

Syntheses and Reactions of Arsinic Imines

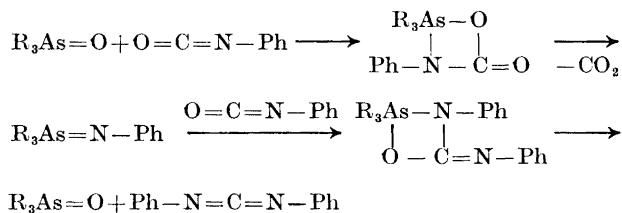
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Syntheses of triphenylarsine benzoylimine resp. acetylimine from triphenylarsine oxide and benzoyl- resp. acetylisocyanate are reported. The benzoyl derivative was also synthesized from triphenylarsine dibromide and benzamide. Some reactions of the arsinic imines are studied.

Contrary to phosphine imines, very few arsinic imines are reported in the literature. The arsinic imines reported have been prepared by the action of arsinics on chloramine salts,¹ or by treating amino arsonium salts with sodamide in liquid ammonia.²

It has been suspected, however, that arsinic imines are generated as intermediates in the reaction between arsinic oxides and phenyl isocyanate leading to diphenyl carbodiimide.³

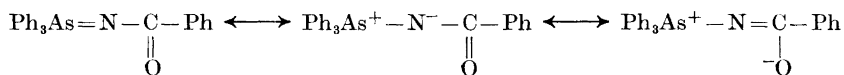


Scheme 1.

The initial step of this reaction is believed to be formation of the arsinic imine, $\text{R}_3\text{As}=\text{N}-\text{Ph}$, in a slow reaction between arsinic oxide and one molecule of phenyl isocyanate. In a second, and much faster step, the arsinic imine is thought to react with a new molecule of isocyanate to afford the carbodiimide (Scheme 1).

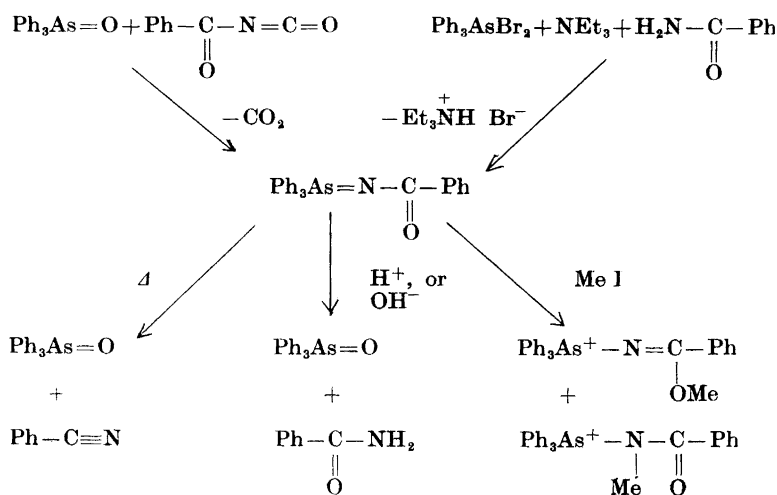
Kinetic data available for phosphine oxides which undergo the same reaction, shows that phosphine imines react 10^5-10^7 times faster with phenyl isocyanate than corresponding phosphine oxides.⁴ If there is a similar rate ratio between the two steps in corresponding arsinic compounds, it would be

impossible to trap the arsine imines in this reaction. However, assuming that the postulated mechanism in Scheme 1 is correct, one might expect that stabilized isocyanates might produce fairly stable arsine imine intermediates. This assumption was confirmed when it was found that the reaction of triphenylarsine oxide and benzoyl- resp. acetyl isocyanate gave excellent yields of the corresponding arsine imines. In these cases the arsine imines will be strongly stabilized through resonance with the carbonyl group:



The low infrared stretching frequency of the carbonyl group at 1530 cm^{-1} resp. 1550 cm^{-1} , clearly demonstrates the importance of the above resonance structures. The delocalization of electronic density between nitrogen, arsenic, and oxygen, lowers the nucleophilicity of nitrogen and correspondingly reduces its reactivity towards the carbonyl carbon of the isocyanate. This is also illustrated by the fact that triphenylarsine benzoylimine undergoes alkylation with methyl iodide to afford a mixture of the *O*-alkylated and *N*-alkylated products.

The present isolation of triphenyl arsine benzoyl- resp. acetyl imines strongly supports the postulated imine intermediate in the carbodiimide syntheses and are in agreement with the mechanism shown in Scheme 1; a nucleophilic attack of the oxygen of phosphine oxide resp. arsine oxide on the carbonyl carbon of the isocyanate.³ The first step is thus completed by the attack of the imine nitrogen on phosphorus, resp. arsenic through formation of a four-membered ring transition state, forming carbon dioxide and phosphine, resp., arsine imine.⁴

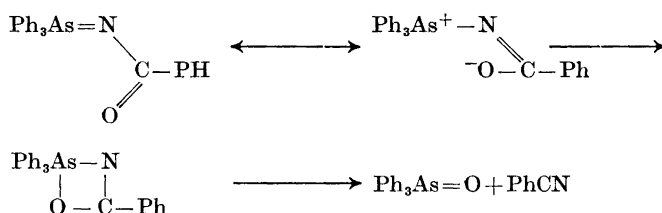


Scheme 2.

In the present study triphenylarsine benzoylimine has also been synthesized by the action of triethylamine and benzamide on triphenylarsine dibromide. Several phosphine imines have earlier been synthesized by this method,⁵ but as far as the author knows, the method has not been used for synthesis of arsine imines. An attempt to synthesize triphenylarsine acetylimine along the same route was unsuccessful.

In Scheme 2 an outline of the synthesis and some reactions of triphenylarsine benzoylimine are presented.

It is seen that triphenylarsine benzoylimine decomposes to triphenylarsine oxide and benzonitrile when heated. This reaction seems to proceed in a manner analogous to that for the triphenylphosphine benzoylimine,⁶ probably *via* a four-membered transition state:



The arsine imines are stable on exposure to the atmosphere and to water, but are hydrolysed in basic as well as acidic media. They seem to be more unstable to hydrolysis than the corresponding phosphine imines.

EXPERIMENTAL

Triphenylarsine oxide was carefully freed from water by azeotropic distillation with benzene, and thereafter recrystallized from the warm benzene solution, m.p. 192°, lit.⁷ 192°. Benzoyl isocyanate was synthesized according to the method of Billeter.⁸ His procedure was, however, slightly modified. To a suspension of silver isocyanate in absolute benzene was added a solution of an equimolecular amount of benzoyl chloride in absolute benzene; the reaction was carried out under dry nitrogen with vigorous stirring. After dropwise addition of the benzoyl chloride, the mixture was heated during 2 h. Upon distillation excellent yield of benzoyl isocyanate was obtained, b.p.₁₂: 87°, lit.⁸ b.p.₁₀ 88°. The product crystallized in the condenser during distillation. All operations with benzoyl isocyanate were carried out under dry nitrogen because of its extreme reactivity towards humidity.

Acetyl isocyanate was synthesized in an analogous manner from acetyl chloride and silver isocyanate, b.p. 81°, lit.⁹ 80°.

Triphenylarsine benzoylimine. a) *From triphenylarsine oxide and benzoyl isocyanate.* The reaction was carried out by dropwise addition of 0.002 mole of benzoyl isocyanate in absolute benzene to a suspension of 0.64 g (0.002 mole) of triphenylarsine oxide in absolute benzene. Dry nitrogen was passed through the apparatus during the operations. The reaction mixture was heated for 10 min after the addition was completed. Most of the benzene was distilled off, and the product crystallized in quantitative yield. It was recrystallized from a mixture of benzene and petroleum ether, m.p. 184–185°. IR spectrum: peaks at 1330 cm⁻¹ (strong), probably: As=N, and 1535 cm⁻¹ (strong) C=O. (Found: C 71.14; H 4.58. Calc. for C₂₅H₂₀AsNO: C 70.60; H 4.74).

b) *From triphenylarsine and benzamide.* In a four-necked flask fitted with a stirrer, dropping funnel, nitrogen inlet, and a condenser with drying tube, was placed 3.0 of

triphenylarsine dissolved in dry benzene. 1.6 g of bromine dissolved in benzene was added dropwise, then 1.7 g of triethylamine, and finally 1.2 g of benzamide in dry benzene. Stirring was continued over night. Triethylammonium bromide was then filtered off, whereafter most of the benzene in the filtrate was distilled off. The product crystallized on cooling of the concentrated solution. It was recrystallized two times, m.p. 184–185°C. The melting point of a mixture of the products from method a) and b) showed no depression, and the infrared spectra of the two products were identical.

Triphenylarsine acetylimine. a) *From triphenylarsine oxide and acetyl isocyanate.* The reaction was carried out exactly as for triphenylarsine benzoylimine. The product was recrystallized from benzene-petroleum ether, m.p. 170°. The infrared spectrum showed strong absorptions at 1310 cm^{-1} (As=N) and 1550 cm^{-1} (C=O).

b) *From triphenylarsine and acetamide.* The reaction was carried out as for the benzoylimine analogue, but no triphenylarsine acetylimine could be detected from this reaction. The product, a crystalline solid, insoluble in water and benzene, has not been identified.

Alkaline hydrolysis of triphenylarsine benzoylimine. 0.5 g of triphenylarsine benzoylimine was heated with stirring in a 10 % solution of NaOH for 1 to 2 h. The mixture was cooled, and the precipitate filtered off. This was freed from water by azeotropic distillation with benzene, and had after recrystallization m.p. 192°C. The compound was shown by its IR spectrum to be triphenylarsine oxide. From the water solution was isolated a compound with m.p. 126°. This compound was shown to be benzamide by its infrared spectrum.

Acid hydrolysis of triphenylarsine benzoylimine. 0.5 g of the imine was dissolved in 20 ml ethanol and 3 ml 1 N HCl was added. The mixture was boiled a short time, and the ethanol was distilled off. The concentrated water solution was neutralized with 0.1 N NaOH, and the precipitate collected, dried by azeotropic distillation with benzene, and recrystallized, m.p. 192°. It was shown to be triphenylarsine oxide by comparison with an authentic sample. The filtrate was concentrated by evaporation *in vacuo*. The precipitated solid was recrystallized from water, m.p. 124–126°. Its IR spectrum showed it to be benzamide contaminated with a small amount of triphenylarsine oxide.

Pyrolysis of triphenylarsine benzoylimine. 0.5 g of the substance was placed in a semimicro distillation apparatus and heated a little above its melting point. The distillate had the characteristic smell of phenyl cyanide, and was identified by its infrared spectrum. The residue was recrystallized from benzene-petroleum ether, m.p. 192°. Its infrared spectrum was identical with that of an authentic sample of triphenylarsine oxide.

Alkylation of triphenylarsine benzoylimine. A mixture of triphenylarsine benzoylimine and methyl iodide was refluxed for 5 h. Most of the methyl iodide was distilled off, and to the remaining concentrated solution was added a little petroleum ether. A red oil separated which crystallized on treatment with petroleum ether. The NMR spectrum of this compound showed, in addition to the phenyl protons at δ 7.4–8, signals at 3.5, 3, and 3.08 δ . The ratio between the latter 3 signals and the phenyl protons was 3:20. The peak at 3.5 δ probably arises from the methyl group on nitrogen, and the peaks at 3.0 and 3.08 δ from the *O*-alkylated product. The infrared spectrum of the compound shows a strong, broad absorption band at 1640 cm^{-1} .

REFERENCES

1. Appel, R. and Wagner, D. *Angew. Chem.* **72** (1960) 209.
2. Mann, F. G. and Chaplin, E. J. *J. Chem. Soc.* **1937** 527.
3. Monagle, J. J. *J. Org. Chem.* **27** (1962) 3851.
4. Aksnes, G. and Frøyen, P. *To be published.*
5. Horner, L. and Hoffmann, H. *Angew. Chem.* **68** (1956) 473.
6. Staudinger, H. and Hauser, E. *Helv. Chim. Acta* **4** (1921) 861.
7. Pascal, P. *Bull. Soc. Chim. France* **33** (4) (1923) 171.
8. Billeter, O. *C. Ber.* **36** (1903) 3218.
9. Billeter, O. *C. Ber.* **36** (1903) 3213.

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