8.30, m	12H	Aromatic	1578	965
	7.30, s	1H	Olefinic		
	1.25, s	2H	$>CH_2$		
IVc	7.45—8.60, m	12H	Aromatic		
	7.27, s	1H	Olefinic		
	1.60, s	2H	$>CH_2$		
IVd	7.58—8.45, m	12H	Aromatic	1590	952
	7.35, s	1H	Olefinic		
	1.40, s	2H	$>CH_2$		
IVe	7.50—8.10, m	14H	Aromatic		
	7.35, s	1H	Olefinic		
	1.29, s	2H	$>CH_2$		
IVf	7.60—8.60, m	11H	Aromatic	1598	962
	7.23, s	1H	Olefinic		
	1.53, s	2H	$>CH_2$		
IVg				1595	958
IVh	7.70—8.60, m	11H	Aromatic	1600	969
	7.45, s	1H	Olefinic		
	1.63, s	2H	$>CH_2$		
IVj	7.60—8.40, m	11H	Aromatic	1595	970
	7.33, s	1H	Olefinic		
	1.50, s	2H	$>CH_2$		
VIb	6.34—7.95, m	13H	Aromatic	1592	950
	6.24, q	2H	Olefinic		
VIc				1588	952
VIe	6.90—7.75, m	15H	Aromatic	1613	966
	6.60, q	2H	Olefinic		

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

were prepared by the treatment of α-bromo compounds with triphenylarsine in benzene at reflux temperature, as reported previously [7—9,13].

(a) Preparation of 9-arylidene-10-hydroanthracenes (IVa—IVj)

To a suspension of ylides (IIa—IIe), prepared from 4 mmol of salts (Ia—Ie) and sodamide (0.19 g, 5 mmol) in anhydrous benzene (100 ml) under nitrogen, was added 4 mmol of 9-anthrone (IIIa, IIIb). The reaction mixture was heated under reflux for 48 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 chloroform and chromatographed. Elution with benzene afforded new 9-arylidene-10-hydroanthracenes (IVa—IVj) in 50—75% yields. The products were crystallized from appropriate solvents (Table 2).

TABLE 2

PHYSICAL PROPERTIES OF ANTHRACENE DERIVATIVE IVa—IVj, VIa—VIe

Compound	X	Ar	Yield (%)	Recryst. solvent	M.p. (°C)	Molecular formula	Analysis found (calcd.) (%)	
							C	H
IVa	H	2-$NO_2C_6H_4$	65	EtOH	250—251	$C_{21}H_{15}NO_2$	80.48 (80.52)	4.76 (4.80)
IVb	H	3-$NO_2C_6H_4$	58	$CHCl_3$/EtOH	120—122	$C_{21}H_{15}NO_2$	80.54 (80.52)	4.75 (4.80)
IVc	H	4-$NO_2C_6H_4$	75	EtOH	212—214	$C_{21}H_{15}NO_2$	80.46 (80.52)	4.79 (4.82)
IVd	H	4-IC_6H_4	65	$CHCl_3$	171—173	$C_{21}H_{15}I$	63.92 (63.96)	3.84 (3.81)
IVe	H	1-Br-2-$C_{10}H_6$	68	EtOH	122—124	$C_{25}H_{17}Br$	75.51 (75.56)	4.25 (4.28)
IVf	2-Cl	2-$NO_2C_6H_4$	60	EtOH	174—175	$C_{21}H_{14}NO_2Cl$	72.58 (72.53)	4.24 (4.27)
IVg	2-Cl	3-$NO_2C_6H_4$	52	$CHCl_3$	194—195	$C_{21}H_{14}NO_2Cl$	72.58 (72.53)	4.23 (4.27)
IVh	2-Cl	4-$NO_2C_6H_4$	70	EtOH	182—183	$C_{21}H_{14}NO_2Cl$	72.50 (72.53)	4.24 (4.27)
IVi	2-Cl	4-IC_6H_4	58	$CHCl_3$/EtOH	180—182	$C_{21}H_{14}ClI$	58.83 (58.79)	3.27 (3.24)
IVj	2-Cl	1-Br-2-$C_{10}H_6$	60	EtOH	186—188	$C_{25}H_{16}BrCl$	69.57 (69.52)	3.78 (3.75)
VIa		2-$NO_2C_6H_4$	80	$CHCl_3$/EtOH	102—103	$C_{22}H_{15}NO_2$	81.26 (81.23)	4.64 (4.61)
VIb		3-$NO_2C_6H_4$	75	AcOH	160—162	$C_{22}H_{15}NO_2$	81.18 (81.23)	4.65 (4.61)
VIc		4-$NO_2C_6H_4$	90	EtOH/$CHCl_3$	221—222	$C_{22}H_{15}NO_2$	81.25 (81.23)	4.63 (4.61)
VId		4-IC_6H_4	60	AcOH	142—144	$C_{22}H_{15}I$	65.27 (65.24)	3.67 (3.69)
VIe		1-Br-2-$C_{10}H_6$	65	AcOH	166—167	$C_{26}H_{17}Br$	76.25 (76.28)	4.18 (4.16)

(b) Preparation of 1-aryl-2-(9-anthryl) ethylenes (VIa—VIe)

To a stirred solution of 4 mmol of arsonium salts (Ia—Ie) in 120 ml of methanol, was added 4 mmol of methanolic sodium methoxide followed by 4 mmol 9-anthraldehyde (V) under an atmosphere of nitrogen. The mixture was stirred at room temperature for 20 h, the solvent evaporated and the residue extracted with chloroform. The extract was then evaporated and the residue chromatographed on alumina. Elution with benzene/petroleum ether (2 : 1) afforded *trans*-ethylenes (VIa—VIe) in 60—90% yields. The products were crystallized from appropriate solvents (Table 2).

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