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HYPERVALENT IODINE IN SYNTHESIS XXXI: FORMATION OF PHOSPHINIMINES AND ARSINIMINES BY NITRENE ROUTE OR NON-NITRENE ROUTE

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Abstract: N-sulfonyltriphenylphosphinimines and N-sulfonyltriphenylarsinimines are prepared by the reaction of triphenylphosphine or triphenylarsine under nitrene-producing conditions with I-N ylide ($PhI{=}NSO_2R$).Triphenylarsinimines can also be generated by a non-nitrene route from triphenylarsine, iodobenzene diacetate, and sulfonamides via triphenylarsine diacetate, $Ph_3As(OAc)_2$.

The phosphinimines were discovered in 1919[1] by Staudinger and are, in principle, extremely interesting intermediates for synthesis of a wide variety of compounds with carbon-nitrogen bond.[2-6]

N-sulfonyltriphenylphosphinimines are members of the family of phosphinimines. In early years, Frederick [7] treated phosphines with anhydrous Chloramine-T to afford the imines, but anhydrous Chloramine-T is explosive and not easily

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available. To date, some other methods to prepare the imines were developed, such as the reaction of sulfonyl azides with triphenylphosphine[8-9], treatment of triphenylphosphine with tetraalkylammonium N-chloro-p-toluenesulfonamides[10], the reaction of triphenylphosphine and sulfonamides with diethyl azodicarboxylate[11], the three-component reaction of triphenylphosphine, carbon tetrachloride and sulfonamide in the presence of triethylamine[12], and the substitution of parent phosphimine with sulfonyl chlorides[13]. In our course of studies on the applications of hypervalent iodine reagents in organic synthesis, we have found that I-N ylide (PhI=NSO_2R), an excellent imido group transfer reagent, can react with triphenylphosphine to afford imines[14] . To the stirred solution of triphenylphosphine in acetonitrile was added an appropriate I-N ylide(1). It was refluxed for required time until the I-N ylide almost completely disappeared. After workup and isolation, the corresponding N-sulfonyltriphenylphosphinimine(2) was obtained in 57-78% yield (Scheme 1 and Table I).

$$Ph_3P + \underset{\mathbf{1}}{PhI{=}NSO_2R} \xrightarrow[-PhI]{CH_3CN} \underset{\mathbf{2}}{Ph_3P{=}NSO_2R}$$

	a	b	c	d
R=	Ph	p-$CH_3C_6H_4$	p-ClC_6H_4	m-$NO_2C_6H_4$

(Scheme 1)

A plausible mechanism for the generation of imines(2) is illustrated in Scheme 2. First, the I-N ylide(1) decomposes to give a nitrene intermediate along with the

expulsion of a molecule of iodobenzene. Subsequently, the nitrene intermediate is captured by triphenylphosphine to give imines(2).

$$\underset{\mathbf{1}}{PhI{=}NSO_2R} \longrightarrow [\,{:}NSO_2R\,] + PhI$$

$$[\,{:}NSO_2R\,] + Ph_3P \longrightarrow \underset{\mathbf{2}}{Ph_3P{=}NSO_2R}$$

(Scheme 2)

Analogous to the imination of triphenylphosphine, imination of triphenylarsine with $PhI{=}NSO_2R$ also occurred readily in a single step to afford corresponding N-sulfonyl-triphenylarsinimine(3) as shown in Scheme 3 and Table I.

$$\underset{}{Ph_3As} + \underset{\mathbf{1}}{PhI{=}NSO_2R} \xrightarrow[-PhI]{CH_3CN} \underset{\mathbf{3}}{Ph_3As{=}NSO_2R}$$

	a	**b**	**c**	**d**
R=	Ph	p-$CH_3C_6H_4$	p-ClC_6H_4	m-$NO_2C_6H_4$

(Scheme 3)

However, a similar reaction with triphenylstibine did not yield the expected N-sulfonyl-triphenylstibinimine, but $Ph_3Sb{=}O$ was isolated instead. It is possible that the imine is formed but is quite unstable relative to hydrolysis.even in the presence of minute quantities of water, and thus produces the oxide and amide.[15]

$$Ph_3Sb + PhI{=}NSO_2R \longrightarrow Ph_3Sb{=}NSO_2R \xrightarrow{H_2O} Ph_3Sb{=}O + RSO_2NH_2$$

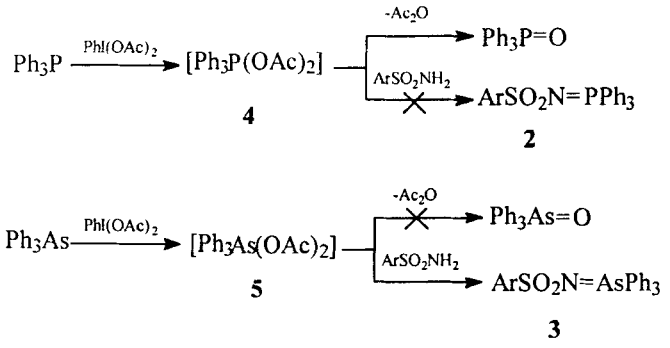
Table I. Synthesis triphylphosphinimines and triphenylarsinimines by a nitrene route.

entry	reaction time (min)	yield * (%)	m.p. (℃)	lit. m.p. (℃)	recryst. solvent
2a	60	57	151-152	157-158[11]	benzene
2b	60	69	187-189	190[11]	ethanol
2c	60	78	215-217	212-215[11]	chloroform
2d	30	75	159-160	168[11]	ethanol
3a	60	68	153-155	152-155[11]	benzene
3b	60	65	189-192	192-193[16]	ethanol
3c	30	85	217-220	—	methanol
3d	5	81	136-138	141-142[16]	ethanol

* isolated yields.

Combined with the fact that, in general, I-N ylide ($PhI{=}NSO_2R$) can be prepared by reaction of iodobenzene diacetate with sulfonamides, we thought that a one pot reaction of iodobenzene diacetate, sulfonamides and triphenylphosphine or triphenylarsine for preparing their imines is possible. According to this, we allowed sulfonamides to react with $PhI(OAc)_2$ and triphenylphosphine or triphenylarsine in dichloromethane at room temperature. After workup and isolation, only arsinimines were obtained as shown in Table II. Instead of the expected phosphinimines, $Ph_3P{=}O$ was isolated. This adumbrates a new non-nitrene route. Analogous to the reaction of sulfonamide, triphenylarisine with lead

tetraacetate[17], we believe that arsinimines formation proceeds via reaction of iodobenzene diacetate with triphenylarsine to give triphenylarsine diacetate(5), which then reacts with the amide. When triphenylphosphine was used, an elimination of postulated intermidiate(4) readily occurred to afford $Ph_3P{=}O$.(Scheme 4)



(Scheme 4)

We also treated triphenylstibine with $PhI(OAc)_2$ and sulfonamides. Only $Ph_3Sb(OAc)_2$ was obtained. It fails to react with sulfonamides or to eliminate from acetic anhydride even in the presence of base.

In the summary, we have simple methods for the preparation N-sulfonyl-triphenylphosphinimines and N-sulfonyltriphenylarsinimines. They have some advantages over others such as mild reactiom conditions, simple procedure and avoiding the use of toxic agents, such as LTA and azides.

Table II. Synthesis triphenylarsinimines by a non-nitrene route.

Entry	reaction time (h)	yield* (%)
3a	2	56
3b	1.5	72
3c	1	78
3d	2	63

* isolated yields.

Experimental:

^{1}HNMR spectra were recorded on PMX-60 spectrometer. Infrared spectra were determined on PE-683 Infrared Spectrophotometer. Elemental analyses were performed on a Carlo Erbal 1107 instrument. Dichloromethane was distilled from CaH_2, acetonitrile from P_2O_5 prior to use.

Typical procedure for the preparation of N-sulfonyltriphenylphosphinimines and N-sulfonyltriphenylarsinimines by a nitrene route: Under stirring, 5 mmol of appropriate I-N ylide was added to the solution of 5 mmol triphenylphosphine or triphenylarsine in 20 mL dry MeCN, After refluxing for required time (Table 1), the mixture was then diluted with brine and extracted with dichloromethane. The extract was washed with water, and dried over anhydrous $MgSO_4$. After removal of the solvent , the residue was recrystallized from the solvent shown in Table I to give pure triphenylphosphinimines(**2a-d**) or triphenylarsinimines(**3a-d**). Representative spectroscopic and analytical data are shown below.

2a IR (KBr,cm^{-1}) 1270, 1150, 1140, 800. ^{1}HNMR (δ, ppm) 7.2-7.8 (m, 19H).

2b IR (KBr,cm^{-1}) 1270, 1150, 1140, 785. ^{1}HNMR (δ, ppm) 2.25 (s, 3H), 6.9-7.1 (m, 2H), 7.3-7.8 (m, 17H).

2c IR (KBr,cm^{-1}) 1270, 1155, 1140, 800. ^{1}HNMR (δ, ppm) 7.1-7.3 (m, 2H),7.4-8.1 (m, 17H).

2d IR (KBr,cm^{-1}) 1530, 1350, 1280, 1160, 1145, 800. ^{1}HNMR (δ, ppm) 7.2-7.8 (m, 17H), 7.9-8.2 (m, 2H).

3a IR (KBr,cm^{-1}) 1250, 1130, 1040, 800. ^{1}HNMR (δ, ppm) 7.1-7.7 (m, 2H).

3b IR (KBr,cm^{-1}) 1255, 1130, 1040, 815. ^{1}HNMR (δ, ppm) 2.23 (s,3H), 6.9-7.2 (m, 2H), 7.3-7.9 (m, 17H).

3c IR (KBr,cm^{-1}) 1260, 1135, 1030, 820. ^{1}HNMR (δ, ppm) 7.1-7.4 (m, 2H), 7.5-8.2 (m, 17H). Anal. Calcd for $C_{24}H_{19}AsClNO_2S$: C, 58.13; H, 3.86; N, 2.82. Found: C, 58.27; H, 3.93; N, 2.85.

3d IR (KBr,cm^{-1}) 1530, 1350,1265, 1140, 1020, 805. ^{1}HNMR (δ, ppm) 7.1-7.8 (m, 17H), 7.9-8.2 (m, 2H).

Typical procedure for the preparation of N-sulfonyltriphenylarsinimines by a non-nitrene route: Iodobenzene diacetate (1.41 g, 4.4 mmol) was added in small portions to a solution of sulfonamide (4 mmol) and triphenylarsine (3.66 g,

12 mmol) in 30 mL anhydrous methylene chloride with stirring. After the appropriate reaction time as shown in Table II, the mixture was poured into water (150 mL) and extracted with methylene chloride (3 × 50 mL). The extract was washed with water, and dried over anhydrous $MgSO_4$. After removal of the solvent, and the residue was recrystallized from appropriate solvent to give pure arsinimine.

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