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STUDIES ON YLIDES

FORMATION AND REACTIONS OF *ortho*- AND *meta*-NITROBENZYLIDENETRIPHENYLARSENANES

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Summary

Two semi-stabilized arsonium ylides, *ortho*-nitrobenzylidenetriphenylarsenane and *meta*-nitrobenzylidenetriphenylarsenane, were prepared and treated with a range of carbonyl compounds to yield *trans*-olefins. In no case was an epoxide isolated.

Introduction

The growing interest of organic chemists in reactions of arsonium ylides [1], particularly in the ambivalent behaviour of semi-stabilized arsonium ylides towards carbonyl compounds [2-4], indicated the need for more thorough studies of arsonium ylide chemistry.

In extension of our studies of the reactions of semi-stabilized arsonium ylides [4], we have investigated the reactions of *ortho*-nitrobenzylidenetriphenylarsenane (Ia) and *meta*-nitrobenzylidenetriphenylarsenane (Ib) with a series of carbonyl compounds in order to examine the effect of *ortho*-and *meta*-nitrosubstituents on the nature of the products of carbonyl olefination.

Results and discussion

Quaternization of triphenylarsine with *ortho*- and *meta*-nitrobenzyl bromide gave *ortho*-nitrobenzyltriphenylarsonium bromide (IIa) and *meta*-nitrobenzyltriphenylarsonium bromide (IIb), respectively, in good yields. Dehydrohalogenation of these salts IIa-b with sodium methoxide in methanol or sodamide in benzene generated an intense violet or pink colouration due to formation of ylides Ia and Ib respectively (Scheme 1).

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SCHEME 1

$$\mathrm{Ph_3As^+{-}CH_2C_6H_4{-}X\ Br^-} \xrightarrow[\mathrm{MeOH}]{\mathrm{CH_3ONa}} \mathrm{Ph_3As{=}CHC_6H_4{-}X} \updownarrow \mathrm{Ph_3As^+{-}\bar{C}HC_6H_4{-}X}$$

(IIa: X = *o*-NO_2;

IIb: X = *m*-NO_2)

(Ia: X = *o*-NO_2;

Ib: X = *m*-NO_2)

$$\downarrow \mathrm{ArCHO}$$

$$\mathrm{Ph_3AsO + ArCH = CHC_6H_4{-}X}$$

(IIIa-VII)

(III a: Ar = C_6H_5; X = 2-NO_2;

b: Ar = 4-$NO_2C_6H_4$; X = 2-NO_2;

c: Ar = 4-ClC_6H_4; X = 2-NO_2;

d: Ar = 2-CH_3O C_6H_4; X = 2-NO_2;

e: Ar = 3-$CH_3C_6H_4$; X = 2-NO_2;

f: Ar = 3,4-$(CH_3O)_2$-6-BrC_6H_2; X = 2-NO_2)

(IV a: Ar = C_6H_5; X = 3-NO_2;

b: Ar = 4-$NO_2C_6H_4$; X = 3-NO_2;

c: Ar = 4-ClC_6H_4; X = 3-NO_2;

d: Ar = 4-$CH_3C_6H_4$; X = 3-NO_2;

e: Ar = 4-$CH_3OC_6H_4$; X = 3-NO_2;

f: Ar = 3,4-$(CH_3O)_2C_6H_3$; X = 3-NO_2;

g: Ar = 3,4-$(CH_3O)_2$-6-BrC_6H_2; X = 3-NO_2;

h: Ar = 3,4-$(OCH_2O)C_6H_3$; X = 3-NO_2)

(V: Ar = 2-furyl; X = 3-NO_2)

(VI: Ar = 2-pyridyl; X = 3-NO_2)

(VII :Ar = 9-anthryl; X = 3-NO_2)

TABLE 1. *trans*-DIARYL SUBSTITUTED OLEFINS (IIIa-VII) Ar—CH=CHC_6H_4—X

Compound	Ar	X	Yield (%)	Recrystallization solvent	M.p. (°C)	Empirical formula	Analysis found(calcd.)(%) C	H
IIIa	C_6H_5	2-NO_2	60	AcOH	70-71[a]	$C_{14}H_{11}NO_2$	74.64 (74.66)	4.87 (4.88)
IIIb	4-$NO_2C_6H_4$	2-NO_2	85	AcOH	147-148[b]	$C_{14}H_{10}N_2O_4$	62.64 (62.67)	3.71 (3.70)
IIIc	4-ClC_6H_4	2-NO_2	65	EtOH	107-108[c]	$C_{14}H_{10}ClNO_2$	64.73 (64.74)	3.44 (3.46)
IIId	2-$CH_3OC_6H_4$	2-NO_2	50	EtOH	80-81[d]	$C_{15}H_{13}NO_3$	70.56 (70.58)	5.02 (5.00)
IIIe	3-$CH_3C_6H_4$	2-NO_2	50	EtOH (90%)	50-52[e]	$C_{15}H_{13}NO_2$	75.29 (75.31)	5.43 (5.48)
IIIf	3,4-$(CH_3O)_2$-6-BrC_6H_2	2-NO_2	62	AcOH	168-170[f]	$C_{16}H_{14}BrNO_4$	52.76 (52.77)	4.32 (4.34)
IVa	C_6H_5	3-NO_2	65	AcOH	109-110[g]	$C_{14}H_{11}NO_2$	74.65 (74.66)	4.86 (4.88)
IVb	4-$NO_2C_6H_4$	3-NO_2	90	AcOH	218-220[h]	$C_{14}H_{10}NO_4$	62.65 (62.66)	3.70 (3.70)
IVc	4-ClC_6H_4	3-NO_2	70	EtOH (80%)	120-122[i]	$C_{14}H_{10}ClNO_2$	64.75 (64.74)	3.44 (3.46)
IVd	4-$CH_3C_6H_4$	3-NO_2	55	EtOH (90%)	99-100[j]	$C_{15}H_{13}NO_2$	75.29 (75.31)	5.41 (5.48)
IVe	4-$CH_3OC_6H_4$	3-NO_2	58	AcOH	90-91[k]	$C_{15}H_{13}NO_3$	70.54 (70.58)	5.03 (5.09)
IVf	3,4-$(CH_3O)_2C_6H_3$	3-NO_2	60	EtOH	85-90[l]	$C_{16}H_{15}NO_4$	67.34 (67.36)	5.24 (5.26)
IVg	3,4-$(CH_3O)_2$-6-BrC_6H_2	3-NO_2	65	AcOH	145-146[m]	$C_{16}H_{14}BrNO_4$	52.76 (52.77)	4.32 (4.34)
IVh	3,4-$(OCH_2O)C_6H_3$	3-NO_2	70	EtOH	149-150[n]	$C_{15}H_{11}NO_4$	66.87 (66.89)	4.05 (4.09)
V	2-Furyl	3-NO_2	55	EtOH	69-70[o]	$C_{12}H_9NO_3$	66.97 (66.98)	4.01 (4.09)
VI	2-Pyridyl	3-NO_2	55	EtOH	125-126[p]	$C_{13}H_{10}N_2O_2$	68.86 (68.87)	4.40 (4.42)
VII	9-Anthryl	3 NO_2	30	$CHCl_3$ Hexane	115-120[q]	$C_{21}H_{15}NO_2$	80.50 (80.51)	4.77 (4.79)

[a] Lit. [7] 70-72°. [b] Lit. [8] 148°. [c] Lit. [8] 108°. [d] Lit. [8] 81-82°. [e] Lit. [9] 53-54°. [f] Unreported. [g] Lit. [10] 112°. [h] Lit. [10] 220-222°. [i] Lit. [8] 122-123°. [j] Lit. [8] 99°. [k] Lit. [8] 91°. [l, m, n] Unreported. [o] Lit. [11] 70-72°. [p] Lit. [12] 129°. [q] Unreported.

TABLE 2

CHEMICAL SHIFTS δ (ppm) OF *trans*-DIARYL SUBSTITUTED OLEFINS

Compound	Aromatic protons	Olefinic protons	Other groups
IIIa	7.60 - 8.26	7.16	
IIIb	7.64 - 8.40	7.20	
IIId	7.62 - 8.35	7.18	3.88 (OCH_3)
IIIe	7.70 - 8.58	7.28	2.60 (CH_3)
IIIf	7.51 - 8.25	7.16	3.99 (OCH_3)
IVb	7.65 - 8.30	7.28	
IVc	7.64 - 8.42	7.30	
IVe	7.60 - 8.35	7.20	3.90 (OCH_3)
IVf	7.42 - 8.40	7.05	3.98 (OCH_3)
IVg	7.29 - 8.50	7.10	3.94 (OCH_3)
IVh	7.33 - 7.90	7.22	6.12 (O_2CH_2)
V	7.68 - 8.32	7.35	
VII	7.42 - 8.60	7.29	1.25 ($>CH_2$)

The reaction of Ia and Ib with various mono-,di- and tri-substituted benzaldehydes (Scheme 1) at room temperature gave 50-90% yields of *trans-ortho*-nitrostilbenes IIIa-f and *trans-meta*-nitrostilbenes IVa-h. Ylide Ib also reacted smoothly with 2-furfural and picolinealdehyde to give *trans*-2-(*meta*-nitrostyryl) furan (V) and *trans-meta*-nitro-2-stilbazole (VI) respectively. The reaction of ylide Ib with 9-anthrone at elevated temperature gave the exocyclic olefin VII.

In these reactions with carbonyl compounds both ylides Ia and Ib gave olefins to the exclusion of epoxides. This may be due to the electron withdrawing effect of *ortho*-and *meta*-nitro groups.

The *meta*-nitro ylide Ib seems to be more reactive towards carbonyl compounds than the *ortho*-nitro ylide Ia and gives olefins IVa-VII in better yields. The *meta*-nitro ylide reacted equally well with mono-, di- and tri-substituted benzaldehydes and 9-anthrone, whereas the *ortho*-nitro ylide failed to react with 9-anthrone.

The di- and tri-substituted olefins (Table 1) were formed almost exclusively as the *trans*-isomers. Similar exclusive *trans*-olefination has also been reported for the *para*-nitrobenzylidenetriphenylarsenane [4].

The IR spectra of the olefins showed absorptions at 1650-1550 [ν(C = C)] and 985-940 cm^{-1}; the latter absorptions are associated with out-of-plane deformations of hydrogen attached to the *trans*-olefinic system [5]. The NMR spectra ($CDCl_3$) (Table 2) exhibited olefinic protons in the range δ 7.10-7.35 ppm, and aromatic multiplets in the range 7.29-8.60 ppm. The methylene protons in exocyclic olefin VII absorbed at 1.25 ppm.

Experimental

Melting points were determined on a Gallenkamp apparatus and are uncorrected. IR spectra were recorded on a Perkin—Elmer Infrared spectrophotometer in potassium bromide. The NMR spectra ($CDCl_3$) were recorded on a Varian A-60 spectrometer with TMS as an internal standard. All the products were separated and purified by column chromatography using alumina. Purity was checked by TLC.

Preparation of ortho-nitrobenzyltriphenylarsonium bromide (IIa)

A mixture of triphenylarsine (9.18 g, 0.03 mol) and *ortho*-nitrobenzyl bromide (9.28 g, 0.043 mol) was heated as a melt at 100° for 20 h. The mixture was then allowed to stand for one week at room temperature. The resulting solid was washed with ether and crystallized from chloroform/ethyl acetate (1/4) to give white microcrystals of *ortho*-nitrobenzyltriphenylarsonium bromide (IIa) in 20% (3.6 g) yield, m.p. 129-130° (lit. [6] 135°). NMR spectrum ($CDCl_3$):δ 7.29-8.10 (19H, aromatic, multiplet) and 6.00 ppm (2H, methylene protons, singlet). (Found: C, 57.44; H, 4.01. $C_{25}H_{21}AsBrNO_2$ calcd.: C, 57.47; H, 4.02%.)

Preparation of meta-nitrobenzyltriphenylarsonium bromide (IIb)

A mixture of triphenylarsine (9.18 g, 0.03 mol) and *meta*-nitrobenzyl bromide (9.28 g, 0.043 mol) was heated on a steam bath for 3 h. The resulting solid was washed with ether and crystallized from chloroform/n-hexane (1/4) to yield pale yellow crystals of *meta*-nitrobenzyltriphenylarsonium bromide (IIb), yield 14.5 g (80%), m.p. 166-167° (lit. [6] 167-168°). NMR spectrum: δ 7.60-8.25 (19H, aromatic multiplet) and 5.98 ppm (2H, methylene, singlet). (Found C, 57.46; H, 4.00. $C_{25}H_{21}AsBrNO_2$ calcd.: C, 57.47; H, 4.02%.)

Reaction of ylides Ia, Ib with aromatic aldehydes

To a suspension of ylide Ia or Ib, generated from 2.0 g (4 mmol) of salt IIa or IIb and sodium methoxide (4 mmol) in methanol (100 ml) 4 mmol of aromatic aldehyde was added under nitrogen. The mixture was stirred at room temperature for 24 h, the solvent was then evaporated off and the residue was extracted with chloroform. The extract was washed with water, dried and evaporated on a steam bath. The resulting product was chromatographed to yield *trans*-diaryl substituted olefin IIIa-VI (Table 1) which was further purified by crystallization from appropriate solvent.

Reaction of ylide Ib with 9-anthrone

To a suspension of ylide Ib, prepared from 2.0 g (4 mmol) of salt IIb and sodamide (0.19 g, 5 mmol) in anhydrous benzene (120 ml) under nitrogen was added, 0.77 g (4 mmol) of 9-anthrone, and the mixture stirred at 70° for 30 h. Triphenylarsine oxide and unreacted sodamide were removed by filtration, and the filtrate was concentrated on a steam bath under reduced pressure. The residual oil was extracted with benzene and chromatographed to give the exocyclic olefin VII (Table 1).

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