

Ylide Reactions of Triphenylarsine Phenylimine

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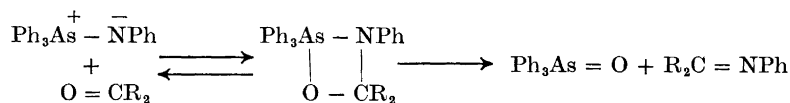
Triphenylarsine phenylimine reacts with aldehydes, ketones, isocyanates, isothiocyanates, nitroso compounds, quinones, carbon disulfide, sulfur dioxide, dimethyl acetylenedicarboxylate, and nitrile oxides. The compound also easily undergoes alkylation and protonation. The reaction with ketones and aldehydes leads to ketimines and aldimines. In the reaction with nitrile oxides and dimethyl acetylenedicarboxylate 1:1 adducts are formed.

Some time ago the present author reported that treatment of certain isocyanates and *N*-sulfinyl amides with triphenylarsine oxide leads to the corresponding triphenylarsine imines in high yield.¹

Almost no chemical studies have been reported for arsine imines, and an examination of their properties seemed to be of importance. The only members of this class of compounds known so far are a series of carbonyl- and sulfonyl-stabilized derivatives where the powerful electron withdrawal effect of the carbonyl resp. sulfonyl group strongly decreases the electron density on the nitrogen atom, thereby making these compounds very poor nucleophiles. In a preliminary experiment the present author tried to react *p*-nitrobenzaldehyde with triphenylarsine *N*-*p*-toluenesulfonylimine in boiling benzene. The reactants were recovered unchanged. In spite of this negative result, arsine imines were assumed to be more reactive than the corresponding phosphine imines since the basicity sequence for the imines is $\text{As} > \text{P}$.² The lack of reactivity in the above-mentioned experiment is attributed to the low nucleophilicity of the imine nitrogen due to delocalization of the negative charge onto the *p*-toluenesulfonyl group. Accordingly, it was decided to prepare some arsine imines where delocalization of the negative charge through the carbon portion of the ylide is less effective. Attempts to prepare triphenylarsine *N*-methylimine was unsuccessful, but the more stable *N*-phenyl and *N*- α -naphthyl derivatives were easily prepared.

Reactions with carbonyl compounds. It is assumed that the mechanism of the reactions between triphenylarsine phenylimine and carbonyl compounds parallels that of the Wittig reaction. If this is so, the first step is a nucleophilic attack by the nitrogen atom of the imine on the carbonyl carbon synchronized

with an attack by the oxygen of the carbonyl group on arsenic (Scheme 1). The intermediate thus formed is then converted to triphenylarsine oxide and a Schiff base.



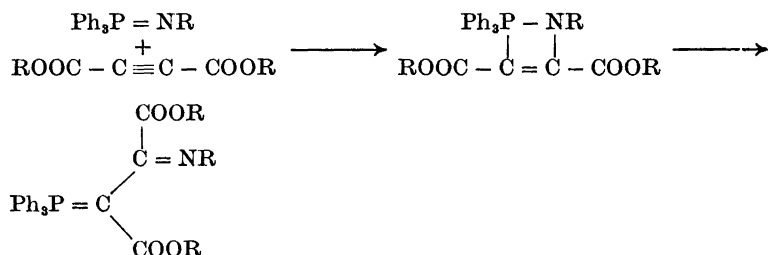
Scheme 1.

This route is probably also followed in the reactions between phosphine imines and carbonyl compounds.^{3,4} There is, however, a marked difference in the reactivity between triphenylarsine phenylimine and its phosphorus analogue. The phosphine imine is reported to react with benzophenone only when heated at 150° for 22 h.⁵ Triphenylarsine phenylimine, however, gives an excellent yield of diphenylmethyldene aniline when heated for a few minutes with benzophenone in boiling benzene.

The enhanced reactivity of the triphenylarsine phenylimine is also demonstrated by its reaction under mild conditions with quinones and nitroso compounds.⁶ The difference in reactivity between triphenylarsine resp. triphenylphosphine phenylimine in these reactions must be attributed to a much higher reactivity of the former in the first step (Scheme 1). The increased nucleophilicity of the arsenic compound indicates that the ionic structure $\text{Ph}_3\text{As}^+ - \text{NPh}^-$ contributes more to the actual structure, $\text{Ph}_3\text{As}^+ - \text{NPh}^- \leftrightarrow \text{Ph}_3\text{As} = \text{NPh}$, than does $\text{Ph}_3\text{P} - \text{NPh}$ in the analogous phosphorus case. This conclusion is in accordance with that expressed by Johnson on the basis of studies of arsonium resp. phosphonium fluorenylides that arsenic is less capable than phosphorus of stabilizing the negative charge on the adjacent carbanion by valence shell expansion.⁷ Triphenylarsine phenylimine is less reactive, however, than its phosphorus analogue in the reaction with carbon dioxide and phenyl isocyanate. In an attempt to react the compound with carbon dioxide the triphenylarsine phenylimine was recovered unchanged when carbon dioxide had been bubbled through a solution of the compound in boiling benzene for 14 h. The low reactivity against phenyl isocyanate is also remarkable, since triphenylphosphine phenylimine reacts very rapidly with this compound, even at low temperatures. As demonstrated by its fast reaction with carbonyl compounds, it is evident that triphenylarsine phenylimine is a far better nucleophile than its phosphorus analogue. It is possible, however, that the rate of the second step of the reaction is decreased when phosphorus is replaced with arsenic, and that the decomposition of the penta-covalent cyclic intermediate in certain cases becomes rate controlling. This may be the reason why the arsenic compound shows decreased reactivity towards phenyl isocyanate and carbon dioxide as compared to its phosphorus analogue. It should be mentioned, however, that the failure of triphenylarsine phenylimine to react with carbon dioxide may be

partly ascribed to the low concentration of this compound in the reaction mixture, as the reaction was carried out in boiling benzene.

The reaction with dimethyl acetylenedicarboxylate. Triphenylarsine phenylimine reacts with dimethyl acetylenedicarboxylate under formation of a 1 : 1 adduct, m.p. 177°C. IR spectra show two different carbonyl groups at 1734 and 1658 cm^{-1} . It seems, therefore, that the reaction with acetylenes is strictly analogous to that of phosphine imines:⁸



The reaction with triphenylacetoneitrile N-oxide. Recently several workers have been concerned with the reactions of phosphorus ylides with 1,3 dipoles, especially nitrile oxides.⁹⁻¹¹

In the reaction between triphenylarsine phenylimine and triphenylacetoneitrile *N*-oxide a 1 : 1 adduct is formed



The structure assigned to the product 1,2,4,5- As^{V} -oxadiazarsole (1) is based on the analogous reaction of methylene triphenylphosphorane with benzonitrile *N*-oxide where the product is shown to be the 4,5-dihydro-1,2,5 P^{V} -oxazaphosphole (2).¹²



EXPERIMENTAL

4-Nitrobenzylidene aniline. In a four-necked flask fitted with a stirrer, dropping funnel, nitrogen inlet, and a condenser with a drying tube, 2.4 g of triphenylarsine oxide dissolved in dry benzene was placed. 0.89 g of phenyl isocyanate dissolved in benzene was added dropwise. The temperature of the reaction mixture was held at 5–6° during the addition. 1.0 g of *p*-nitrobenzaldehyde dissolved in absolute benzene was then added and most of the benzene was distilled off. The product was dissolved in ether and recrystallized; yield 0.7 g. The infrared spectrum of the compound was identical with that of an authentic sample of 4-nitrobenzylidene aniline, m.p. 93°, lit.¹⁸ 93°.

Diphenylmethylidene aniline. To a solution of triphenylarsine phenylimine prepared from 1.6 g triphenylarsine oxide and 0.58 g phenyl isocyanate a solution of 0.9 g benzoquinone in dry benzene was added. The reaction mixture was heated for 1 hour after the addition was completed. Most of the benzene was distilled off and the product was freed from triphenylarsine oxide by treatment with ether; yield 0.9 g. The melting point after recrystallization from ethanol was 112°. Lit.¹⁴ 116°. The product was shown by mixture melting point and thin layer chromatography to be identical with a sample prepared by the method of Reddelien.¹⁵

N,N'-Diphenyl p-benzoquinone diimine. To a solution of 0.01 mol of triphenylarsine phenylimine prepared as previously described, 0.005 mol of benzoquinone was added. The resulting deep red solution was concentrated in vacuum. After addition of ether to the concentrated solution most of the triphenylarsine oxide was filtered off. The ether soluble product was recrystallized from absolute ethanol, m.p. 180°, undepressed by admixture of an authentic sample. The product was also identified by its infrared spectrum.

N-Phenyl p-benzoquinone imine. A benzene solution of triphenylarsine phenylimine was prepared from 1.5 g phenyl isocyanate and 4.1 g triphenylarsine oxide. Benzoquinone (0.9 g) was added and it was observed that the yellow colour of the arsine imine solution was discharged immediately, producing the intense red colour of the benzoquinone imine. Most of the benzene was distilled off and the product recrystallized from ligroin. Yield 1.2 g, m.p. 101°, lit.¹⁶ 100–101°. The infrared spectrum of the compound was identical with that of an authentic sample.

N,N'-Diphenyl 1,4-naphthoquinone diimine was synthesized in an analogous way from triphenylarsine phenylimine and 1,4-naphthoquinone. The product was crystallized from ether. M.p. 185°, lit.¹⁷ 187°. For further identification 0.2 g of the product was dissolved in 3 ml 48 % sulfuric acid. The solution was allowed to stand a few minutes, whereafter 3 ml of water were added. The mixture was then partially neutralized with 0.1 N sodium hydroxide solution, and the product was extracted with ether. Most of the ether was distilled off and the residue was dissolved in ethanol and recrystallized several times, m.p. 123°. An authentic sample of 1,4-naphthoquinone had m.p. 120–124°. The infrared spectra of the two compounds were identical. The aqueous solution was made alkaline with sodium hydroxide solution and extracted with benzene. The benzene solution was dried, whereafter 6 ml acetic anhydride were added. The solvent was evaporated at reduced pressure and the residue recrystallized, m.p. 113°, undepressed by admixture of an authentic sample of acetanilide.

Diphenylcarbodiimide. To a solution of 0.01 mol of triphenylarsine phenylimine in benzene 0.01 mol of phenyl isothiocyanate was added. The reaction mixture was heated for 2 h. The product was identified by its infrared spectrum without isolation. The infrared spectra showed a quantitative transformation of the isothiocyanate into diphenylcarbodiimide. 1.9 g of triphenylarsine sulphide was separated before running the infrared spectra. M.p. 160–162°, lit.¹⁸ 162°.

Phenyl isothiocyanate. A solution of 0.01 mol of triphenylarsine phenylimine in benzene was prepared as previously described. Excess of carbon disulphide was added and the reaction mixture was heated for 2–3 h. Most of the benzene was distilled off and 2.7 g of triphenylarsine sulphide was filtered away. The filtrate was shown to be a mixture of phenyl isothiocyanate and diphenylcarbodiimide by its infrared spectrum.

N-Sulfinyl aniline. 0.01 mol of triphenylarsine phenylimine was dissolved in 100 ml benzene and dry sulphur dioxide was bubbled through the warm solution. Gas chromatographic analysis of the reaction mixture showed the presence of *N*-sulfinyl aniline.

Adduct from dimethyl acetylenedicarboxylate and triphenylarsine phenylimine. 1.3 g of the ester was added to an equivalent amount of triphenylarsine phenylimine prepared as previously described. The solvent was removed and the resulting oil was triturated with ether until it solidified.

The product was recrystallized two times from chloroform-ether. The adduct, 2.5 g, had m.p. 177°C (Found: C 67.06; H 4.96; N 2.83. Calc. for C₃₀H₂₆AsNO₄: C 66.8; H 4.86; N 2.60). IR spectrum: peaks (strong) at 1734 cm⁻¹ (ester carbonyl) and 1658 cm⁻¹ (ester carbonyl, the frequency of the stretching vibration is displaced downwards due to a strong contribution from the enolate structure in the resonance hybrid.) The PMR spectrum exhibited singlets at δ 3.24 (3H) and 3.60 (3H) and multiplets at δ 6.15–7.80 (20H).

Adduct from triphenylacetoneitrile N-oxide and triphenylarsine phenylimine. 1.2 g of triphenylacetoneitrile N-oxide was added to the warm solution of an equivalent quantity of the arsine imine in benzene. The reaction mixture was heated for 2 h with stirring, whereafter most of the benzene was distilled off. Ether was added and the product crystallized after several days. Recrystallization from benzene+ether yielded 0.7 g of a white solid, m.p. 182°. IR spectrum: Peak at 1690 cm^{-1} (strong), probably: C=N. The spectrum also indicated the presence of water of crystallization. (Found: C 75.35; H 5.30; N 3.80. Calc. for $\text{C}_{44}\text{H}_{35}\text{AsN}_2\text{O}\cdot\text{H}_2\text{O}$: C 75.41; H 5.32; N 3.99.) The mass spectrum showed no parent molecular ion peak M at m/e 700. The ready expulsion of triphenylarsine oxide accounts for the total absence of M in the spectrum and represents just what one would have expected of a molecule of the proposed structure. The principal high mass peaks occurred at m/e 378 (M - Ph_3AsO) 321, 243 (Ph_3C), 229, 227 and a series of other skeletal rearrangement products from triphenylarsine.

Reaction with methyl iodide. The triphenylarsine phenylimine was heated a short time with a large excess of methyl iodide in boiling benzene. Most of the solvent was removed and the product washed several times with hot benzene. The resulting red oil was characterized by its PMR spectrum which, besides the low field part of the spectrum due to the phenyl groups, shows a high field signal at 2.82 ppm. The signals due to the methyl and phenyl groups, respectively, are in the ratio 3 : 20 to each other.

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