Formation of Arsinimines by Reactions of Triphenylarsine with Compounds Generally Believed to be Nitrene Precursors

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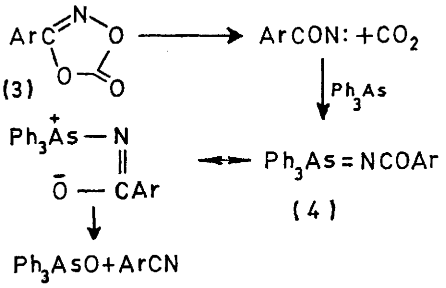
Summary The little known triphenylarsinimines ($Ph_3As{=}NX$, where $X{=}C_6F_5$, 4-6-dimethylpyrimidyl, EtO_2C, p-$Me{\cdot}C_6H_4{\cdot}SO_2$, $MeSO_2$, CN, Bz, p-$NO_2{\cdot}C_6H_4{\cdot}CO$) are prepared either by reaction of triphenylarsine under nitrene-producing conditions with azides (XN_3), 3-aryl-1,4,2-dioxazolidin-5-ones, *N*-*p*-nitrobenzenesulphonoxy-urethane and -toluene-*p*-sulphonamide, and/or by a non-nitrene route from triphenylarsine, lead tetra-acetate, and amides *via* triphenylarsine diacetate, $Ph_3As(OAc)_2$, now isolated.

FOLLOWING previous unsuccessful attempts[1,2] we now report conditions under which triphenylarsine reacts with a variety of azides to give the little known *N*-substituted triphenylarsinimines (**1**).[3] Thus, reaction of the electrophilic nitrene precursors, ethyl azidoformate, cyanogen azide, and toluene-*p*-sulphonyl azide at their decomposition points in a melt or solution of triphenylarsine gave the corresponding arsinimines (**1**; $X{=}EtO_2C$ 66%, CN 40%, p-$Me{\cdot}C_6H_4{\cdot}SO_2$ 14%). The use of electrolytic copper in catalytic quantities lowered the decomposition point and gave better yields in the case of methane- and toluene-*p*-sulphonyl azides (74 and 90%). The absence of reaction below the decomposition points of the azides suggests nitrene or copper–nitrenoid[4] participation rather than reaction *via* the intermediate (**2**). In accord with this, thermolysis of benzoyl and *p*-nitrobenzoyl azides, which proceed *via* a non-nitrene Curtius rearrangement, in triarylarsine did not give the corresponding arsinimines, whereas thermolysis of 3-phenyl-1,4,2-dioxazolidin-5-one (**3**; Ar=Ph) which is known to give benzoyl nitrene,[5] in triphenylarsine gave triphenylarsine oxide and benzonitrile, suggesting the intermediacy of the required *N*-benzoylarsinimine (**4**; Ar=Ph) (Scheme).[6]

$$XN_3 \rightarrow XN \xrightarrow{Ph_3As} XN{=}AsPh_3 \quad (\mathbf{1})$$

$$XN_3 + Ph_3As \rightarrow XN{=}N{-}N{=}AsPh_3 \quad (\mathbf{2})$$



SCHEME

The use of copper led to a lowering of the decomposition points of the nitrene precursors (**3**), a technique which may be useful generally with these reagents, with the resulting isolation of *N*-aroylarsinimines (**4**; Ar=Ph 63%, p-$NO_2{\cdot}C_6H_4$ 84%) from 3-phenyl- and 3-*p*-nitrophenyl-1,4,2-dioxazolidin-5-ones (**3**). Photolysis or thermolysis, with or without copper, of phenyl azide in triphenylarsine gave tars. Application of the concept[7] of the electrophilic aryl nitrene by copper-catalysed decomposition of 2-azido-

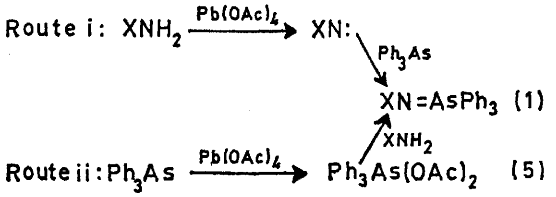
4,6-dimethylpyrimidine in molten triphenylarsine (120°) gave the corresponding *N*-arylarsinimine [**1**; X = 2-(4,6-Me_2-pyrimidyl) 76%]; a similar but uncatalysed reaction of the electrophilic nitrene from perfluorphenyl azide gave *N*-perfluorophenyltriphenylarsinimine (**1**; X=C_6F_5 38%).

N-Ethoxycarbonyl- and *N*-toluene-*p*-sulphonyl-triphenyl arsinimines (**1**; X = CO_2Et or *p*-$Me{\cdot}C_6H_4{\cdot}SO_2$) were also produced in 73 and 17% yields, respectively, by base-induced α-elimination[8] from *p*-nitrobenzenesulphonoxyurethane and *N*-*p*-nitrobenzenesulphonoxytoluene-*p*-sulphonamide.

Confirmation that the arsinimine (**1**; X = EtO_2C) was produced *via* ethoxycarbonyl nitrene in both the azidoformate and α-elimination routes was provided by competition reactions involving mixtures of tris-*p*-methoxyphenyl- and tris-*p*-tolyl-arsine in each case. N.m.r. analysis of the resulting arsinimines gave a ratio $K^{MeO}_{Me} = 1{\cdot}30$ for the azidoformate route and $K^{MeO}_{Me} = 1{\cdot}32$ for the α-elimination method.

These experiments suggest that triphenylarsine might be useful as a nitrene trap.

Since there have been many suggestions[9] that amino-compounds, including amides, are oxidised by lead tetra-acetate to nitrenes, we allowed methane- and toluene-*p*-sulphonamides, and benzamide to react with triphenylarsine and $Pb(OAc)_4$ in methylene chloride. Isolation of *N*-methanesulphonyltriphenylarsinimine (**1**; X = $MeSO_2$ 62%) and the *N*-toluene-*p*-sulphonyl- and *N*-benzoyl-analogues (**1**; X = *p*-$Me{\cdot}C_6H_4{\cdot}SO_2$ 90%, Bz 58%) adumbrates a new route to arsinimines which might, at first sight, be thought to proceed *via* nitrenes subsequently captured by the arsine (Route i). That nitrenes are not involved, however, follows from the failure of these amides to react with $Pb(OAc)_4$ in the absence of the arsine. This suggests reaction *via* a first formed triphenylarsine diacetate $Ph_3As(OAc)_2$ (**5**) hitherto unknown, with the amide (Route ii).



Reaction *via* Route ii is confirmed by the isolation of the postulated diacetate (**5**) as a crystalline solid [m.p. 53—56° (softening) 87%] from reaction of $Pb(OAc)_4$ with triphenylarsine. The arsine diacetate reacted rapidly in methylene chloride with benzamide, toluene-*p*-sulphonamide, and methanesulphonamide, but not with the less nucleophilic *p*-nitrobenzamide, to give the arsinimines (**1**; X = *p*-Me·-$C_6H_4{\cdot}SO_2$ 65%, $MeSO_2$ 62%, Bz 56%) thus fully supporting Route (ii). At higher temperatures, *e.g.* in boiling ethylene dichloride, *p*-nitrobenzamide also gave the arsinimine (51%).

These investigations, besides providing simple new routes to arsinimines and to the potentially synthetically useful, reactive, arsine diacetate (**5**), have implications concerning the possible participation of nitrenes in $Pb(OAc)_4$ oxidations of amides, amino-, and *N*-amino-compounds, in general, particularly if the "nitrene trap" being employed is potentially readily attacked by lead tetra-acetate.

Indeed our confimation[10] of the lack of reaction between $Pb(OAc)_4$ and toluene-*p*-sulphonamide at 40° appears to invalidate the suggestion[9c] that toluene-*p*-sulphonylnitrene is involved in the formation of *N*-tosyldimethylsulphilimine from toluene-*p*-sulphonamide, $Pb(OAc)_4$ and dimethyl sulphide in ether.

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