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REACTION OF PHENACYL- (OR BENZYL-)TRIPHENYLARSONIUM BROMIDE WITH AROMATIC DIAZONIUM SALTS: SYNTHESIS OF 1,4-DIHYDRO-1,2,4,5-TETRAZINES THROUGH ARSENIC YLIDE *

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Summary

The reaction of phenacyl- (or benzyl-)triphenylarsonium bromide with aromatic diazonium salts provides a simple method for synthesizing 1,4-dihydro-1,2,4,5-tetrazines in good yield. The reaction proceeds via the nitrilimine intermediate and the latter dimerizes to yield the corresponding 1,4-dihydro-1,2,4,5-tetrazines. Many 1,4-dihydro-1,2,4,5-tetrazines have been prepared by this method.

Introduction

The chemistry of ylides has attracted a good deal of attention because of their important synthetic applications. As only limited work has been done so far on arsenic ylides, we began a study of their synthetic utility, and have reported the synthesis of some indoles and benzindoles from arsenic ylides [1,2]. We now describe the synthesis of some 1,4-dihydro-1,2,4,5-tetrazines by treatment of phenacyl- (or benzyl-)triphenylarsonium bromide with aromatic diazonium salts.

Huisgen et al. reported the synthesis of some 1,4-dihydro-1,2,4,5-tetrazines by thermolysis of 2,5-disubstituted tetrazoles [3], and suggested that a 'nitrilimine' intermediate was involved [4]. However, the thermolysis was not clean and a number of side-products were formed [4]. The reaction of phenylhydrazones of α-chlorobenzaldehyde [5,6] and α-chloroglyoxalic acid [7] with a base also gives 1,4-dihydro-1,2,4,5-tetrazines, but again the yield is unsatisfactory.

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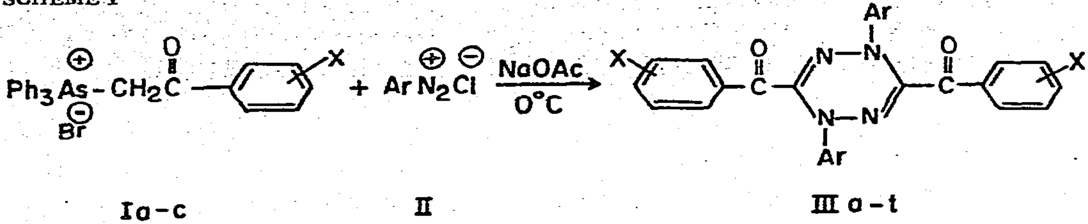
Results and discussion

Phenacyltriphenylarsonium bromide (Ia—Ic) reacted with various aryl diazonium salts (II) in methanol at 0°C in the presence of sodium acetate to give the corresponding 1,4-diaryl-3,6-diaroyl-1,4-dihydro-1,2,4,5-tetrazines (IIIa-t) (Scheme 1).

SCHEME 1



The reactions of aryldiazonium salts with *N*-phenacylpyridinium bromide [8,9] and phenacyldimethylsulphonium bromide [10] have also been studied. In these cases, it was suggested that the diazonium salt reacts directly with the pyridinium or the sulphonium salt to give the ylide [8—10] but this appears to be contrary to the observed facts. The diazonium salt, being electrophilic in nature would be expected to react with the nucleophilic species and it therefore seemed more probable that the arsonium salt would first be converted into the ylide, which would then react with the diazonium salt. Our results support this suggestion. On stirring the arsonium salt with sodium acetate, a yellow colour develops, indicating the generation of the ylide (IV). When the diazonium salt solution is added to the ylide solution, the acetate ion, being a stronger base than the ylide, neutralizes the excess of acid present in the diazonium salt solution and thus the ylide is left to interact with the diazonium salt to yield the species V. The latter subsequently changes into the nitrilimine (VII), which finally undergoes 1,3-dipolar dimerization to yield the 1,4-dihydro-1,2,4,5-tetrazines (III). The suggested mechanism is outlined in Scheme 2.

A similar reaction of benzyltriphenylarsonium bromide (VIII) with phenyldiazonium salt (II) afforded 1,3,4,6-tetraphenyl-1,4-dihydro-1,2,4,5-tetrazine (IX) (Scheme 3), which was identical with the compound prepared by Bamberger et al. [11] by iodine oxidation of benzaldehyde phenylhydrazone.

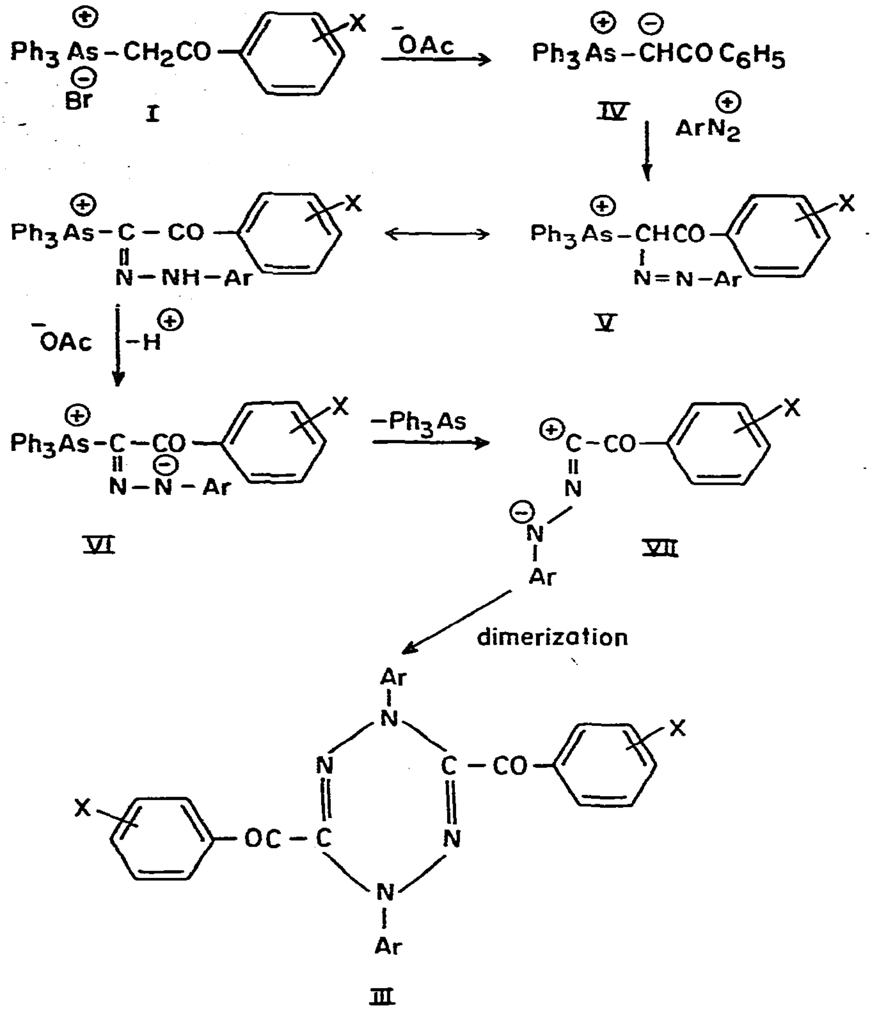
The reactions of phenacyltriphenylarsonium bromide with α- and β-naphthyl diazonium salts were also studied but the yields were poor and the products could not be isolated pure. The low yield can be attributed to steric hindrance by the bulky naphthyl groups.

All the tetrazines, most of which are new, were characterized on the basis of elemental analysis and IR and PMR spectra. In the IR, a sharp peak in the region of 1670—1640 cm^{-1} is attributable to C=O stretching frequency (PhCO). In the PMR spectrum, only a multiplet was observed in the region δ 6.8—8.2 ppm, corresponding to the aromatic protons. In the compounds having methyl group a singlet was observed in the region δ 1.8—2.2 ppm, as expected for methyl protons.

The physical data of the 1,4-dihydro-1,2,4,5-tetrazines (IIIa—IIIt, IX) are summarized in Table 1.

(continued on p. 298)

SCHEME 2



SCHEME 3

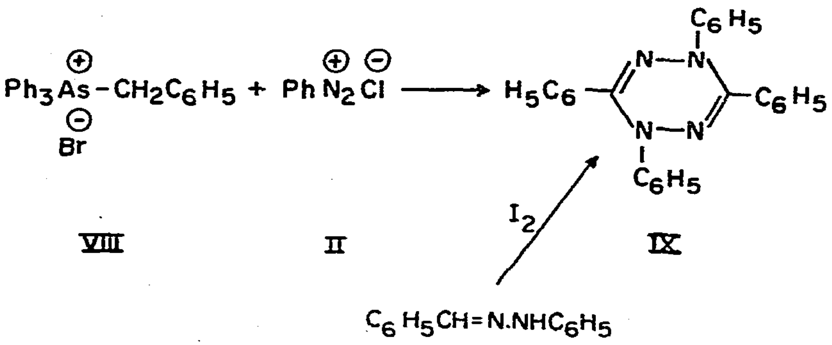


TABLE 1

PHYSICAL CONSTANTS AND ANALYSES FOR THE 1,4-DIHYDRO-1,2,4,5-TETRAZINES

Compound	X	Ar	M.p. (°C)	Yield (%)	Molecular formula	Analysis (Found (calcd.) (%))		
						C	H	N
IIIa	H	C_6H_5	196 [a]	65	$C_{28}H_{20}N_4O_2$	75.64 (75.66)	4.53 (4.54)	12.57 (12.60)
IIIb	H	*p*-MeC_6H_4	148	48	$C_{30}H_{24}N_4O_2$	76.20 (76.25)	5.10 (5.12)	11.83 (11.86)
IIIc	H	*p*-ClC_6H_4	202	76	$C_{28}H_{18}N_4O_2Cl_2$	65.48 (65.49)	3.50 (3.50)	10.82 (10.91)
IIId	H	*p*-$NO_2C_6H_4$	217	72	$C_{28}H_{18}N_6O_6$	62.90 (62.92)	3.38 (3.39)	15.68 (15.72)
IIIe	H	*p*-BrC_6H_4	188	68	$C_{28}H_{18}N_4O_2Br_2$	55.80 (55.81)	2.99 (2.99)	9.21 (9.30)
IIIf	H	*p*-IC_6H_4	179	61	$C_{28}H_{18}N_4O_2I_2$	48.25 (48.27)	2.53 (2.58)	8.00 (8.04)
IIIg	H	*p*-$MeOC_6H_4$	163	50	$C_{30}H_{24}N_4O_4$	71.41 (71.42)	4.79 (4.79)	11.08 (11.10)
IIIh	H	*p*-$EtOC_6H_4$	152	45	$C_{32}H_{28}N_4O_4$	72.16 (72.18)	5.27 (5.26)	10.49 (10.52)
IIIi	*m*-NO_2	C_6H_5	186	60	$C_{28}H_{18}N_6O_6$	62.90 (62.92)	3.36 (3.36)	15.69 (15.72)
IIIj	*m*-NO_2	*p*-$NO_2C_6H_4$	196	67	$C_{28}H_{16}N_8O_{10}$	53.80 (53.84)	2.52 (2.56)	17.89 (17.94)

IIIk	*m*-NO_2	*p*-ClC_6H_4	150—152	60	$C_{28}H_{16}N_6Cl_2O_6$	55.70 (55.72)	2.64 (2.65)	13.90 (13.93)
III l	*m*-NO_2	*p*-MeC_6H_4	178—180	55	$C_{30}H_{22}N_6O_6$	64.02 (64.05)	3.92 (3.94)	14.90 (14.94)
IIIm	*m*-NO_2	*p*-$MeOC_6H_4$	146—147	48	$C_{30}H_{22}N_6O_8$	60.60 (60.61)	3.73 (3.73)	14.12 (14.14)
IIIn	*m*-NO_2	*p*-BrC_6H_4	202	57	$C_{28}H_{16}N_6O_6Br_2$	48.55 (48.55)	2.32 (2.31)	12.10 (12.13)
IIIo	*m*-NO_2	*p*-IC_6H_4	173—174	61	$C_{28}H_{16}N_6O_6I_2$	42.71 (42.74)	2.01 (2.03)	10.60 (10.69)
IIIp	*p*-CH_3	C_6H_5	208—210	56	$C_{30}H_{24}N_4O_2$	76.23 (76.25)	5.11 (5.12)	11.83 (11.86)
IIIq	*p*-CH_3	*p*-$NO_2C_6H_4$	218—220	71	$C_{30}H_{22}N_6O_6$	64.04 (64.05)	3.72 (3.94)	14.90 (14.94)
IIIr	*p*-CH_3	*p*-ClC_6H_4	184—185	73	$C_{30}H_{22}N_4O_2Cl_2$	66.51 (66.54)	4.04 (4.06)	10.16 (10.35)
IIIs	*p*-CH_3	*p*-MeC_6H_4	169—171	62	$C_{32}H_{28}N_4O_2$	76.78 (76.80)	5.57 (5.60)	11.10 (11.20)
IIIt	*p*-CH_3	*p*-BrC_6H_4	158—160	54	$C_{30}H_{22}N_4O_2Br_2$	57.29 (57.30)	3.49 (3.49)	8.81 (8.88)
IX	—	—	202—204 [b]	40	$C_{26}H_{20}N_4$	80.38 (80.39)	5.18 (5.19)	14.40 (14.42)

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[a] Lit. [10] 196°C. [b] Lit. [3] 203—204°C.

Experimental

Melting points are uncorrected. The compounds were purified by recrystallization and their purity checked by TLC. The IR spectra were recorded with KBr pellets on a Perkin—Elmer 337 Grating IR spectrophotometer. The PMR spectra were recorded on a Perkin—Elmer RB-12 spectrometer with tetramethylsilane as internal standard. The spectra of the compounds containing methyl groups were recorded in $CDCl_3$, and other spectra in acetone.

The amines used for the preparation of the diazonium salts, were purified either by distillation or by recrystallization, and an A.R. grade of sodium acetate was used in all the reactions. The arsonium salts were prepared as described in the literature [2].

Reaction of phenacyl- (or benzyl-)triphenylarsonium bromide with aryl diazonium salt

The following general procedure was used for all the reactions. A mixture of arsonium salt (10 mmol in 50 ml methanol) and sodium acetate (50 mmol in 20 ml water) was cooled in an ice bath and stirred, whereupon a yellow colour developed. A separately prepared diazonium salt solution (10 mmol) was added and the mixture was kept in an ice bath for further 3 h. The solid which separated was recrystallized to yield the tetrazine.

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