

Syntheses of Some Arsinic Imine Derivatives

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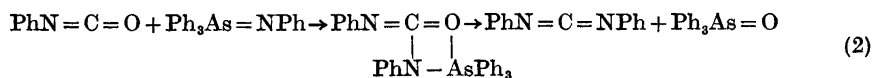
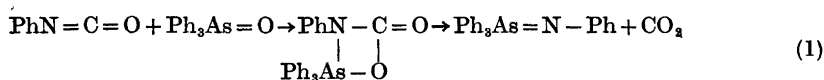
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Syntheses of triphenylarsine imine derivatives from triphenylarsine oxide and a variety of isocyanates, *N*-sulfinyl amines, and *N*-sulfinyl amides are reported. The general applicability of the reaction in the syntheses of arsinic imines have been studied. *N*-Sulfinyl derivatives, where electron withdrawing substituents as phosphoryl or sulfonyl are attached to the cumulene system, react much faster with triphenylarsine oxide than *N*-sulfinyl amines. This is in contrast to the behaviour of the analogous isocyanates in the same reaction.

In a previous paper,¹ syntheses of arsinic imine derivatives from benzoyl isocyanate or acetyl isocyanate, respectively, and triphenylarsine oxide were reported. Continuing along this line, the reactions of several other isocyanates, *N*-sulfinyl amines and *N*-sulfinyl amides, with triphenylarsine oxide, have been studied.

A point of special interest, in this context, has been the synthesis of triphenylarsine phenylimine. None of the methods reported in the literature for preparation of arsinic imines is applicable in this case.

The reaction between triphenylarsine oxide and phenyl isocyanate has been studied by Monagle.² The reaction led to formation of diphenyl carbodiimide and carbon dioxide; triphenylarsine oxide was recovered. This result seemed to indicate that the formation of the arsinic imine was the slow step in the postulated reaction scheme:

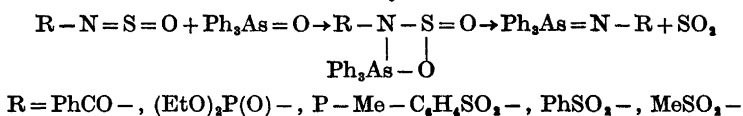
*Scheme 1.*

Such a conclusion seemed very reasonable, since kinetic data available for triphenylphosphine oxide, which undergoes the same reaction, show that triphenylphosphine phenylimine reacts 10^6 – 10^7 times faster with phenyl

isocyanate than triphenylphosphine oxide.³ The present isolation of triphenylarsine phenylimine from the reaction between phenyl isocyanate and triphenylarsine oxide shows, however, that the second step in the reaction, step (2) in Scheme 1, is rate determining.

When the reaction is carried out under mild conditions, no diphenyl carbodiimide is formed. The reaction stops at the arsine imine stage. If the temperature is increased, the reaction is completed with the formation of diphenyl carbodiimide. Similarly, arsine imine derivatives were made from *p*-toluene sulfonyl isocyanate, diphenylphosphinyl isocyanate, and α -naphthyl isocyanate. All the reactions were completed in a few minutes in refluxing benzene.

N-Sulfinyl amides react similarly with triphenylarsine oxide to give high yields of the corresponding arsine imines. Sulfur dioxide is evolved during the reactions, and the mechanism is thought to parallel rather closely the mechanism of the reaction between isocyanates and arsine oxides:



The reactions are completed in a few minutes in refluxing benzene.

N-Sulfinylaniline shows a somewhat different behaviour. In this case, the reaction with triphenylarsine oxide in refluxing benzene is very slow, and only traces of sulphur dioxide is evolved. No triphenylarsine imine could be isolated, but a red addition complex was formed during the reaction. The reactivity of *N*-sulfinyl *p*-nitroaniline, however, is vastly enhanced by the electron withdrawing *p*-nitro group, and the reaction with the arsine oxide is completed in a very short time.

It is interesting to compare the reactivity of isocyanates with that of *N*-sulfinylamides or amines, respectively, in these reactions. Phenyl isocyanate reacts spontaneously with triphenylarsine oxide in the cold, whereas *N*-sulfinylaniline does not afford any triphenylarsine phenylimine when heated for 24 h with excess triphenylarsine oxide. However, the reactivity of *N*-sulfinyl-*p*-toluenesulfonylamide seems to be comparable with that of *p*-toluenesulfonyl isocyanate, and the reactivity of the latter is comparable with that of phenyl isocyanate. It appears that the nitrogen atom in the *N*-sulfinyl compounds must be attached to electron withdrawing substituents, if the reaction is to take place. Highly polar groups, such as sulfonyl or phosphoryl, leave the sulfur atom more susceptible to nucleophilic attack, but their greatest effect lies doubtless in their ability to stabilize the negative charge on the nitrogen atom in the transition state of the reaction.

The fact that triphenylarsine oxide is far more reactive than triphenylphosphine oxide in the first step of these reactions, may, as argued by Monagle,² be attributed to the higher dipole moment of the former (5.50 D) compared to that of triphenylphosphine oxide (4.31 D). Steric hindrance of the groups attached to the metalloïd atom to the formation of the four-membered ring transition state may also, as proposed by the same author, be of less importance in the case of triphenylarsine oxide. From the same arguments, however, one

should expect a higher reactivity for the arsenic compound also in the second step, since the triphenylarsine phenylimine must be expected to have a greater contribution from the dipolar form $\text{Ph}_3\text{As}^+\text{N}^-\text{Ph}$ than the analogous phosphorus compound. However, triphenylphosphine phenylimine is far more reactive than the corresponding arsine imine in the reaction with phenyl isocyanate. It is reasonable to expect that the much stronger P=O bond, as compared with the As=O bond, may play an important role in these reactions. Dainton⁴ has discussed the respective bond energies in As_4O_{10} and P_4O_{10} . The heat of formation of As_4O_{10} is not very well established, but from the available data, Dainton deduces the energy of the apical arsenic oxygen bond $E(\text{As}-\text{O})$ to be 93 kcal. The same author reports a value of 156 kcal for the corresponding P=O bond in P_4O_{10} . If the relative strengths of the bonds in triphenylarsine oxide and triphenylphosphine oxide are of the same order of magnitude, it seems probable that the chief reason for the reluctance of triphenylarsine phenylimine to react with phenyl isocyanate may be attributed to the relatively weak arsenic-oxygen bond formed in triphenylarsine oxide. It is evident that the formation of this bond will provide considerably less driving force for the reaction than the triphenylphosphine oxide formed in the analogous reaction of triphenylphosphine phenylimine.

EXPERIMENTAL

N-Sulfinyl-diethylphosphoramidate was synthesized according to the description of Wieczorkowski,⁵ b.p. 75°/0.7 mm, lit.⁵ 77°/1 mm.

N-Sulfinyl-benzamide was synthesized from *N,N*-bis-trimethylsilyl-benzamide and thionyl chloride, b.p. 73°/0.2 mm, lit.⁵ 68–70°/0.1 mm.

N-Sulfinylaniline, *N*-sulfinyl- β -naphthylamine, and *N*-sulfinyl *p*-nitroaniline were made from the respective amines on treatment with thionyl chloride.⁷

N-Sulfinylsulfonamides were synthesized according to the descriptions of Kresze and Maschke.⁸

p-Toluenesulfonyl isocyanate was obtained from *p*-toluenesulfonyl chloride on treatment with silver cyanate in boiling mesitylene.

Diphenylphosphinic isocyanate was synthesized in an analogous manner from diphenylphosphinic chloride and excess silver cyanate in acetonitrile.⁹

Phenyl isocyanate and α -naphthyl isocyanate were obtained from Fluka and used as received.

Triphenylarsine oxide (Fluka) was freed from water by azeotropic distillation with benzene and recrystallized from the warm solution, m.p. 194°C. Lit.¹⁰ 192°C.

Triphenylarsine *N*-diethylphosphorimine. *N*-Sulfinyl diethylphosphoramidate (2.0 g) in dry benzene was added to a solution of 3.2 g triphenylarsine oxide in dry benzene. The reaction mixture was heated for 2 h after the addition was completed. Most of the benzene was distilled off, and petroleum ether was added until a faint opalescence appeared. The product crystallized after standing for several months to afford 3.9 g of the product, m.p. 80–86°C. (Found: C 57.80; H 5.14; N 2.98. Calc. for $\text{C}_{22}\text{H}_{25}\text{AsNO}_2\text{P}$: C 57.78; H 5.51; N 3.06.) Triphenylarsine *N*-benzoylimine, m.p. 185°C. Lit.¹ 184–185°C.

Triphenylarsine *N-p*-toluene sulfonylimine, m.p. 191–192°C. Lit.¹¹ 192–193°C.

Triphenylarsine *N*-benzenesulfonylimine, m.p. 152–155°C, and triphenylarsine *N*-methanesulfonylimine, m.p. 158–165°C, were synthesized from the resp. *N*-sulfinylamides following the same procedure.

Triphenylarsine *N-p*-toluene sulfonylimine was also synthesized according to Mann and Chaplin¹¹ from chloramine-T and triphenylarsine. The melting point of a mixture of the products from the two different reactions showed no depression, and the infrared spectra were identical.

Triphenylarsine *N*-diphenylphosphine imine was made from diphenylphosphinic isocyanate and triphenylarsine oxide in benzene solution. The product was recrystallized from ether, m.p. 137–141°C. (Found: C 68.34; H 4.70. Calc. for C₃₀H₂₅AsNOP: C 69.10; H 4.83.)

Triphenylarsine phenylimine. Procedure A. The reaction was carried out by dropwise addition of 0.005 mol of phenyl isocyanate in absolute benzene to a solution of 0.005 mol of triphenylarsine oxide in absolute benzene. Dry nitrogen was passed through the apparatus during the operations. The temperature of the reaction mixture was held at 5°C during the addition, whereafter the temperature was allowed to rise. Finally, the reaction mixture was heated a short time at 80°C. The infrared spectrum of the yellow solution showed no absorption at 2146 cm⁻¹ (diphenylcarbodiimide) or 2274 cm⁻¹ (isocyanate). Most of the benzene was distilled off, and the product crystallized, m.p. 134–143°C. (Found: C 70.16; H 5.49; N 3.41. Calc. for C₂₄H₂₀AsN: C 72.55; H 5.07; N 3.52.) Heating of the triphenylarsine phenylimine with an equimolecular amount of phenyl isocyanate in dry benzene afforded diphenylcarbodiimide and triphenylarsine oxide in quantitative yield.

Procedure B. A mixture of equimolecular amounts of *N*-sulfinyl aniline and triphenylarsine oxide in dry benzene was heated at 80°C for 24 h. No triphenylarsine phenylimine could be detected in this reaction. An attempt to synthesize triphenylarsine *N*-β-naphthylimine along the same route was also unsuccessful. In both instances a red addition complex was formed. These products have not yet been identified.

REFERENCES

1. Frøyen, P. *Acta Chem. Scand.* **23** (1969) 2935.
2. Monagle, J. J. *J. Org. Chem.* **27** (1962) 3851.
3. Aksnes, G. and Frøyen, P. *Acta Chem. Scand.* **23** (1969) 2697.
4. Dainton, F. S. *Trans. Faraday Soc.* **43** (1947) 244.
5. Wiczorkowski, J. *Chem. Ind. (London)* **1963** 825.
6. Scherer, O. J. and Schmitt, R. *Chem. Ber.* **101** (1968) 3302.
7. Michaelis, A. *Ann.* **274** (1893) 173.
8. Kresze, G. and Maschke, A. *German pat.* 1117566 (1962); *Chem. Abstr.* **57** (1962) 11110.
9. Popoff, I. C. *Chem. Abstr.* **59** (1963) 3947f.
10. Pascal, P. *Bull. Soc. Chim. France* (4) **33** (1923) 171.
11. Mann, F. G. and Chaplin, E. J. *J. Chem. Soc.* **1937** 527.

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