Formation of Triphenylarsinimines (*AsAsAs*-Triphenylarsine Imides) by Non-nitrene Routes: Co-oxidation of Triphenylarsine and Amines or Amides with Lead Tetra-acetate, and Related Reactions. Preparation of Diacetoxytriphenylarsorane

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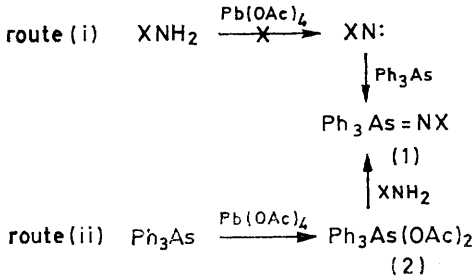
Contrary to earlier suggestions, toluene-*p*-sulphonamide does not react with lead tetra-acetate (LTA) at low temperatures to give *p*-tolylsulphonylnitrene. Reaction of LTA with triphenylarsine in the presence of toluene-*p*-sulphonamide gives triphenyl-*N*-*p*-tolylsulphonylarsinimine (*AsAsAs*-triphenylarsine *p*-tolylsulphonylimide) (90%) *via* the intermediacy of the hitherto unknown diacetoxytriphenylarsorane [$Ph_3As(OAc)_2$]. *N*-Methylsulphonyl- and *N*-benzoyltriphenylarsinimines were formed similarly (58—62%). Reaction of triphenylarsine with LTA gave diacetoxytriphenylarsorane as a crystalline reactive solid (87%) which reacted with relevant amides to give the above arsinimines and also the *N*-*p*-nitrobenzoyl analogue (51%). These observations led to a simple one-pot reaction of amides with triphenylarsine oxide in acetic anhydride to give the above arsinimines and also *N*-diphenylphosphinyltriphenylarsinimine [$Ph_3As{=}NP(O)Ph_2$] in 65—90% yields. Reaction of LTA with *N*-aminophthalimide in the presence of triphenylarsine gives triphenyl(phthalimidoamino)arsonium acetate (10). Unlike the case of toluene-*p*-sulphonamide this reaction may be occurring, at least in part, *via* a nitrene mechanism to give the corresponding *N*-phthalimidotriphenylarsinimine ylide (11).

In the preceding paper [1] routes to a wide range of *N*-substituted triarylarsinimines (*AsAsAs*-triarylarsine imides) ($Ar_3AsN{=}X$) were described, involving reaction of triarylarsines under nitrenogenic conditions with nitrene precursors such as various azides, 3-aryl-1,4,2-dioxazolidin-5-ones, and *N*-*p*-nitrophenylsulphonyloxyurethane and -toluene-*p*-sulphonamide. As a corollary it was thus shown that triarylarsines are useful nitrene traps.

There have been many suggestions [2-4] that amino-compounds, including amides are oxidised to nitrenes by lead tetra-acetate (LTA). On the other hand it has been stated that carboxamides [5] and sulphonamides [6] do not react either at all [6] or 'appreciably' [5] with LTA in methylene chloride at room temperature. It was of interest, therefore, to attempt to extend our nitrene-based synthesis of arsinimines by allowing LTA to react with amino-compounds in the presence of triphenylarsine. In the event, although arsinimines were produced, it became clear that nitrenes were not involved in most of, if not all, the cases studied. This conclusion not only led to a new and by far the simplest route to arsinimines so far recorded, but also implied that the questions of nitrene participation in LTA oxidations of amino-compounds must generally be treated with circumspection with full regard to the conditions and components of the reactions under investigation.

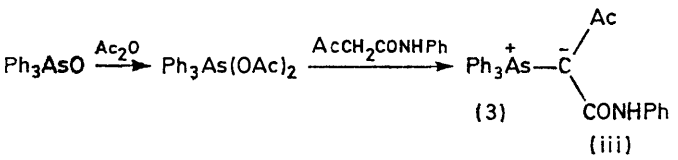
Reactions with Acyl, Sulphonyl, and Phosphinyl Amides.—We allowed methane- and toluene-*p*-sulphonamides, and benzamide to react with triphenylarsine and LTA in methylene chloride at room temperature. The reaction mixture became warm and subsequent isolation of *N*-methylsulphonyltriphenylarsinimine (1; X = $MeSO_2$) (62%) and the *N*-*p*-tolylsulphonyl (90%) and *N*-benzoyl (58%) analogues, in addition to providing a new route to arsinimines, seemed to give support for the suggestion that the reactions proceeded *via* the intermediate formation of nitrenes which were subsequently captured by triphenylarsine [route (i)]. That nitrenes are not involved in these reactions clearly follows, however, from the results of control experiments which confirm earlier reports [5,6] and show that these amides do not react appreciably at room temperature with LTA in the absence of triphenylarsine. This suggests that arsinimine formation proceeds *via* reaction of LTA with triphenylarsine to give diacetoxytriphenylarsorane (2) which then reacts with the amide [route (ii)].



The postulated intermediate (2) has recently been suggested [7] as an intermediate in the formation of arsenic ylides from triphenylarsine oxide and active methylene compounds in acetic anhydride [equation (iii)], but before this investigation it had never been isolated or detected. We have now produced this compound, by direct reaction of LTA with triphenylarsine, as colourless crystals, easily hydrolysed to triphenylarsine oxide. In accord with the proposed route (ii) the diacetoxyarsorane reacted at room temperature, in methylene chloride, with methane- and toluene-*p*-sulphonamides and with benzamide, but not with the less nucleophilic *p*-nitrobenzamide, to give the corresponding arsinimines: (1; X = $MeSO_2$) (69%); (1; X = *p*-$MeC_6H_4SO_2$) (65%); (1;

[1] J. I. G. Cadogan and I. Gosney, preceding paper.
[2] B. V. Ioffe and M. A. Kuznetsov, *Russ. Chem. Rev.*, 1972, **41**, 131.
[3] B. Acott, A. L. J. Beckwith, and A. Hassanali, *Austral. J. Chem.*, 1968, **21**, 185.
[4] T. Ohasi, K. Matsunaga, M. Okahara, and S. Komori, *Synthesis*, 1971, **2**, 96.
[5] H. E. Baumgarten and A. Staklis, *J. Amer. Chem. Soc.*, 1965, **87**, 1141.
[6] R. A. Abramovitch, 'Chem. Soc. Special Publ. No. 24,' 1970, p. 323.
[7] I. Gosney and D. M. G. Lloyd, *Tetrahedron*, 1973, **29**, 1697.

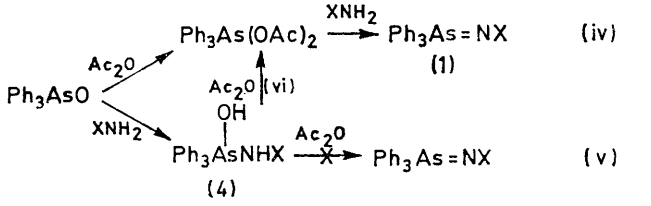
X = Bz) (56%). Higher temperatures (boiling ethylene dichloride) were necessary to convert *p*-nitrobenzamide into the arsinimine (1; X = *p*-$NO_2C_6H_4CO$) (51%). We



(3) (iii)

are also able to support the suggestion [7] that diacetoxytriphenylarsorane (2) is an intermediate in the formation of arsenic ylides [equation (iii)] because reaction of preformed (2) with acetoacetanilide in boiling benzene gave the ylide (3) (39%) identical with that produced from the arsine oxide, acetic anhydride, and acetoacetanilide.

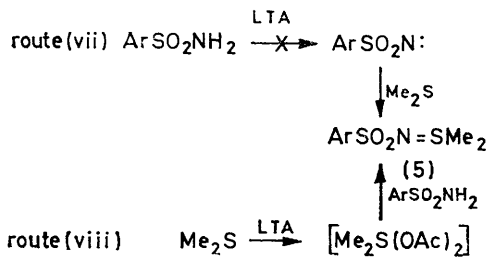
This demonstration of the effective equivalence of diacetoxytriphenylarsorane with a mixture of triphenylarsine oxide with acetic anhydride has led to what appears to be the simplest route to arsinimines yet recorded: reaction of triphenylarsine oxide with hot acetic anhydride in the presence of methane-, benzene-, and toluene-*p*-sulphonamide, benzamide, *p*-nitrobenzamide, and diphenylphosphinamidate [$Ph_2P(O)NH_2$] gave within a few minutes the corresponding arsinimines [1; X = $MeSO_2$, $PhSO_2$, *p*-$MeC_6H_4SO_2$, Bz, *p*-$NO_2C_6H_4CO$, or $Ph_2P(O)N$] in good yields (65—90%).



(4) (iv) (v)

At first sight it would appear that these reactions proceed *via* the sequence $Ph_3AsO \longrightarrow Ph_3As(OAc)_2 \longrightarrow Ph_3As{=}NX$ as in route (iv). Since it is known [8] that amides form adducts of the type (4) with triarylarsine oxides, an observation confirmed in this investigation, it is necessary to consider the possibility of reaction *via* the adduct (4) and thence by displacement to give the diacetoxyarsorane [route (vi)] and/or dehydration to give the arsinimine directly [route (v)]. A control experiment established that reaction of benzamidotriphenylarsonium hydroxide (4; X = Bz) with cold acetic anhydride gave diacetoxytriphenylarsorane and not the arsinimine (1; X = Bz) which appeared only on subsequent warming of the reaction mixture. This points to route (vi), and hence (iv), and discounts (v). It was also shown that reaction of triphenylarsine oxide with acetic anhydride with gentle warming gave diacetoxytriphenylarsorane, thus establishing the first step of route (iv), as a competitor to reaction *via* route (vi). Although direct dehydration of the intermediate (4; X = Bz) to the arsinimine [route (v)] does not occur under these conditions, we were able to establish that under the more forcing circumstances (P_2O_5–NEt_3 in boiling benzene) a low conversion into the arsinimine (1; X = Bz) did occur.

Our present observations support Abramovitch's report [6] that LTA does not react with toluene-*p*-sulphonamide in cold methylene chloride and invalidates the suggestion [4] that *p*-tolylsulphonylnitrene is involved in the formation of dimethyl-*N*-*p*-tolylsulphonylsulphimide (5) from reaction of toluene-*p*-sulphonamide with dimethyl sulphide and LTA in ether, as depicted in route (vii). Since it is known that LTA reacts with dialkyl sulphides,[9] probably *via* a dialkyl sulphide diacetate, it is likely that the mode of formation of the sulphimide (5) parallels that of our arsinimines, *i.e. via* route (viii),



especially since it is known that sulphoxides condense readily with amides in acetic anhydride to yield sulphimides, presumably *via* the diacetate.[10]

Reactions with N-*Aminophthalimide.*—Oxidation of *N*-aminophthalimide (6) with LTA in the presence of sulphoxides is known to give the corresponding sulphoximides (7).[11] There is no direct evidence that nitrenes are involved in this reaction but the nitrene mechanism has been used as a good working hypothesis. On the other hand thermolysis or photolysis of the sulphoximide (7) does appear to give *N*-phthalimidonitrene (8) which can be trapped by alkenes [11] and by 2-acetylbenzofuran [12] to give aziridines such as (9).

Reaction of a solution of *N*-aminophthalimide with one mol. equiv. of LTA in the presence of an excess of triphenylarsine at room temperature gave the crystalline aminoarsonium acetate (10), which can be hydrolysed to give triphenylarsine oxide and *N*-aminophthalimide and whose n.m.r. spectrum indicated that it exists as an equilibrating mixture of the ionic and covalent forms (10a and b). This suggests that the arsinimine (11) was formed first, followed by reaction with co-produced acetic acid to give the arsonium acetate (10). This was confirmed by generating phthalimidonitrene (8) by thermolysis of Jones' *N*-phthalimidoaziridine (9) [12] and trapping it with triphenylarsine, as described earlier,[1] in the presence of acetic acid to give the salt (10).

[8] F. G. Mann, *J. Chem. Soc.*, 1932, 958.

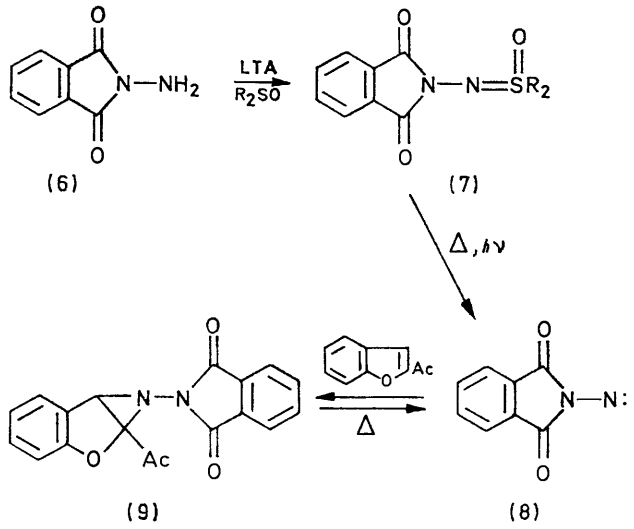
[9] H. E. Barron, G. W. K. Cavill, E. R. Cole, P. T. Gilham, and D. H. Solomon, *Chem. and Ind.*, 1954, 76; R. Criegee, 'Oxidation in Organic Chemistry,' ed. K. B. Wiberg, Academic Press, New York, 1965.

[10] J. G. Moffatt, 'Oxidation,' eds. R. L. Augustine and D. J. Trecker, Dekker, New York, 1971, vol. II; D. S. Tarbell and C. Weaver, *J. Amer. Chem. Soc.*, 1941, **63**, 2939.

[11] D. J. Anderson, D. C. Horwell, E. Stanton, T. L. Gilchrist, and C. W. Rees, *J.C.S. Perkin I*, 1972, 1317.

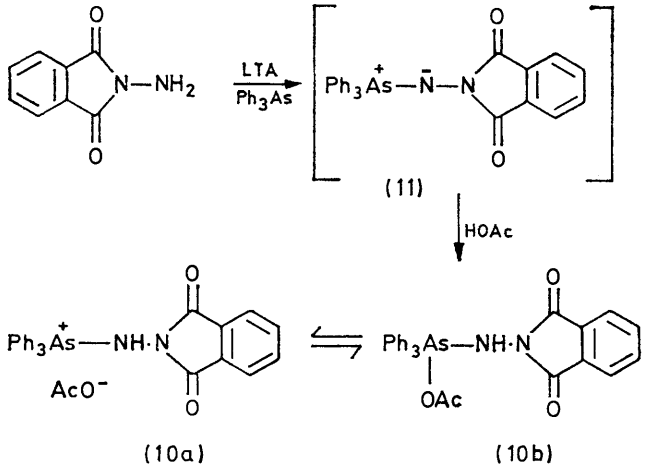
[12] D. W. Jones, *J.C.S. Chem. Comm.*, 1972, 884; *J.C.S. Perkin I*, 1972, 225.

Attempts to isolate the pure parent arsinimine (11), in the absence of acetic acid, were frustrated by its extreme ease of hydrolysis under the mildest conditions,

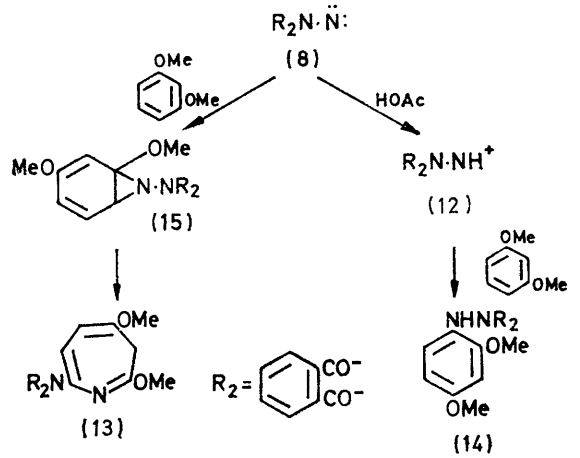


to give triphenylarsine oxide and *N*-aminophthalimide. This hydrolytic instability contrasts with the high stability of the corresponding sulphoximide, and reflects the relatively high dipolar character of the $\overset{+}{As}-\overset{-}{N}-$ *vs.* the $=\overset{+}{S}-\overset{-}{N}-$ bond previously noted for the corresponding *S*-ylides *vis à vis* their arsenic analogues.[13]

The arsonium acetate (10) was also produced by reaction of diacetoxytriphenylarsorane with *N*-aminophthalimide, indicating a reaction path similar to that established for amides, above. Unlike amides, however,



N-aminophthalimide was consumed rapidly by LTA in the absence of triphenylarsine at low temperature. Hence the arsonium acetate (10), in addition to being produced by the non-nitrene mechanism involving diacetoxytriphenylarsorane, also may be competitively formed by a trapping reaction of triphenylarsine with a reactive species formed by LTA attack on *N*-aminophthalimide. This could be a lead derivative, the nitrene, or the *N*-phthalimidonitrenium ion (12). In this connection there is evidence that this nitrenium ion may be involved in LTA oxidations of *N*-aminophthalimide. Jones has recently reported [14] that, whereas *N*-phthalimidonitrene produced by thermolysis of the *N*-phthalimidoaziridine (9) reacted with 1,3-dimethoxybenzene by addition to give mainly the azepine (13), reaction of *N*-aminophthalimide with LTA gave mainly the insertion product (14) and little azepine (13). Nitrene participation was assumed in each case and the dichotomy was attributed to diversion of the intermediate benzaziridine (15) (Scheme), formed by nitrene addition, by acetic acid to give the insertion product. An attractive alternative explanation is that thermolysis of the *N*-phthalimidoaziridine (9) does indeed give the nitrene which adds in the expected fashion to give ultimately the azepine, but that LTA oxidation of *N*-aminophthalimide leads to the nitrenium ion (12) by protonation of the nitrene which then reacts *via* normal electrophilic substitution with the highly nucleophilic



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1,3-dimethoxybenzene. This is supported by Jones' own observation [14] that thermolysis of the *N*-phthalimidoaziridine (9) in the presence of acetic acid as well as 1,3-dimethoxybenzene led to a diversion of azepine to insertion product.

EXPERIMENTAL

Reaction of Triphenylarsine with Lead Tetra-acetate: Formation of Diacetoxytriphenylarsorane.—(a) Lead tetra-acetate (1·55 g, 0·0035 mol) was added during 5 min to a stirred solution of triphenylarsine (1·22 g, 0·004 mol) in anhydrous methylene chloride (30 ml). After 10 min the mixture was filtered and the solid washed with anhydrous methylene chloride (2 × 10 ml). The combined filtrate and washings were concentrated to *ca.* 5 ml and anhydrous ether was added until a faint opalescence appeared. On standing colourless needles of the *diacetate* separated (1·08 g, 87%), m.p. 53—56° (softening) (Found: C, 62·3; H, 5·3. $C_{22}H_{21}AsO_4$ requires C, 62·3; H, 5·0%), $\nu_{max.}$ (Nujol) 2560br, 1755, 1705br, 1255br, 865, and 843 cm^{-1} among others, τ ($CDCl_3$) 1·9—2·7 (15H, m) and 8·19 (6H, s).

[13] B. H. Freeman, D. Lloyd, and M. I. C. Singer, *Tetrahedron*, 1972, **28**, 343.

[14] D. W. Jones, *J.C.S. Chem. Comm.*, 1973, 67.

(b) The combined filtrate and washings from (a) were shaken with water (3 × 100 ml), dried ($MgSO_4$), and evaporated. Crystallisation of the residue from benzene gave triphenylarsine oxide hydrate (0·91 g, 71%) as indicated by comparison of its i.r. spectrum with that of an authentic sample.

Preparation of Arsinimines by Condensation of Amides with Diacetoxytriphenylarsorane from the Reaction of Triphenylarsine and Lead Tetra-acetate.—(i) *Triphenyl-*N-*p-tolylsulphonylarsinimine.* Lead tetra-acetate (1·95 g, 0·0044 mol), dried by pressing between filter papers, was added in small portions to a solution of toluene-*p*-sulphonamide (0·68 g, 0·004 mol) and triphenylarsine (3·66 g, 0·012 mol) in anhydrous methylene chloride (30 ml) with stirring. The reaction was exothermic; after 1·5 h the mixture was poured into water (150 ml) and extracted with methylene chloride (3 × 50 ml). The extract was washed with water, solvent removed, and the oily residue crystallised from ether to give the arsinimine (1·54 g, 82%), m.p. 186—189°, undepressed by admixture with a sample prepared from triphenylarsine and toluene-*p*-sulphonyl azide.[1]

(ii) N-*Methylsulphonyltriphenylarsinimine.* This was prepared similarly (62%) and was identical (m.p., i.r., n.m.r.) with the product from methanesulphonyl azide and triphenylarsine.[1]

(iii) N-*Benzoyltriphenylarsinimine.* Benzamide (0·48 g, 0·004 mol) was dissolved in anhydrous methylene chloride (40 ml) containing triphenylarsine (3·66 g, 0·012 mol) and lead tetra-acetate (1·95 g, 0·0044 mol) was added during 5 min with vigorous stirring. After 3 h the mixture was filtered and the filtrate concentrated to *ca.* 5—10 ml. Addition of anhydrous ether (100 ml) and cooling to 0° gave the arsinimine (0·98 g, 58%), identical (m.p., i.r., n.m.r.) with a sample prepared as described previously.[1]

(iv) N-p-*Nitrobenzoyltriphenylarsinimine.* This was prepared similarly and was identical (m.p., i.r., n.m.r.) with the product previously obtained.[1]

Reactions (i)—(iii) were also carried out by the alternative procedure involving the inverse addition of the amide to a mixture of 1 mol. equiv. of triphenylarsine and lead tetra-acetate in methylene chloride. This method gave the arsinimines in 56—90% yield.

(v) *Triphenyl(phthalimidoamino)arsonium acetate.* (a) Finely ground *N*-aminophthalimide[15] (0·65 g, 0·004 mol) and triphenylarsine (3·66 g, 0·012 mol) were dissolved in methylene chloride (40 ml) and lead tetra-acetate (1·95 g, 0·0044 mol) was added in small portions with stirring. The mixture was stirred for a further 1 h, then filtered, and the solids washed with methylene chloride. Evaporation of the filtrate and washings gave a yellow oil from which almost colourless crystals (1·05 g, 50%) of the acetate slowly separated on addition of ether. An analytical sample prepared by two recrystallisations from absolute alcohol had m.p. 219—223°, $\nu_{max.}$ (Nujol) 2680br, 1790, 1728, 1695, and 1535 cm^{-1}, τ ($CDCl_3$) −0·8br (1H, s), 2·15—2·4 (10H, m), 2·4—2·7 (9H, m), and 7·90(s)—8·29(s) (total integration 3H) (Found: C, 63·5; H, 4·4; N, 5·4. $C_{28}H_{23}AsN_2O_4$ requires C, 63·9; H, 4·4; N, 5·3%).

(b) A solution of the phthalimidoaziridine[12] (0·96 g, 0·003 mol), triphenylarsine (2·76 g, 0·009 mol), and acetic acid (0·18 g, 0·003 mol) in anhydrous ethylene chloride (30 ml) was boiled under reflux for 3 h. Most of the solvent was evaporated and ether (40 ml) added to the concentrate. A creamy-coloured solid slowly deposited which was collected and recrystallised from ethanol–ether to give the acetate (0·61 g, 48%), identical with that obtained in (a).

The same reaction in the absence of acetic acid afforded an oily residue after removal of solvent, whose i.r. spectrum, taken immediately, showed no absorption at 880 cm^{-1} (As–O). Prolonged exposure to the atmosphere resulted in the appearance of bands of increasing intensity at 3400br, 1660, and 880 cm^{-1}, indicative of triphenylarsine oxide hydrate formation. Addition of ethanolic picric acid solution to the residue produced an immediate yellow precipitate. Filtration and recrystallisation from hot ethanol gave triphenylarsine hydroxypicrate as bright yellow needles (1·20 g, 73%), m.p. and mixed m.p. 165—167°. Examination of the filtrate by t.l.c. indicated the presence of *N*-aminophthalimide.

Formation of Arsinimines by Condensation of Triphenylarsine Oxide with Amides in Acetic Anhydride.—The method is exemplified by the preparation of triphenyl-*N*-*p*-tolylsulphonylarsinimine.

A mixture of triphenylarsine oxide (1·29 g, 0·004 mol), toluene-*p*-sulphonamide (0·68 g, 0·004 mol), and freshly distilled acetic anhydride (15 ml) was heated under reflux for 2 min. On cooling and scratching, colourless crystals of the arsinimine separated which were filtered off, washed with ether, and recrystallised from absolute ethanol (1·80 g, 91%). The product was identical (m.p. and mixed m.p., i.r. and n.m.r. spectra) with an authentic specimen.[1]

Similarly prepared were triphenyl-*N*-phenylsulphonylarsinimine (62%), m.p. 154—156° (lit.,[16] 152—155°) (Found: C, 62·3; H, 4·4; N, 3·0. Calc. for $C_{24}H_{20}AsNO_2S$: C, 62·5; H, 4·4; N, 3·0%), *N*-*p*-nitrobenzoyltriphenylarsinimine (47%), m.p. and mixed m.p. 190—193°, *N*-benzoyltriphenylarsinimine (64%), m.p. and mixed m.p. 182—183°, *N*-methylsulphonyltriphenylarsinimine (96%), m.p. and mixed m.p. 205—208°, and N-*diphenylphosphinyltriphenylarsinimine* (45%), m.p. 167—169° (colourless needles from hexane–benzene) (Found: C, 69·2; H, 4·8; N, 2·5. $C_{30}H_{25}AsNOP$ requires C, 69·1; H, 4·8; N, 2·7%), $\nu_{max.}$ (Nujol) 1176, 1115, and 1080 cm^{-1} τ ($CDCl_3$) 2·0—2·5 (10H, m), and 2·5—3·0 (15H, m). Frøyen [16] claimed to have obtained this material from diphenylphosphinyl isocyanate and triphenylarsine oxide but reported m.p. 137—141°.

Reaction of Triphenylarsine Oxide with Benzamide in Benzene.—(i) A mixture of triphenylarsine oxide (1·61 g, 0·005 mol) and benzamide (0·61 g, 0·005 mol) in anhydrous benzene (30 ml) was boiled under reflux for 3 h and then concentrated *in vacuo* to *ca.* 10 ml to give colourless crystals of N-*benzamidotriphenylarsonium hydroxide* which was recrystallised from ethyl acetate (1·86 g, 84%), m.p. 109—110°, $\nu_{max.}$ (Nujol) 3310br, 3140br, 1670, 1628, and 882 cm^{-1} among others (Found: C, 67·7; H, 4·9; N, 3·2. $C_{25}H_{22}AsNO_2$ requires C, 67·7; H, 5·0; N, 3·2%).

(ii) A mixture of the arsonium hydroxide (1·10 g, 0·0025 mol) and phosphorus pentoxide (1·5 g) in benzene (25 ml) and triethylamine (12·5 ml) was boiled under reflux. After 1·5 h the solvent was decanted while hot and evaporated to dryness to give a colourless oil. Trituration with anhydrous ether gave *N*-benzoyltriphenylarsinimine (0·53 g, 50%), contaminated to a minor extent with triphenylarsine oxide hydrate.

(iii) *N*-Benzamidotriphenylarsonium hydroxide (1·20 g) in freshly distilled acetic anhydride (10 ml) was stirred at room temperature. After 1 h a colourless precipitate of

[15] H. D. K. Drew and H. H. Hatt, *J. Chem. Soc.*, 1937, 16.
[16] P. Frøyen, *Acta Chem. Scand.*, 1971, **25**, 983.

diacetoxytriphenylarsorane (54%), identical (m.p., i.r.) with that obtained above, was formed.

Reaction of Triphenylarsine Oxide with Acetic Anhydride.—Triphenylarsine oxide (1·0 g) was heated below 55° in freshly distilled acetic anhydride (10 ml) until dissolved. When cool, this gave diacetoxytriphenylarsorane (0·65 g, 49%), identified by comparison with samples obtained previously.

Reaction of Diacetoxytriphenylarsorane with Acetoacetanilide.—A mixture of diacetoxytriphenylarsorane (1·27 g, 0·003 mol) and acetoacetanilide (0·53 g, 0·005 mol) in anhydrous benzene (30 ml) containing 2 drops of acetic anhydride was boiled under reflux for 30 min. Solvent was evaporated and the residue triturated with ether to give a colourless solid (0·72 g). Recrystallisation from nitromethane gave triphenylarsonium acetyl-(*N*-phenylcarbamoyl)methylide as prisms (0·51 g, 39%), m.p. 200—202°, undepressed by admixture with an authentic sample.[7]

[3/1467 *Received*, 12*th July*, 1973]