

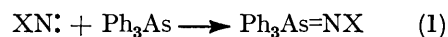
Reactions of Triarylsines with Nitrene Precursors: Formation of Triarylsarinimines (*AsAsAs*-Triarylsarsine Imides) and Related Compounds †

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Copper catalysed or uncatalysed thermolyses of azides in triarylsines provide good routes (40–90%) to the little known *N*-substituted triarylsarinimines (*AsAsAs*-triarylsarsine imides) ($\text{Ar}_3\text{As}=\text{NX}$) including *N*-pentafluorophenyl-, *N*-4,6-dimethyl-2-pyrimidyl-, *N*-ethoxycarbonyl-, *N*-cyano-, *N*-*p*-tolylsulphonyl-, and *N*-methylsulphonyl-triphenylarsininimes. Reaction of *p*-nitrophenyl azide with triphenylarsine and copper in boiling wet dioxan gave a monohydrate of the arsinimine [$\text{Ph}_3\text{As}(\text{OH})\text{NHAr}$]. Benzoyl and *p*-nitrobenzoyl azides in the presence of triarylsines underwent Curtius rearrangement rather than reaction to give the corresponding *N*-arylsarinimines which were instead obtained by copper catalysed thermolysis of the corresponding 3-aryl-1,4,2-dioxazolidin-5-ones with triphenylarsine. *N*-Ethoxycarbonyl- and *N*-*p*-tolylsulphonyl-triphenylarsininimes were also obtained by base induced α -elimination from *N*-*p*-nitrophenylsulphonyloxy-urethane and -toluene-*p*-sulphonamide respectively. Circumstantial evidence is presented which suggests that triarylsines are acting as nitrene traps in at least some of these reactions. The foregoing use of copper is recommended generally for lowering the temperature at which dioxazolidin-5-ones decompose to give aroylnitrenes.

ALKENES,¹ dialkyl sulphides,² and dialkyl sulphoxides³ are the recognised traps for nitrenes produced by a variety of routes. New traps for nitrenes would be valuable, however, because none of these reagents is universal in the sense that it captures all types of nitrenes produced under all types of conditions: phenyl-nitrene has yet to be trapped by any of these reagents, for example. This paper describes an investigation of the potential of the readily available triphenylarsine as a trapping agent for nitrenes. We expected that triphenylarsine would be sufficiently active as a donor to

react with the electron deficient nitrene to give *N*-substituted triphenylarsininimes (*AsAsAs*-triphenylarsine imides) [reaction (1)] and yet not be nucleophilic



enough to interact directly with the nitrene precursor itself. Thus we hoped to circumvent the difficulty associated with the use of the much more nucleophilic triphenylphosphine in this connection, which cannot be

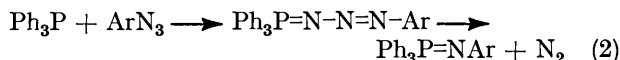
¹ W. Lwowski, *Angew. Chem. Internat. Edn.*, 1967, **6**, 897.

² T. Ohasi, K. Matsunaga, M. Okahara, and S. Komari, *Synthesis*, 1971, **2**, 96; M. Okahara and D. Swern, *Tetrahedron Letters*, 1969, 3301.

³ L. Horner and A. Christmann *Chem. Ber.*, 1963, **96**, 388.

† Preliminary communication, J. I. G. Cadogan and I. Gosney, *J.C.S. Chem. Comm.*, 1973, 586.

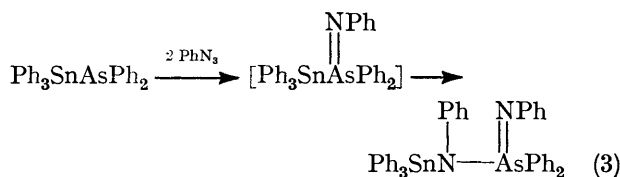
used diagnostically to trap arylnitrenes produced from aryl azides, for example, because direct reaction with undecomposed azide occurs very readily [reaction (2)].⁴



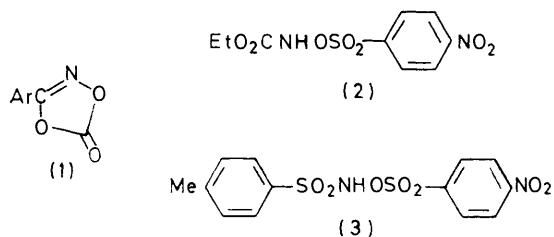
Similar difficulties are associated with other possible routes to nitrenes^{1,5} [e.g. $(\text{RO})_3\text{P} + \text{ArNO}_2$; $\text{ArSO}_2\text{-ONHCO}_2\text{Et} + \text{Et}_3\text{N}$].

A second objective of this work was development of a simple route to the hitherto relatively unexplored triarylarasinimines which are of potential synthetic interest because they are isoelectronic with arsenic ylides which are themselves intermediate between phosphorus and sulphur ylides in chemical behaviour.

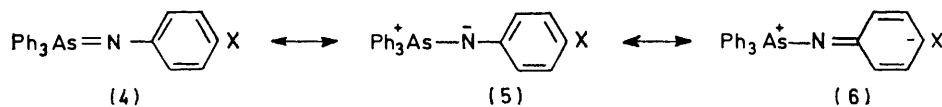
The few arsinimines hitherto reported were prepared by condensation of triarylar sine oxides with isocyanates,^{6,7} *N*-sulphinylamines⁷ or *N*-sulphinylamides,^{7,8} by reaction of triphenylarsine dibromide with activated amides,⁹ by treatment of triphenylarsine with sodium *N*-chlorotoluene-*p*-sulphonamide¹⁰ (chloramine T) or *NN'*-dichlorotoluene-*p*-sulphonamide,¹¹ and, in one case,



by the action of base on an aminoarsonium salt.¹² The simple approach of reaction of an azide with a tertiary



arsine appears to have been used only once and then with only partial success. In this case¹³ a stannyl-substituted arsine on reaction with two moles of the azide gave



an organostannylphenylaminoarsinimine [reaction (3)] rather than the simple arsinimine, which was possibly an intermediate. On the other hand, Wittig¹⁴ and

Staudinger¹⁵ have reported that phenyl azide does not react with triphenylarsine.

In this paper we describe the conversion of triarylar sinines into the corresponding *N*-substituted triarylar sinimines and related compounds *via* their reactions with a variety of nitrene precursors including copper catalysed and uncatalysed reactions of aryl, acyl, ethoxycarbonyl, sulphonyl, and cyanogen azides, and 3-aryl-1,4,2-dioxazolidin-5-ones (1), and base-induced α -eliminations from *N*-*p*-nitrophenylsulphonyloxy-urethane (2) and -toluene-*p*-sulphonamide (3).

Reactions of Triphenylarsine with Azides.—(i) *Aryl azides.* In accord with previous workers we were unable to detect tetraphenylarsinimine (4; X = H) among the products of photolysis or thermolysis at 130°, either alone or with copper, of phenyl azide in the presence of triphenylarsine. Only traces of azobenzene and tars were isolated. A possible explanation for this failure lies in the theory that phenyl nitrene is weakly electrophilic^{16,17} and hence could not be captured by the weakly nucleophilic arsine. Alternatively it is possible that tetraphenylarsinimine, if formed, is unstable under the conditions of the reactions. In either case, the introduction of electron-withdrawing substituents in the aryl nitrene should facilitate arsinimine formation by both increasing the electrophilicity of the nitrene and by stabilising the highly polar As-N bond by delocalisation (5) \longleftrightarrow (6).

In accord with this, thermolysis of pentafluorophenyl azide in molten triphenylarsine at 120°, *i.e.* at the decomposition point of the azide, gave *N*-pentafluorophenyltriphenylarsinimine (38%) (7) as a colourless, crystalline solid which was stable in dry air but decomposed slowly in solution. That no reaction occurred below the decomposition point of the azide is in accord with, but does not prove, nitrene participation [reaction (4)] in this case.

Decomposition of 2-azido-4,6-dimethylpyrimidine, which would be expected to give an electrophilic nitrene,¹⁶ did not occur below 180°, however. At this temperature the reaction with triphenylarsine produced charred products. Modification of the reaction by the introduction of copper bronze reduced the decomposition

⁴ H. Staudinger and E. Hauser, *Helv. Chim. Acta*, 1921, **4**, 861; M. I. Kabachnik and V. A. Gilyarov, *Izvest. Akad. Nauk S.S.S.R. Otdel. khim. Nauk*, 1956, 790 (*Chem. Abs.*, 1957, **51**, 1823).

⁵ J. I. G. Cadogan, *Quart. Rev.*, 1968, **22**, 222.

⁶ P. Frøyen, *Acta Chem. Scand.*, 1969, **23**, 2935.

⁷ P. Frøyen, *Acta Chem. Scand.*, 1971, **25**, 983.

⁸ A. Senning, *Acta Chem. Scand.*, 1965, **19**, 1755.

⁹ B. D. Chernokal'skii, S. S. Nasybullina, R. R. Shagidullin, I. A. Lamanova, and G. Kamai, *Izvest. Vyssh. Ucheb. Zaved. khim. khim. Tekhnol.*, 1966, **9**, 768 (*Chem. Abs.*, 1967, **66**, 76,112w).

¹⁰ F. G. Mann and E. J. Chaplin, *J. Chem. Soc.*, 1937, 527.

¹¹ A. Schonberg and E. Singer, *Chem. Ber.*, 1969, **102**, 2557.

¹² R. Appel and D. Wagner, *Angew. Chem.*, 1960, **72**, 209.

¹³ H. Schumann and A. Roth, *Chem. Ber.*, 1969, **102**, 3731.

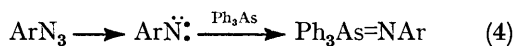
¹⁴ G. Wittig and H. Hellwinkel, *Angew. Chem. Internat. Edn.*, 1962, **1**, 53.

¹⁵ H. Staudinger and J. Meyer, *Helv. Chim. Acta*, 1919, **2**, 635.

¹⁶ R. Huisgen and K. von Fraunberg, *Tetrahedron Letters*, 1969, 2595.

¹⁷ R. A. Abramovitch, S. R. Challand, and E. F. V. Scriven, *J. Org. Chem.*, 1972, **37**, 2705.

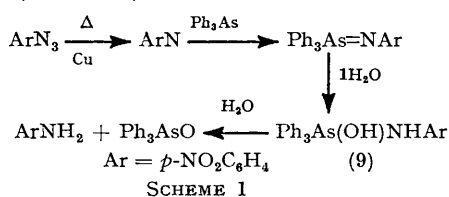
complex ArNCu , as suggested previously by Kwart and Khan¹⁸ for the copper catalysed decomposition of benzenesulphonyl azide.



p-Nitrophenyl azide also gave intractable tars at its decomposition point (160°) in molten triphenylarsine but was similarly induced to give isolable products at a



lower temperature by reaction with copper bronze in boiling dioxan. The reaction mixture decomposed on alumina to give triphenylarsine oxide and *p*-nitroaniline only, suggesting that *N-p*-nitrophenyltriphenylarsinimine (4; X = NO₂) had been formed only to be subsequently hydrolysed. Thermolysis of the azide in wet dioxan in the presence of triphenylarsine and copper bronze led to the isolation of a product corresponding to one mole of *N-p*-nitrophenyltriphenylarsinimine with one mole of water (56%), as a yellow crystalline solid. Spectroscopic evidence (n.m.r., i.r.), detailed in the Experimental section, led to its formulation as the hydrated arsinimine (9) similar in type to compounds such as $\text{Ar}_3\text{As}(\text{OH})\text{NHSO}_2\text{Ar}$ which are readily formed from triarylsarsine oxides and a weak acid such as toluene-*p*-sulphonamide.¹⁹ In accord with this, reaction of *p*-nitroaniline with triphenylarsine oxide gave a product (92%) identical in all respects with the hydrated arsinimine (9). We envisage the hydrated arsinimine (9) to be formed *via* nitrene or nitrenoid (ArNCu) capture to give *N-p*-nitrophenyltriphenylarsinimine (4; X = NO₂) followed by hydration of the highly polar As-N bond. Further hydrolysis leads to the arsine oxide and *p*-nitroaniline (Scheme 1).

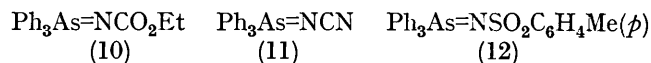


Similarly, the arsinimine (4; X = CN) could not be isolated *via* chromatography from the products of the reaction of *p*-cyanoaniline with triphenylarsine and copper in a melt at 125°. *p*-Cyanoaniline (78%) and the arsine oxide (66%) were isolated.

(ii) *Ethyl azidoformate, cyanogen, sulphonyl, and acyl azides.* Reaction of triphenylarsine with other highly electrophilic nitrenes gave equally successful results. Thus ethyl azidoformate gave *N*-ethoxycarbonyltriphenylarsinimine (10) (66%), at the temperature (130°) required for generation of ethoxycarbonylnitrene, as a colourless, deliquescent, crystalline solid stable at room

¹⁸ H. Kwart and A. A. Khan, *J. Amer. Chem. Soc.*, 1967, **89**, 1950.

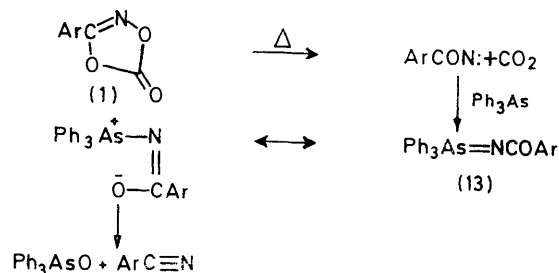
temperature for a few days. It is of interest that the use of copper in this reaction led to the suppression of arsinimine. Reaction of cyanogen azide in acetonitrile afforded the more stable *N*-cyanotriphenylarsinimine (11) (40%) again at the decomposition temperature (50°) of the parent azide, while toluene-*p*-sulphonyl azide gave triphenyl-*N-p*-tolylsulphonylarsinimine (12) in 14% yield, increased to 92% by the use of added electrolytic copper. Similar results were obtained with methanesulphonyl azide which gave *N*-methylsulphonyltriphenylarsinimine $\text{Ph}_3\text{As}=\text{NSO}_2\text{Me}$, m.p. 205–209°, in 74% yield which was markedly different from that claimed to have been prepared (m.p. 158–165°) from



triphenylarsine oxide and the corresponding isocyanate.⁷

Reactions of benzoyl azide with triphenylarsine and *p*-nitrobenzoyl azide with tris-*p*-methoxyphenylarsine proceeded, as expected, *via* non-nitrene Curtius rearrangement, to give the isocyanates, rather than to give the corresponding *N*-aryltriphenylarsinimines.

Reactions of Triarylsarsines with Non-azidic Precursors.—(i) *With 3-aryl-1,4,2-dioxazolidin-5-ones* (1). Unlike the preceding reaction, which does not involve a nitrene, thermal decompositions of 3-aryl-1,4,2-dioxazolidin-5-ones (1) are believed²⁰ to give aroylnitrenes. The use of these precursors with triphenylarsine was therefore expected to lead to the formation of the corresponding *N*-aryltriphenylarsinimines, which eventually proved to be the case. Simple thermolysis, in a melt, of triphenylarsine and 3-phenyl-1,4,2-dioxazolidin-5-one (1; Ar = Ph) gave triphenylarsine oxide and benzonitrile, however, suggesting the intermediacy of the required *N*-benzoylarsinimine (13; Ar = Ph) which is known to fragment in this manner⁶ (Scheme 2). The use of copper led to



SCHEME 2

a reduction in the temperature of decomposition of the azide, however, with the resulting isolation of *N*-benzoyl- and *N-p*-nitrobenzoyl-triphenylarsinimines in 63 and 84% yield respectively. This use of copper is recommended generally for lowering the temperature at which the dioxazolidin-5-ones (1) decompose to give aroylnitrenes.

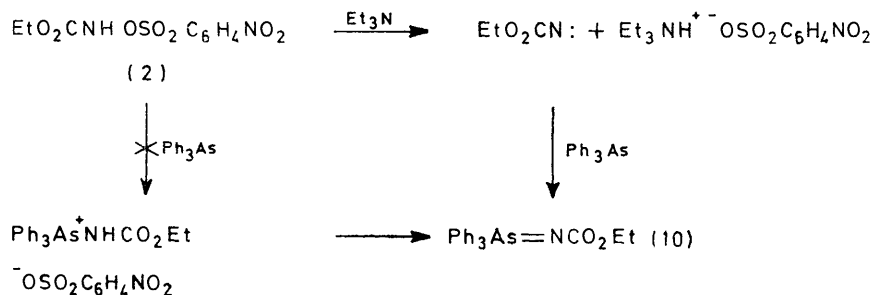
(ii) *With p-nitrophenylsulphonyloxyurethane* (2) and *N-p-nitrophenylsulphonyloxytoluene-p-sulphonamide* (3). α -Elimination from *p*-nitrophenylsulphonyloxyurethane

¹⁹ (a) F. G. Mann, *J. Chem. Soc.*, 1932, 958; (b) D. W. Allen, F. G. Mann, and J. C. Tebby, *J.C.S. Perkin I*, 1972, 2793.

²⁰ J. Sauer and K. K. Mayer, *Tetrahedron Letters*, 1968, 319.

(2) under the influence of triethylamine is a useful low temperature route to ethoxycarbonylnitrene.^{1,21} When carried out in methylene chloride in the presence of triphenylarsine, this reaction gave a high (73%) yield of *N*-ethoxycarbonyltriphenylarsininime (10) as shown by n.m.r. This was not as useful a preparative route as that involving ethyl azidoformate, described above, however, due to the difficulty of separation of triethylammonium *p*-nitrobenzenesulphonate also formed in the reaction.

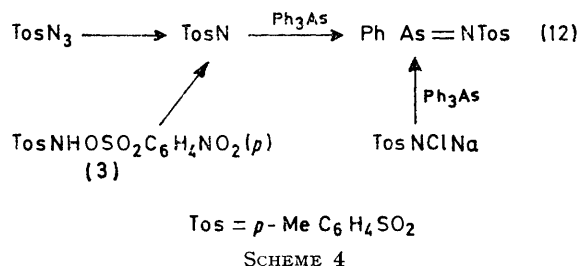
In theory, the arsinimine (10) could also be formed *via* direct displacement by triphenylarsine on the urethane (2), followed by proton transfer, *i.e.* without the intermediacy of the nitrene (Scheme 3). This is indeed the



SCHEME 3

case in the corresponding conversion of tri-*p*-tolylphosphine to *N*-ethoxycarbonyltriphenylphosphininime ($\text{Ar}_3\text{P}=\text{NCO}_2\text{Et}$).²² We know that this does not occur in the present arsinimine case, however, because no reaction between triphenylarsine and the urethane takes place until triethylamine is added.

The production of the *N*-ethoxycarbonylarsininime (10) by two different routes, *i.e.* by the above α -elimination and from ethyl azidoformate, enabled us to employ



SCHEME 4

the classic competition test to provide evidence for or against a common intermediate such as ethoxycarbonylnitrene. Thus reaction of ethyl azidoformate with an excess of an equimolar mixture of tris-*p*-methoxyphenylarsine and tri-*p*-tolylarsine gave a mixture of the corresponding *N*-ethoxycarbonylarsininimes which by n.m.r. analysis corresponded to a reactivity ratio of $K_{\text{MeO}}^{\text{MeO}} = 1.30$. The corresponding competition experiment using *p*-nitrophenylsulphonyloxyurethane (2) led to an almost identical ratio $K_{\text{MeO}}^{\text{MeO}} = 1.32$, thus suggesting a common intermediate. Taken alone, this result cannot be considered to be very significant because the

²¹ 'Nitrenes,' ed. W. Lwowski, Interscience, New York, 1970.

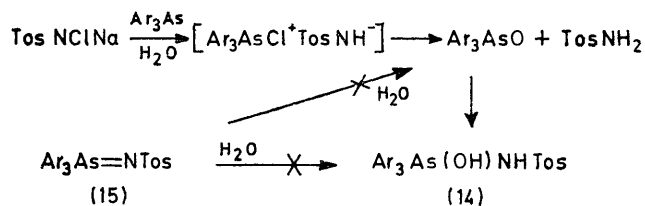
²² J. I. G. Cadogan and I. Gosney, unpublished results.

two reactions used were, of necessity, carried out at different temperatures.

In a closely related reaction, α -elimination from *N*-*p*-nitrophenylsulphonyloxytoluene-*p*-sulphonamide (3) was used to convert triphenylarsine into triphenyl-*N*-*p*-tolylsulphonylarsininime (12) (17%) identical with that produced from *p*-tolylsulphonyl azide with triphenylarsine, and from the arsine oxide and chloramine τ ¹⁰ (Scheme 4). The yield from (3) was reduced considerably by competing Lössen-type rearrangement.²³

Finally, it is noteworthy that triphenyl-*N*-*p*-tolylsulphonylarsininime (12) is remarkably stable towards hydrolysis. This is relevant to previous mechanistic

suggestions advanced^{19a} to explain the formation of the hydroxysulphonamide derivatives (14) from triarylarisines and hydrated chloramine τ wherein it was assumed that an arsinimine (15) was the first product, being subsequently hydrated to give the hydrate (14). Alternatively, it was suggested that the route to (14) involved rapid hydrolysis of (15) to give the arsine oxide and toluene-*p*-sulphonamide followed by condensation of these products (Scheme 5). In view of the high stability of triphenyl-*N*-*p*-tolylsulphonylarsininime (12), now demonstrated, these explanations are less likely than the alternative of direct oxidation of triarylarisine by chloramine τ followed by condensation of the resulting arsine oxide and toluene-*p*-sulphonamide to give the observed product.



SCHEME 5

The related reaction^{19b} of triarylphosphines with hydrated chloramine τ is also more likely to proceed *via* a mechanism analogous to Scheme 5, rather than *via* hydrolysis of $\text{Ar}_3\text{P}=\text{NTos}$, as postulated,¹⁹ in view of (a) the known higher nucleophilicity of triarylphosphine compared with triarylarisine and (b) the greater stability of phosphorus-nitrogen ylides towards hydrolysis. We

²³ W. Lwowski and E. Scheffele, *J. Amer. Chem. Soc.*, 1965, **87**, 4359.

have shown in this connection that (*p*-tolyl)₃P=NTos is completely unchanged under the conditions in question.

EXPERIMENTAL

M.p.s are uncorrected. N.m.r. spectra were recorded on a Varian HA-100 spectrophotometer using deuteriochloroform solutions of the compounds and tetramethylsilane as the internal standard. Column chromatography was carried out over alumina (Brockmann activity 1).

Anhydrous solvents were used at all times. Methylene chloride (spectrograde) was dried over molecular sieves (type 4A). Light petroleum had b.p. 40–60°.

Commercial triphenylarsine oxide was freed from water of crystallisation or hydration by azeotropic distillation with benzene. The sample so prepared was dried at 140° *in vacuo* and stored in a desiccator until use.

Thermal Decomposition of Azides and Dioxazolidinones in Arsines.—*N-Cyanotriphenylarsinimine.* Triphenylarsine (9.18 g, 0.03 mol) was added to cyanogen azide²⁴ (0.01 mol) in anhydrous acetonitrile (35 ml) at room temperature and the resulting solution was heated at *ca.* 50° under nitrogen with stirring. After the evolution of nitrogen had ceased solvent was removed under reduced pressure and the crystalline residue washed with ether-acetone (1:1) to give the pure *arsinimine* (1.35 g, 40%). An analytical sample was obtained as colourless prisms by recrystallisation from benzene, m.p. 176–179° (softening), ν_{\max} (Nujol) 2130 (C≡N) and 1180 cm⁻¹ (Found: C, 65.9; H, 4.4; N, 8.1. C₁₉H₁₅N₂As requires C, 65.9; H, 4.4; N, 8.1%).

N-Ethoxycarbonyltriphenylarsinimine. Ethyl azidoformate²⁵ (0.70 g, 0.006 mol) was added dropwise to a well-stirred melt of triphenylarsine (3 g) at 130° under nitrogen. When the addition was complete, the mixture was cooled and taken up in anhydrous ether (40 ml), filtered rapidly, and the filtrate cooled to separate the *arsinimine* as colourless prisms (1.60 g, 66%). An analytical sample was recrystallised from benzene-ether, m.p. 144–147°, ν_{\max} (Nujol) 1600 (C=O) and 1260br cm⁻¹ among others, τ (CDCl₃) 2.1–2.7 (15H, m), 5.95 (2H, q), and 8.77 (3H, t) (Found: C, 64.0; H, 5.0; N, 3.8. C₂₁H₂₀AsNO₂ requires C, 64.1; H, 5.1; N, 3.6%).

N-4,6-Dimethyl-2-pyrimidyltriphenylarsinimine. A finely ground mixture of triphenylarsine (2.78 g, 0.009 mol), 2-azido-4,6-dimethylpyrimidine²⁶ (0.41 g, 0.003 mol), and copper bronze (0.5 g) was placed in a flask which was flushed continuously with oxygen-free nitrogen. The flask was immersed in an oil-bath at 120° until nitrogen ceased to be evolved (*ca.* 5–10 min). Methylene chloride (30 ml) was added to the cooled mixture and the insoluble materials filtered off. The filtrate was evaporated to dryness and the oily residue triturated with ether to give the *arsinimine* (0.98 g, 76%), m.p. 214–216°. An analytical sample was obtained as colourless prisms by recrystallisation from benzene, m.p. 216–218°, ν_{\max} (Nujol) 1555br, 1408, and 1330 cm⁻¹, τ (CDCl₃) 2.1–2.3 (6H, m), 2.4–2.8 (9H, m), 4.00 (1H, s), and 7.98 (6H, s) (Found: C, 67.4; H, 5.0; N, 9.7. Calc. for C₁₄H₂₂AsN₃: C, 67.4; H, 5.2; N, 9.8%).

Triphenyl-N-p-tolylsulphonylarsinimine. Tosyl azide (0.60 g, 0.003 mol) and triphenylarsine (2.78 g, 0.009 mol) were dissolved in anhydrous ether (10 ml) and evaporated to dryness. Electrolytic copper (0.5 g) was added and the process repeated. The reaction flask was flushed with

oxygen-free nitrogen for 10 min and plunged into an oil-bath preheated to 120°. When nitrogen evolution was complete (5–10 min) the cooled mixture was leached with chloroform and the leachings filtered. Removal of solvent gave a viscous clear oil from which colourless crystals (1.40 g, 95%) of the *arsinimine* separated upon addition of ether. Recrystallisation from absolute ethanol gave an analytical sample, m.p. 189–191° (lit.,¹⁰ m.p. 192–193°), τ (CDCl₃) 2.15–2.7 (17H, m), 3.08 (2H, d, *J* 8 Hz), and 7.76 (3H, s), ν_{\max} (Nujol) 1250, 1130, 1090 (doublet), and 1035 cm⁻¹ (Found: C, 63.1; H, 4.5; N, 2.9. Calc. for C₂₅H₂₂AsNO₂S: C, 63.1; H, 4.7; N, 3.0%).

The same reaction carried out without copper catalyst required prolonged heating to complete the evolution (*ca.* 1 h) of nitrogen and gave much tar. Identical work-up gave 0.15 g (14%) of the *imine* (identical m.p. and i.r. spectrum with the authentic sample).

N-Methylsulphonyltriphenylarsinimine. Methanesulphonyl azide²⁷ (0.36 g, 0.003 mol), triphenylarsine (2.76 g, 0.009 mol), and copper powder (0.5 g) were mixed together intimately and heated in a melt at 110° as described above. Similar work-up gave the *arsinimine* as a cream-coloured solid (0.96 g, 74%). Recrystallisation from ethyl acetate (twice) gave an analytical sample, m.p. 205–209°, ν_{\max} (Nujol) 1255, 1110, and 1055br cm⁻¹, τ (CDCl₃) 2.1–2.6 (15H, m) and 7.27 (3H, s) (Found: C, 57.4; H, 4.7; N, 3.5. C₁₉H₁₈AsNO₂S requires C, 57.1; H, 4.6; N, 3.5%). It should be noted that Frøyen⁷ reported m.p. 158–165° for material claimed to be this compound.

N-Benzoyltriphenylarsinimine. 3-Phenyl-1,4,2-dioxazolidin-5-one²⁸ (0.49 g, 0.003 mol), triphenylarsine (2.76 g, 0.009 mol), and a catalytic amount of copper bronze were mixed together intimately and heated in a melt at 130° as described above until the evolution of nitrogen had ceased (*ca.* 5 min). Work-up gave the *arsinimine* as colourless prisms (0.81 g, 63%). Recrystallisation from benzene furnished an analytical sample, m.p. 181–183° (lit.,⁶ m.p. 184–185°), ν_{\max} (Nujol) 1586, 1530 (C=O), and 1330 cm⁻¹ among others, τ (CDCl₃) 1.6–1.8 (2H, m), 2.1–2.3 (6H, m), and 2.4–2.7 (12H, m) (Found: C, 70.7; H, 4.8; N, 3.4. Calc. for C₂₅H₂₀AsNO: C, 70.6; H, 4.8; N, 3.3%).

N-p-Nitrobenzoyltriphenylarsinimine. A mixture of 3-*p*-nitrophenyl-1,4,2-dioxazolidin-5-one²⁰ (0.62 g, 0.003 mol), triphenylarsine (2.76 g, 0.009 mol), and a catalytic amount of copper bronze in a melt at 150° similarly gave (5 min) the *arsinimine*, m.p. 188–191° (1.20 g, 84%), as pale yellow microcrystals. An analytical sample from benzene had m.p. 194–197°, ν_{\max} (Nujol) 1545 and 1325 cm⁻¹ among others, τ (CDCl₃) 1.58 (2H, d, *J* 9 Hz), 1.81 (2H, d, *J* 9 Hz), and 2.1–2.7 (15H, m) (Found: C, 63.8; H, 4.0; N, 6.0. C₂₅H₁₉AsN₂O₃ requires C, 63.8; H, 4.1; N, 6.0%).

N-Pentafluorophenyltriphenylarsinimine. To a stirred melt of triphenylarsine (*ca.* 3 g) under nitrogen was added dropwise, at 120°, over 15 min, pentafluorophenyl azide²⁹ (0.63 g, 0.003 mol) (*caution*). Trituration with benzene gave colourless crystals of the *arsinimine* (0.51 g, 38%). Recrystallisation from benzene gave an analytical sample as fine needles, m.p. 168–170°, ν_{\max} (Nujol) 1493 (doublet), 1443 (doublet), 1175, 1020, and 980 cm⁻¹, τ (CDCl₃) 2.1–2.4 (6H, m) and 2.4–2.7 (9H, m), ¹⁹F n.m.r., δ 156.5 (2F, m),

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168.2 (2F, m), and 178.7 (1F, m), p.p.m. upfield from Arcton (Found: C, 59.6; H, 3.1; N, 2.7. $C_{24}H_{15}AsF_5N$ requires C, 59.2; H, 3.1; N, 2.9%).

Thermolysis of *p*-Cyanophenyl Azide in Molten Triphenylarsine.—*p*-Cyanophenyl azide³⁰ (0.47 g, 0.003 mol), triphenylarsine (2.76 g, 0.009 mol), and copper bronze (0.5 g) were heated in a melt at 125° under nitrogen (20 min). Chromatography on alumina and elution with light petroleum gave triphenylarsine (2.16 g). Elution with ether-benzene (1:1 v/v) gave 4,4'-dicyanoazobenzene (0.07 g), m.p. 266–268° (from EtOH) (lit.,³¹ m.p. 270°), m/e 232 (M^+). Elution with ether gave *p*-aminobenzonitrile (0.31 g, 78%), identical with an authentic sample (m.p. and i.r. spectrum). Elution with ethyl acetate-ethanol (9:1 v/v) gave triphenylarsine oxide (0.63 g, 66%) identified as the hydroxypicrate, yellow needles (from EtOH), m.p. 164–166° (lit.,³² m.p. 162–163°) undepressed by admixture with an authentic sample obtained directly from triphenylarsine oxide hydrate.

Thermolysis of *p*-Nitrophenyl Azide in Wet Dioxan containing Triphenylarsine.—A mixture of *p*-nitrophenyl azide (0.49 g, 0.003 mol), triphenylarsine (2.78 g, 0.009 mol), and copper bronze (0.5 g) in wet dioxan (40 ml) was boiled under reflux for 6 h after which time the evolution of N_2 had subsided. Solvent was evaporated and the semi-crystalline residue triturated with ether to give tan-coloured crystals (0.75 g, 56%) of *p*-nitro-*N*-[triphenyl(hydroxy)arsoranyl]aniline. Recrystallisation from benzene gave an analytical sample as yellow prisms, m.p. 170–172°, ν_{max} . (Nujol) 3335, 3140, and 878 cm^{-1} , τ ($CDCl_3$) 2.05 (2H, d, J 9 Hz), 2.2–2.6 (15H, m), 3.44 (2H, d, J 9 Hz), and 4.60br (2H, s, disappeared on addition of D_2O) (Found: C, 62.9; H, 4.6; N, 6.2. $C_{24}H_{21}AsO_3N_2$ requires C, 62.6; H, 4.6; N, 6.1%).

An identical product (m.p., and i.r., n.m.r. spectra) was obtained by heating a solution of triphenylarsine oxide (0.97 g, 0.003 mol) and *p*-nitroaniline (0.41 g, 0.003 mol) in benzene (30 ml), under reflux overnight. On cooling, yellow prisms of the hydrated imine separated and were collected (1.10 g, 80%).

Attempts to dehydrate the product to the arsinimine with phosphorus pentoxide-triethylamine, *NN'*-dicyclohexylcarbodi-imide, and sodium hydride in benzene were unsuccessful.

Formation of Arsinimines by α -Elimination Procedure.—**Triphenyl-*N*-*p*-tolylsulphonylarsinimine.** To a stirred solution of *p*-nitrophenylsulphonyloxytoluene-*p*-sulphonamide (1.86 g, 0.005 mol), prepared by the method of Lwowski and Scheiffele,³³ in anhydrous methylene chloride (30 ml) containing triphenylarsine (6 g) was added triethylamine (0.61 g, 0.005 mol) in anhydrous methylene chloride (10 ml) over 15 min. Standard work-up gave the arsinimine (0.40 g, 17%), identical (m.p., i.r. spectrum) with the product prepared from triphenylarsine and toluene-*p*-sulphonyl azide (see above). (*N.B.* no reaction occurred until triethylamine was added to the reaction mixture.)

***N*-Ethoxycarbonyltriphenylarsinimine.**—*N*-*p*-Nitrophenylsulphonyloxyurethane³³ (2.90 g, 0.01 mol) reacted with triphenylarsine (6.0 g) in the presence of triethylamine (1.11 g,

0.011 mol) as described above. Removal of solvent gave a viscous yellow oil which was triturated with anhydrous ether to give a pale yellow crystalline solid (4.70 g) consisting of 3 parts of *N*-ethoxycarbonyltriphenylarsinimine and 5 parts of triethylammonium *p*-nitrobenzenesulphonate [analysed by n.m.r. by comparison of the integration ratio of the signal at τ 5.94 (OCH_2CH_3) with that at 6.83 (NCH_2CH_3)]. The yield of the crude arsinimine is calculated to be 73%.

Reactions of Ethoxycarbonylnitrene with Tris-*p*-methoxyphenyl- and Tri-*p*-tolyl-arsines.—(i) **With tris-*p*-methoxyphenylarsine.**³⁴ The reaction was carried out as described in the preceding experiment. N.m.r. analysis of the concentrate from the reaction showed it to consist of ca. 3 parts of the *N*-ethoxycarbonyltris-*p*-methoxyphenylarsinimine, τ ($CDCl_3$) 2.37 (d, J 9 Hz), 2.98 (d, J 9 Hz), 5.94 (q, CH_2CH_2O), and 6.19 (s, $CH_3OC_6H_4$), and 5 parts of triethylammonium *p*-nitrobenzenesulphonate. Addition of cold absolute ethanol to the mixture precipitated unchanged arsine. Filtration and treatment of the filtrate with picric acid gave tris-*p*-methoxyphenylarsine hydroxypicrate as yellow needles (2.38 g, 74%), m.p. 168–172° (from EtOH) (Found: C, 50.5; H, 3.7; N, 6.8. Calc. for $C_{22}H_{24}AsN_3O_{11}$: C, 50.6; H, 3.8; N, 6.6%), τ ($CDCl_3$) 1.31 (2H, s), 2.37 (6H, d, J 9 Hz), 2.93 (6H, d, J 9 Hz), and 6.17 (9H, s).

(ii) **With tri-*p*-tolylarsine.**—A similar reaction with tri-*p*-tolylarsine³⁵ yielded a straw-coloured oil consisting of about equal parts of the corresponding arsinimine, τ ($CDCl_3$) 4.94 (q, OCH_2CH_3), 7.60 (s, $CH_3C_6H_4$) among other signals, and triethylammonium *p*-nitrobenzenesulphonate. Trituration with cold ethanol and filtration to remove unchanged arsine, followed by addition of picric acid to the filtrate afforded 2.10 g (71%) of tri-*p*-tolylarsine hydroxypicrate as yellow needles, m.p. 183–185° (from ethanol) (lit.,¹⁹ 184–185°), τ ($CDCl_3$) 1.32 (2H, s), 2.42 (d, J = 9 Hz), 2.63 (d, J = 9 Hz; total integration, 12H), 7.57 (9H, s).

(iii) **With an equimolar mixture of tris-*p*-methoxyphenyl- and tri-*p*-tolylarsines.** The standard procedure was followed using equimolar quantities of the two arsines (0.005 mol), *N*-*p*-nitrophenylsulphonyloxyurethane (1.45 g, 0.005 mol), and triethylamine (0.56 g, 0.005 mol). After 3 h solvent was removed and the yellow, oily concentrate was analysed by n.m.r. by comparing the integration ratio of the aryl methyl absorptions at τ 6.19 (CH_3O) with that at 7.60 (CH_3) due to the respective *N*-ethoxycarbonylarsinimines. The relative reactivities (K_{Me}^{MeO}) of the two arsines was calculated to be 1.32.

Reaction of an Equimolar Mixture of Tris-*p*-methoxyphenyl- and Tri-*p*-tolylarsines with Ethoxycarbonylnitrene formed by Thermolysis of Ethyl Azidoformate.—Ethyl azidoformate (0.58 g, 0.005 mol) was decomposed in a melt of tris-*p*-methoxyphenylarsine (1.98 g, 0.005 mol) and tri-*p*-tolylarsine (1.74 g, 0.005 mol) at 140° as described above. N.m.r. analysis of the mixture gave a value of 1.30 for K_{Me}^{MeO} .

[3/1466 Received, 12th July, 1973]

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