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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

$$Ph_{3}As \longrightarrow \ddot{C}HR$$

$$+$$

$$O \longrightarrow C$$

$$R''$$

$$(Oletin)$$

$$R''$$

$$(Oletin)$$

$$R''$$

$$(Epoxide)$$

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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

$$Ph_3As$$
 — CH_2Ar Br $NaNH_2/Benzene$ Ph_3As — $CHAR$ $CHAR$ $MeONa/MeOH$

$$(\Pi a - \Pi e)$$

(a) Ar =
$$2-NO_2C_6H_4$$
; (b) Ar = $3-NO_2C_6H_4$; (c) Ar = $4-NO_2C_6H_4$;
(d) Ar = $4-IC_6H_4$; (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).

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

$$\square a - \square e$$
 + $\square C$ — $\square C$

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 CH₂ 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 (CDCl₃) 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 (CE	C1 ₃)		IR data (KBr) (cr	m ⁻¹)
	δ (ppm) ^a	Number of protons	Assignment	C=C stretching vibrations	Out-of-plane deformations of hydrogen attached to olefinic bond
	· · · · · · · · · · · · · · · · · · ·			1575	966
IVa		_ ~			
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	å-a-	
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		
IVi	7.60-8.40, m	11H	Aromatic	1595	970
	7.33, s	1 H	Olefinic		
	ร่.จีป, 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-IVI, VIa-VIC

17a	Compound	×	Ar	Yield (%)	Recryst.	M.p.	Molecular	Analysis found (calcd.) (%)	(calcd.) (%)
H $2.NO_2G_6H_4$ 66 $E1OH$ $250-251$ $G_1H_15NO_2$ 80.48 H $3.NO_2G_6H_4$ 68 $CHCl_3/EIOH$ $120-122$ $G_1H_15NO_2$ 80.64 H $4.NO_2G_6H_4$ 65 $CHCl_3$ $171-173$ $G_1H_15NO_2$ 80.46 H $4.NO_2G_6H_4$ 65 $CHCl_3$ $171-173$ $G_1H_15NO_2$ 80.46 H $4.NO_2G_6H_4$ 66 $CHCl_3$ $171-173$ $G_1H_15NO_2$ 80.46 2-Cl $2.NO_2G_6H_4$ 60 $E1OH$ $122-124$ G_2H_17BT G_1B_1 G_1B_2 2-Cl $3.NO_2G_6H_4$ 60 $E1OH$ $174-175$ $G_1H_14NO_2Cl$ 72.58 2-Cl $4.NO_2G_6H_4$ 68 $CHCl_3$ $194-196$ $G_1H_14NO_2Cl$ 72.58 2-Cl $4.NO_2G_6H_4$ 68 $CHCl_3/EIOH$ $182-183$ $G_2H_14NO_2Cl$ 72.58 2-Cl $4.NO_2G_6H_4$ 68 $CHCl_3/EIOH$ $180-182$ $G_2H_16NO_2Cl$ 72.58 2-Cl $4.NO_2G_6H_4$ 69 $CHCl_3/EIOH$ $180-162$ $G_2H_16NO_2$ 81.26 3-NO_2G_6H_4 70 $CHCl_3/EIOH$ $160-162$ $G_2H_15NO_2$ 81.26 4-NO_2G_6H_4 60 $CHCl_3/EIOH$ $160-162$ $G_2H_15NO_2$ 81.26 66.57 66.57 66.57 66.57 66.57 67.69					solvent	(3)	formula	Ö	I
H $3.NO_2G_6H_4$ 58 $CHCl_3/EtOH$ $120-122$ $C_21H_1SNO_2$ (80.52) H $4.NO_2G_6H_4$ 75 $EtOH$ $212-214$ $C_21H_1SNO_2$ 80.46 H $4.VG_6H_4$ 65 $CHGl_3$ $171-173$ $C_21H_1SNO_2$ 80.46 H $1.BP.2-G_10H_6$ 68 $EtOH$ $122-124$ C_21H_1SI 63.92 2-C1 $2.NO_2G_6H_4$ 60 $EtOH$ $122-124$ C_2H_1BC (72.53) 2-C1 $2.NO_2G_6H_4$ 52 $CHGl_3$ $194-195$ $C_21H_1ANO_2GI$ (72.53) 2-C1 $4.NO_2G_6H_4$ 70 $EtOH$ $182-183$ $C_21H_1ANO_2GI$ (72.53) 2-C1 $4.NO_2G_6H_4$ 70 $EtOH$ $180-183$ $C_21H_1ANO_2GI$ (72.53) 2-C1 $4.NO_2G_6H_4$ 70 $EtOH$ $180-182$ $C_2H_1GNO_2$ (81.23) 2-C1 $4.NO_2G_6H_4$ 80 $CHGl_3/EtOH$ $102-103$ $C_22H_1SNO_2$ (81.23) <	IVa	н	2-NO ₂ C ₆ H ₄	66	Етон	250-251	C21H15NO2	80.48	4.76
H $3.00_2G_6H_4$ 68 $CHCl_3/ELOH$ $120-122$ $C_21H_1SNO_2$ 60.64 H $4.NO_2G_6H_4$ 75 $ELOH$ $212-214$ $C_21H_1SNO_2$ 60.62 H $4.1G_6H_4$ 65 $CHCl_3$ $171-173$ $C_21H_1SNO_2$ 60.62 H $1.9P_2-C_10H_6$ 68 $ELOH$ $122-124$ C_2H_1PBr 75.51 $2.C1$ $2.NO_2G_6H_4$ 60 $ELOH$ $174-175$ $C_21H_1HO_2CI$ 75.58 $2.C1$ $3.NO_2G_6H_4$ 70 $ELOH$ $182-183$ $C_21H_1HO_2CI$ 72.58 $2.C1$ $4.NO_2G_6H_4$ 70 $ELOH$ $180-182$ $C_21H_1HO_2CI$ 72.58 $2.C1$ $4.1C_6H_4$ 58 $CHCl_3$ ELOH $180-182$ $C_21H_1GNO_2CI$ 72.58 $2.C1$ $1.9E-2C_1OH_6$ 60 $ELOH$ $102-103$ $C_22H_1SNO_2$ 69.57 $4.NO_2G_6H_4$ 75 $AcOH$ $160-167$ $C_2H_1SNO_2$ 60.27 $4.$								(80.52)	(4.80)
H $4\text{-NO}_2G_6H_4$ 75 EtOH $212-214$ $G_1H_1 \circ NO_2$ (80.52) H $4\text{-}1G_6H_4$ 65 $CHCl_3$ $171-173$ $C_21H_1 \circ NO_2$ (80.52) H $1\text{-}Br^2\text{-}C_10H_6$ 68 $EtOH$ $122-124$ $C_21H_1 \circ NO_2$ (83.96) 2-C1 $2\text{-}NO_2C_6H_4$ 60 $EtOH$ $174-176$ $C_21H_1 \circ NO_2C$ (75.56) 2-C1 $3\text{-}NO_2C_6H_4$ 60 $EtOH$ $182-183$ $C_21H_1 \circ NO_2C$ (72.53) 2-C1 $4\text{-}NO_2C_6H_4$ 70 $EtOH$ $182-183$ $C_21H_1 \circ NO_2C$ (72.53) 2-C1 $4\text{-}NO_2C_6H_4$ 58 $CHCI_3/EtOH$ $186-188$ $C_21H_1 \circ NO_2C$ (12.53) 2-C1 $1\text{-}Br^2\text{-}C_10H_6$ 60 $CHCI_3/EtOH$ $186-188$ $C_21H_1 \circ NO_2C$ (12.53) 2-C2 $4\text{-}NO_2C_6H_4$ 80 $CHCI_3/EtOH$ $160-182$ $C_22H_1 \circ NO_2C$ (81.23) 2-NO_2C_6H_4 60 $AcOH$ $142-144$ $C_22H_1 \circ NO_2C$	IVb	æ	$3.NO_2C_6H_4$	58	CHCl3/EtOH	120 - 122	C21H15N02	80.54	4.76
H $4 \cdot 10_{2} \cdot 10_{44}$ 76 EtOH $212 - 214$ $C_{21} \cdot 11_{15}$ 60.46 H $4 \cdot 10_{6} \cdot 14_{4}$ 65 $CHGl_{3}$ $171 - 173$ $C_{21} \cdot 11_{15}$ 63.92 H $1 \cdot 1.9 \cdot 2 \cdot C_{10} \cdot 16_{6}$ 68 $EtOH$ $122 - 124$ $C_{21} \cdot 11_{14} \cdot 10_{2}$ (75.56) 2-CI $2 \cdot 10_{2} \cdot C_{6} \cdot 14$ 60 $EtOH$ $174 - 175$ $C_{21} \cdot 11_{14} \cdot 10_{2}$ (75.56) 2-CI $2 \cdot 10_{2} \cdot C_{6} \cdot 14$ 70 $EtOH$ $182 - 183$ $C_{21} \cdot 11_{14} \cdot 10_{2}$ (72.53) 2-CI $4 \cdot 1C_{6} \cdot 14$ 70 $EtOH$ $182 - 183$ $C_{21} \cdot 11_{14} \cdot 10_{2}$ (72.53) 2-CI $4 \cdot 1C_{6} \cdot 14$ 58 $CHCI_{3} \cdot 10_{2}$ $C_{21} \cdot 11_{2} \cdot 10_{2}$ (72.53) 2-CI $1 \cdot 15 \cdot 2 \cdot 10_{2} \cdot 10_{2}$ 60 $C_{21} \cdot 10_{2} \cdot 10_{2}$ $C_{22} \cdot 10_{2} \cdot 10_{2}$ <t< td=""><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td>(80.52)</td><td>(4.80)</td></t<>								(80.52)	(4.80)
H $4 \cdot 1C_0H_4$ 65 $CHCl_3$ $171-173$ $C_2l_1l_151$ (60.52) H $1 \cdot Br \cdot 2 \cdot C_10H_6$ 68 $EtOH$ $122-124$ $C_2l_1l_16N$ (75.56) $2 \cdot Cl$ $2 \cdot NO_2C_6H_4$ 60 $EtOH$ $174-175$ $C_2l_1l_14NO_2Cl$ 75.56 $2 \cdot Cl$ $3 \cdot NO_2C_6H_4$ 52 $CHCl_3$ $182-183$ $C_2l_1l_14NO_2Cl$ 72.56 $2 \cdot Cl$ $4 \cdot NO_2C_6H_4$ 58 $CHCl_3/EtOH$ $180-182$ $C_2l_1l_14NO_2Cl$ 72.56 $2 \cdot Cl$ $4 \cdot 1C_6H_4$ 58 $CHCl_3/EtOH$ $180-182$ $C_2l_1l_16NO_2Cl$ 72.56 $2 \cdot Cl$ $4 \cdot 1C_6H_4$ 60 $CCCl_3/EtOH$ $CCCl_1l_16NO_2Cl$ $CCCl_1l_16NO_2Cl$ $CCCl_1l_16NO_2Cl$ $CCCl_1l_16NO_2Cl$ $CCCCl_1l_16NO_2Cl$ $CCCCl_1l_16NO_2Cl$ $CCCCl_1l_16NO_2Cl$ $CCCCCl_1l_16NO_2Cl$ $CCCCCCCl_1l_16NO_2Cl$ $CCCCCCCCCCCl_1l_16NO_2Cl$ $CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC$	IVc	н.	4-N02C6H4	76	ЕСОН	212 - 214	C21H15N02	80.46	4.79
H $4+10_6 H_4$ 65 CHGl3 $171-173$ $C_{21}H_151$ 63.92 H $1-Br-2-C_10H_6$ 68 EtOH $122-124$ $C_{25}H_17Br$ $C_{15}H_2$ $2-C1$ $2-NO_2C_6H_4$ 60 EtOH $174-176$ $C_{21}H_14NO_2CI$ $C_{15}H_2$ $2-C1$ $3-NO_2C_6H_4$ 52 $CHCl_3$ $194-195$ $C_{21}H_14NO_2CI$ $C_{25}H_2$ $2-C1$ $4-NO_2C_6H_4$ 70 EtOH $182-183$ $C_{21}H_14NO_2CI$ $C_{25}H_2$ $2-C1$ $4-NO_2C_6H_4$ 70 EtOH $180-182$ $C_{21}H_14NO_2CI$ $C_{25}H_2$ $2-C1$ $4-NO_2C_6H_4$ 58 $CHCl_3/EtOH$ $186-188$ $C_{25}H_16NCI$ $C_{25}H_2$ $2-C1$ $1-Br-2-C_10H_6$ 60 ACH ACH AC_2H_16NCI $C_{22}H_15NO_2$ $C_{21}H_2NO_2$ $2-C1$								(80.52)	(4.82)
H 1-Br-2-C ₁ 0H ₆ 68 EtOH 122-124 $C_{25H_{17}Br}$ $C_{15.50}$ 2-C1 $2-NO_2C_6H_4$ 60 EtOH $174-175$ $C_{11H_{14}NO_2Cl}$ 72.58 2-C1 $3-NO_2C_6H_4$ 52 $CHCl_3$ $194-195$ $C_{11H_{14}NO_2Cl}$ 72.58 2-C1 $4-NO_2C_6H_4$ 70 EtOH $182-183$ $C_{21H_{14}NO_2Cl}$ 72.58 2-C1 $4-NO_2C_6H_4$ 58 $CHCl_3/EtOH$ $180-182$ $C_{21H_{14}NO_2Cl}$ 72.58 2-C1 $1-Br-2-C_1OH_6$ 60 $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ 2-C1 $1-Br-2-C_1OH_6$ 60 $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ 2-C2 $1-Br-2-C_1OH_6$ 60 $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ 3-NO ₂ C ₆ H ₄ 90 ECOH/CHCI3 $\frac{1}{2}$	IVd	Ħ	$4 \cdot 1C_6H_4$	65	CHCl ₃	171-173	$c_{21}H_{15}I$	63,92	3.84
2-Cl $2\cdot NO_2C_6H_4$ 60 EtOH $174-175$ $C_21H_14NO_2Cl$ 72.58 2-Cl $3\cdot NO_2C_6H_4$ 52 CHCl ₃ $194-195$ $C_21H_14NO_2Cl$ 72.58 2-Cl $4\cdot NO_2C_6H_4$ 70 EtOH $182-183$ $C_21H_14NO_2Cl$ 72.59 2-Cl $4\cdot 1C_6H_4$ 58 CHCl ₃ /EtOH $180-182$ $C_21H_14NO_2Cl$ 72.59 2-Cl $1\cdot Br^2\cdot C_10H_6$ 60 EtOH $180-182$ C_21H_14Cl 68.79 68.79 2-Cl $1\cdot Br^2\cdot C_10H_6$ 60 CHCl ₃ /EtOH $102-103$ C_22H_16BrCl 69.57 69.57 2-Cl $1\cdot Br^2\cdot C_10H_6$ 80 CHCl ₃ /EtOH $102-103$ $C_22H_15NO_2$ 81.26 81.28 3-NO ₂ C ₆ H ₄ 90 EtOH/CHCl ₃ $221-222$ $C_22H_15NO_2$ 81.26 81.28 4-1O ₆ H ₄ 60 AcOH $142-144$ $C_22H_15NO_2$ 81.26 (65.24) (65.24) (65.24)	IVe	Ħ	1-Br-2-C10Hc	68	EtOH	122-124	CacHiaBr	75.51	4.25
2-Cl $2\cdot NO_2C_6H_4$ 60 EtOH $174-175$ $C_21H_14NO_2Cl$ 72.58 2-Cl $3\cdot NO_2C_6H_4$ 52 $CHCl_3$ $194-195$ $C_21H_14NO_2Cl$ 72.53 2-Cl $4\cdot NO_2C_6H_4$ 58 $CHCl_3/EtOH$ $180-182$ $C_21H_14NO_2Cl$ 72.53 2-Cl $4\cdot IC_6H_4$ 68 $CHCl_3/EtOH$ $186-188$ C_2H_16BCl 69.57 2-NO $_2C_6H_4$ 76 $AcOH$ $102-103$ $C_2H_16NO_2$ 81.26 3-NO $_2C_6H_4$ 76 $AcOH$ $160-162$ $C_2H_15NO_2$ 81.26 4-IC $_6H_4$ 60 $AcOH$ $160-167$ $C_2H_15NO_2$ 81.26 (81.23) 4-IC $_6H_4$ 60 $AcOH$ $160-167$ $C_2H_15NO_2$ (65.24) (65.24) 1-Br-2- C_1OH_6 65 $AcOH$ $166-167$ C_2H_15N C_2H_15N (65.24) (65.24)								(75,56)	(4.28)
2-CI $3\cdot NO_2C_6H_4$ 52 $CHCl_3$ $194-195$ $C_21H_14NO_2CI$ 72.53 72.58 70 $EtOH$ $182-183$ $C_21H_14NO_2CI$ 72.53 72.53 2 -CI $4\cdot IC_6H_4$ 58 $CHCl_3/EtOH$ $180-182$ C_21H_14CII 58.83 2 -CI $1\cdot Br^2-C_1OH_6$ 60 60 60 60 60 60 60 6	IVÍ	2-C1	$2-NO_2C_6H_4$	09	EtOH	174-175	C21H14N02Cl	72.58	4.24
2-CI $3\cdot NO_2C_6H_4$ 52 $CHCl_3$ $194-195$ $C_21H_{14}NO_2CI$ 72.58 2-CI $4\cdot NO_2C_6H_4$ 70 $EtOH$ $182-183$ $C_21H_{14}NO_2CI$ 72.59 2-CI $4\cdot IC_6H_4$ 58 $CHCl_3/EtOH$ $180-182$ $C_2H_{16}DCI$ 69.57 2-CI $1\cdot Br\cdot 2\cdot C_10H_6$ 60 60 60 60 60 60 60 6	÷							(72,53)	(4.27)
2-Cl $4 \cdot NO_2C_6H_4$ 70 $EtOH$ $182-183$ $C_21H_14NO_2Cl$ 72.50 (72.53) 2-Cl $4 \cdot IC_6H_4$ 58 $CHCl_3/EtOH$ $180-182$ C_21H_14Cll 58.83 (72.53) 2-Cl $1 \cdot Br\cdot 2 \cdot C_10H_6$ 60 $2 \cdot IC_13/EtOH$ $186-188$ C_25H_16BrCl 69.57 (69.52) 2-NO ₂ C ₆ H ₄ 80 $CHCl_3/EtOH$ $102-103$ $C_22H_15NO_2$ 81.26 (81.23) 3-NO ₂ C ₆ H ₄ 75 $AcOH$ $160-162$ $C_2H_15NO_2$ 81.18 (81.23) 4-1O ₆ H ₄ 60 $AcOH$ $142-144$ C_22H_15N 65.27 (65.24) $1 \cdot Br\cdot 2 \cdot C_10H_6$ 65 $AcOH$ $166-167$ C_26H_17Br 76.26	IVg	2-C1	$3-NO_2C_6H_4$	52	CHCl ₃	194-195	C21H14NO2CI	72,58	4.23
2-Cl $4 \cdot NO_2 C_6 H_4$ 70 EtOH $182 - 183$ $C_2 1 H_1 ANO_2 Cl$ 72.50 (72.53) 2-Cl $4 \cdot IC_6 H_4$ 58 $C_1 C_1 C_1 C_2 C_1 C_2 C_2 C_2 C_2 C_2 C_2 C_2 C_2 C_2 C_2$								(72.53)	(4.27)
2-C1 $4\cdot 1C_0H_4$ 58 $CHCl_3/EtOH$ $180-182$ C_21H_14CII 58.83 (72.53) 2-C1 $1\cdot Br\cdot 2\cdot C_10H_6$ 60 ∞ EtOH $186-188$ C_25H_16BrCl 69.57 (69.52) 2-NO ₂ C ₆ H ₄ 80 $CHCl_3/EtOH$ $102-103$ $C_{22}H_15NO_{2}$ 81.26 (81.23) 3-NO ₂ C ₆ H ₄ 75 Λ COH $160-162$ $C_{22}H_15NO_{2}$ 81.18 (81.23) 4-NO ₂ C ₆ H ₄ 60 Λ COH $142-144$ $C_{22}H_15NO_{2}$ (81.23) 4-1C ₆ H ₄ 60 Λ COH $142-144$ Λ C ₂ C ₁ H ₁₅ II (65.24) (65.24) 1-Br·2-C ₁ OH ₆ 65 Λ COH $166-167$ Λ C ₂ C ₁ H ₁₅ II (65.24) (76.28)	IVh	2-CI	$4\cdot NO_2C_6H_4$	70	Етон	182 - 183	C21H14N02Cl	72.50	4.24
2-Cl $4\cdot 1C_0H_4$ 58 $CHCl_3/EtOH$ $180-182$ C_21H_14Cll 58.83 (58.79) (58.79) (58.79) (58.79) (69.57) (69.52) (69.								(72.53)	(4.27)
2-Cl $1-Br-2-C_{10}H_{6}$ 60 EtOH $186-188$ $C_{25}H_{16}BrCl$ (69.57) (69.52) $2-NO_{2}C_{6}H_{4}$ 80 $C_{12}G_{1}G_{1}G_{1}G_{2}G_{1}G_{2}G_{2}G_{2}G_{2}G_{2}G_{2}G_{2}G_{2$	IVi	2-C]	$4 \cdot 1C_0H_4$	58	сноі з/Етон	180-182	C21H14C11	58.83	3.27
2-Cl $1-Br-2-C_{1}OH_{o}$ 60 EtOH $186-188$ $C_{25}H_{16}BrCl$ 69.57 (69.52) 2-NO ₂ C ₆ H ₄ 80 CHCl ₃ /EtOH $102-103$ $C_{22}H_{15}NO_{2}$ 81.26 (81.23) 3-NO ₂ C ₆ H ₄ 75 Λ cOH $160-162$ $C_{22}H_{15}NO_{2}$ 81.18 (81.23) 4-NO ₂ C ₆ H ₄ 90 EtOH/CHCl ₃ $221-222$ $C_{22}H_{15}NO_{2}$ 81.26 (81.23) 4-1C ₆ H ₄ 60 Λ cOH $142-144$ $C_{22}H_{15}I$ 65.27 (65.24) 1-Br-2-C ₁ OH ₆ 65 Λ cOH $166-167$ $C_{26}H_{17}Br$ 76.26 (76.28)								(58.79)	(3.24)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	IVj	2-C]	1-Br-2-C10H6		ЕСОН	186-188	C25H16BrCl	69.57	3.78
$\begin{array}{cccccccccccccccccccccccccccccccccccc$				į				(69.52)	(3.75)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	VIa		$2-NO_2C_6H_4$	80	CHCl3/Etoh	102 - 103	C22H15N02	81.26	4.64
$3 \cdot NO_2 C_6 H_4$ 75 AcOH $160 - 162$ $C_{22} H_{15} NO_2$ 81.18 (81.23) $4 \cdot NO_2 C_6 H_4$ 90 $EtOH/CHCl_3$ $221 - 222$ $C_{22} H_{15} NO_2$ 81.25 (81.23) $4 \cdot IC_6 H_4$ 60 AcOH $142 - 144$ $C_{22} H_{15} I$ (65.27) (65.24) (65.24) (65.24)								(81.23)	(4.61)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Vib		3-NO2C6H4	22	AcOH	160-162	C22H15N02	81.18	4.65
$4\cdot NO_2G_6H_4$ 90 EtOH/CHCl ₃ $221-222$ $G_22H_{15}NO_2$ 81.25 (81.23) (81.23) (81.23) (81.24) (81.								(81.23)	(4.61)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	VIc		$4-NO_2C_6H_4$	06	EtOH/CIICl ₃	221 - 222	C22H15N02	81.25	4.63
$4 \cdot 1C_6H_4$ 60 AcOH $142-144$ $C_{22}H_{15}I$ 65.27 (65.24) (65.24) $1 \cdot Br \cdot 2 \cdot C_{10}H_6$ 65 AcOH $166-167$ $C_{2}6H_{17}Br$ 76.25 (76.28)								(81.23)	(4.61)
(65.24) $1 \cdot Br \cdot 2 \cdot C_{10}H_{6}$ 65 AcOH $166 - 167$ $C_{26}H_{17}Br$ 76.25 (76.28)	VId		$4 \cdot 1C_6H_4$	09	AcOH	142-144	$C_{22}H_{15}I$	65.27	3.67
$1 \cdot Br \cdot 2 \cdot C_{10} H_6$ 65 AcOH $166 - 167$ $C_{26} H_1 \gamma Br$ 76.25 (76.28)								(65.24)	(3.69)
	VIe		1-Br-2-C ₁₀ H ₆	65	АсОН	166-167	$C_{26}H_{17}Br$	76.25	4.18
								(76.28)	(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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