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REACTION OF PHENACYLIDENETRIPHENYLARSENANES WITH α,β-UNSATURATED KETONES: SYNTHESIS OF SOME NEW 2,4,6-TRIARYLPYRIDINES

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Summary

The reaction of some phenacylidenetriphenylarsenanes with substituted benzylideneacetophenones in the presence of ammonium acetate in acetic acid or methanol gave new 2,4,6-triarylpyridines. Ammonium acetate in acetic acid and ammonium acetate in methanol were used as aza cyclization reagents.

Introduction

Arsonium ylides have been the subject of much investigation by synthetic organic chemists [1—8]. They have been used in the synthesis of olefins [1,2,4], epoxides [4], cyclopropanes [4], isoxazolines [8], azirines [4], indoles [8] and a number of heterocyclic systems [3—8]. However, the aza ring closure reaction of arsonium ylides with α,β-unsaturated ketones, leading to the synthesis of pyridine nucleus, has not previously been reported. Continuing our researches on the reactivity of arsonium ylides [9—13], we now describe the reaction of phenylacylidenetriphenylarsenanes with α,β-unsaturated ketones to give some new 2,4,6-triarylpyridines.

Results and discussion

Quaternization of triphenylarsine with substituted phenacyl bromides in anhydrous benzene at reflux temperature gave substituted phenacyltriphenylarsonium bromides (Ia, b) [5—8]. These salts on reaction with sodium ethoxide in ethanol gave substituted phenacylidenetriphenylarsenanes (IIa, b) [5—8] (Scheme 1). The reaction of ylides IIa, b with substituted benzylideneacetophenones (IIIa—j) in the presence of ammonium acetate in acetic acid or meth-

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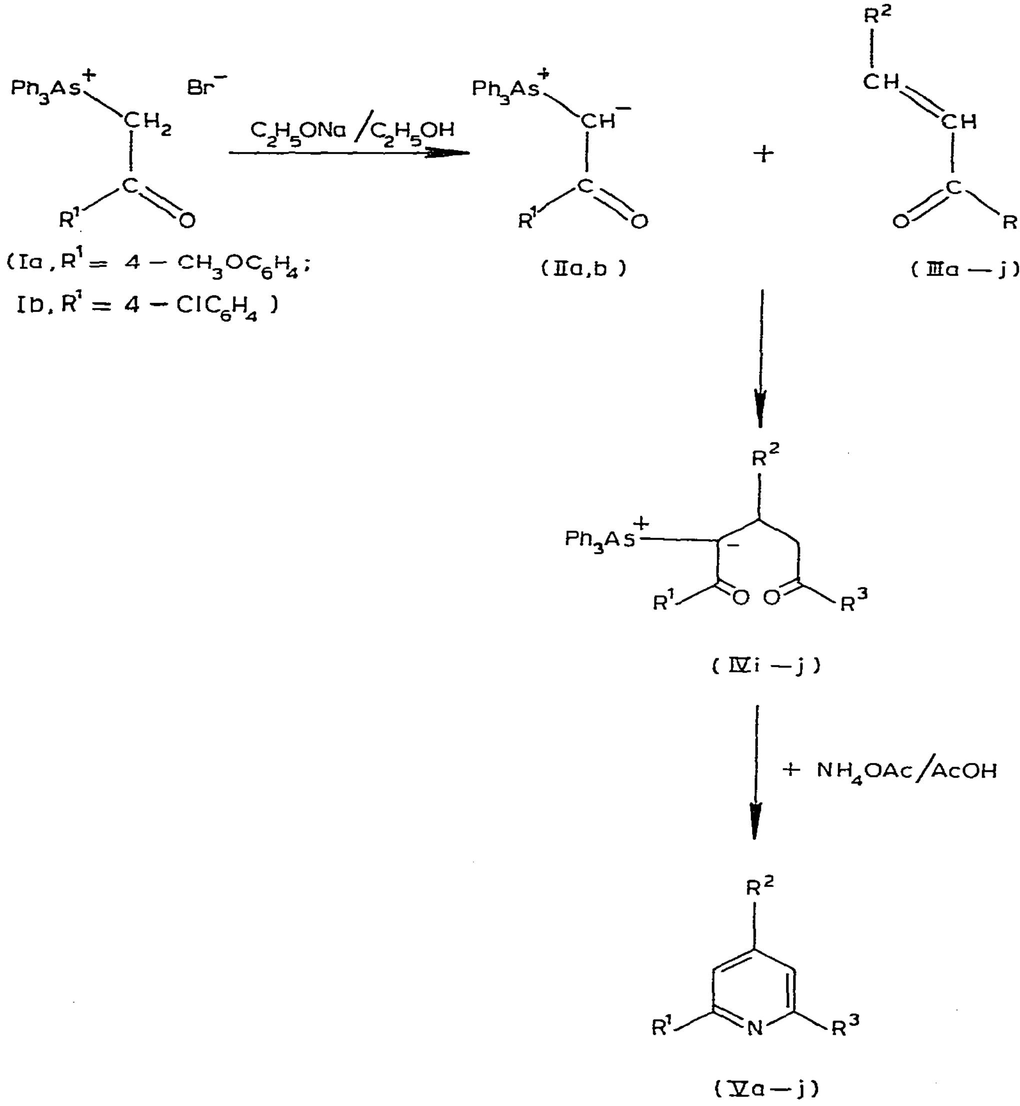
SCHEME 1



anol was carried out under reflux for 4—8 h to give 2,4,6-triarylpyridines (Va—j) in 45—70% yields (Scheme 1). The yield of pyridines Va—j was better when ammonium acetate in acetic acid was used as the aza cyclization reagent.

The reaction presumably proceeds via the nucleophilic attack of ylidic carbanions IIa, b on the β-carbon of the α,β-unsaturated ketones IIIa—j to form 1,5-dionylarsonium betaines (IVa—j), which, in turn, undergo aza ring closure with ammonium acetate to form pyridines Va—j (Scheme 1).

All pyridines Va—j gave satisfactory elemental analyses (Table 1). The structure of the pyridines were confirmed by IR and NMR spectral data (Table 2). The IR spectra of the pyridines show a characteristic absorption band in the region 3025—3000 cm^{-1}, which is assigned to the C—H stretching mode of the

TABLE 1

PHYSICAL PROPERTIES OF 2,4,6-TRIARYLPYRIDINES Va—j

Compound	R^1	R^2	R^3	Yield (%)	Recryst. solvent	M.p. (°C)	Empirical formula	Analysis found(calcd.)(%)		
								C	H	N
Va	4-$CH_3OC_6H_4$	4-$CH_3OC_6H_4$	4-$CH_3C_6H_4$	50	py/MeOH	105—106	$C_{26}H_{23}NO_2$	81.94(81.88)	6.01(6.03)	3.59(3.52)
Vb	4-$CH_3OC_6H_4$	4-$CH_3OC_6H_4$	4-$CH_3OC_6H_4$	55	py/MeCH	131—132	$C_{26}H_{23}NO_3$	78.52(78.58)	5.75(5.79)	3.53(3.50)
Vc	4-$CH_3OC_6H_4$	4-$CH_3OC_6H_4$	4-ClC_6H_4	58	py/MeOH	142—144	$C_{25}H_{21}NO_2Cl$	74.75(74.71)	4.94(4.98)	3.44(3.48)
Vd	4-$CH_3OC_6H_4$	4-$(CH_3O)_2C_6H_3$	4-$OH_3OC_6H_4$	55	py/MeOH	82— 83	$C_{27}H_{25}NO_4$	79.26(79.21)	6.13(6.11)	3.44(3.42)
Ve	4-$CH_3OC_6H_4$	4-ClC_6H_4	4-ClC_6H_4	70	py/MeOH	193—195	$C_{24}H_{17}NOCl_2$	71.15(71.11)	4.21(4.19)	3.41(3.45)
Vf	4-ClC_6H_4	4-$CH_3OC_6H_4$	4-ClC_6H_4	70	py/$CHCl_3$	175—177	$C_{24}H_{17}NOCl_2$	71.14(71.11)	4.17(4.19)	3.43(3.45)
Vg	4-ClC_6H_4	4-$CH_3OC_6H_4$	4-$CH_3OC_6H_4$	65	py/MeOH	169—171	$C_{25}H_{20}NOCl$	77.85(77.82)	5.22(5.18)	3.66(3.63)
Vh	4-ClC_6H_4	3,4-$(CH_3O)_2C_6H_3$	4-$CH_3OC_6H_4$	55	py/$CHCl_3$	130—132	$C_{26}H_{22}NO_3Cl$	72.35(72.30)	5.12(5.09)	3.22(3.24)
Vi	4-ClC_6H_4	C_6H_5	4-ClC_6H_4	50	py/MeOH	124—125	$C_{23}H_{15}NCl_2$	73.45(73.40)	3.95(3.98)	3.74(3.72)
Vj	4-ClC_6H_4	3,4-$O_2CH_2C_6H_3$	4-ClC_6H_4	45	py/MeOH	160—162	$C_{24}H_{15}NO_2Cl_2$	68.61(68.57)	3.59(3.57)	3.30(3.33)

TABLE 2

IR AND NMR SPECTRAL DATA OF PYRIDINES Va—j

Compound	IR data (KBr)(cm^{-1})				NMR data (CDCl$_3$) δ(ppm)
	ν(C=C)	ν(C=N)	ν(C—H)	φ(C—H)	
Va	1585	1515	3020	990	2.35(s, 3 H, CH$_3$); 3.73(s, 6 H, diOCH$_3$); 6.63(s, 1 H, pyH); 6.88(s, 1 H, pyH); 6.97—8.05(m, 12 H, phH).
Vb	1590	1513	3025	995	3.90(s, 9 H, triOCH$_3$); 6.95(s, 1 H, pyH); 7.10(s, 1 H, pyH); 7.20—8.25(m, 12 H, phH).
Vc	1587	1505	3013	988	3.70(s, 6 H, diOCH$_3$); 6.65(s, 1 H, pyH); 6.90(s, 1 H, pyH); 7.20—8.05(m, 12 H, phH).
Vd	1595	1508	3025	993	3.90(s, 12 H, tetraOCH$_3$); 6.90(s, 1 H, pyH); 7.07(s, 1 H, pyH); 7.19—8.20(m, 11 H, phH).
Ve	1598	1510	3008	985	3.75(s, 2 H, OCH$_3$); 6.70(s, 1 H, pyH); 6.80(s, 1 H, pyH); 7.12—8.05(m, 12 H, phH).
Vf	1605	1500	3015	996	3.75(s, 3 H, OCH$_3$); 6.60(s, 1 H, pyH); 6.68(s, 1 H, pyH); 6.70—8.20(m, 12 H, phH).
Vg	1595	1502	3022	988	2.35(s, 3 H, CH$_3$); 3.75(s, 3 H, OCH$_3$); 6.65(s, 1 H, pyH); 6.85(s, 1 H, pyH); 6.98—8.13(m, 12 H, phH).
Vh	1608	1505	3005	980	3.80(s, 9 H, triOCH$_3$); 6.80(s, 1 H, pyH); 6.87(s, 1 H, pyH); 6.95(m, 11 H, phH).
Vi	1615	1498	3020	985	
Vj	1598	1506	3018	992	6.05(s, 2 H, OCH$_2$O); 6.92(s, 1 H, pyH); 7.00(s, 1 H, pyH); 7.15—8.25(m, 11 H, phH).

s = singlet; m = multiplet; py = pyridyl; ph = phenyl.
ν = stretching vibrations; φ = bending (out of plane vibrations).

pyridine nucleus. Two bands in the region 1600 to 1500 cm^{-1} were assigned to the interaction between the C=C and C=N vibration of the pyridine ring. The NMR spectra of the pyridines showed two pyridyl protons in the range δ 6.63—7.00 ppm and the aromatic protons at δ 6.70—8.25 ppm.

Experimental

Melting points were determined on a Gallenkamp apparatus and are uncorrected. IR spectra (KBr) were recorded on a Perkin-Elmer infracord spectrophotometer. The NMR spectra were recorded (CDCl$_3$) on a Varian A-60 spectrometer using TMS as internal standard. All the products were separated and purified by column chromatography using alumina; purity was checked by TLC.

Arsonium salts Ia, b and ylides IIa, b were prepared as previously described [5—8].

Preparation of 2,4,6-triarylpyridines (Va—j)

To a stirred solution of 3 mmoles of ylide IIa, b in 30 ml of glacial acetic acid and ammonium acetate (3 g), a solution of 3 mmoles of α,β-unsaturated ketone IIIa—j in 10 ml of glacial acetic acid was added slowly under nitrogen.

The mixture was refluxed for 5—8 h and left overnight at room temperature. The solution was diluted with cold water (20 ml) and precipitate was separated, washed with methanol and crystallized from suitable solvents to give the required compounds Va—j (Table 1).

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