Preparation and Hydrolysis of Acyliminotriphenylarsoranes; A New, Mild Method for the Hydrolysis of Nitriles

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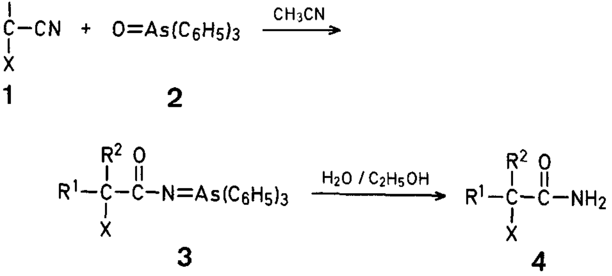
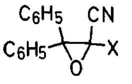
As triphenylarsine oxide (**2**), a nucleophilic reagent, reacts with electrophilic alkynes such as methyl propynoate or dimethyl acetylenedicarboxylate in a reverse Wittig reaction to give arsonium ylids[1], we considered that **2** should also react with cyanides. Compound **2** does not react with normal cyanides such as acetonitrile, phenylacetonitrile, and benzonitrile.

We now report that the reaction of activated cyanides such as trichloroacetonitrile (**1a**), etc., with triphenylarsine oxide (**2**) results in the formation of, e.g., trichloroacetyliminotriphenylarsorane (**3a**) (see Table) and that some of the iminoarsoranes **3** can be easily hydrolysed with aqueous ethanol to give the corresponding amides **4**. Other nitriles **1b–f** react similarly with **2** so that this reaction may offer a convenient method for the selective formation of monoamides from dinitriles under mild conditions without the necessity of isolating the intermediate arsenic compound **3**.

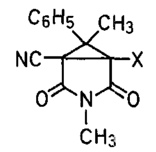


This sequence cannot be employed with malodinitrile or ethyl cyanoacetate as abstraction of hydrogen atoms occurs, giving rise to the corresponding methylenetriphenylarsorane[2]. The reaction has been successfully applied to the dinitriles **5** and **8** to give arsoranes **6** and **9** and amides **7** and **10**, respectively.

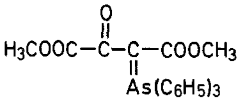
The addition of triphenylarsine oxide to a cyano group is reversible; thermolysis of benzoyliminotriphenylarsorane was reported to give benzonitrile and **2**[3]. Thus, when the arsorane **3e** is heated under reflux with dimethyl acetylenedicarboxylate, transfer of the elements of **2** occurs to give the methylenearsorane **11** in 40% yield[1].



5 X = CN
6 X = CO–N=As(C₆H₅)₃
7 X = CO–NH₂



8 X = CN
9 X = CO–N=As(C₆H₅)₃
10 X = CO–NH₂



$$H_3COOC-\overset{\overset{O}{\|}}{C}-\underset{\underset{As(C_6H_5)_3}{\|}}{C}-COOCH_3$$

11

Triphenylarsine oxide hydrate is dried by melting at 192 °C and subsequently stored under dry nitrogen[5].

Triphenylarsoranes 3a, b, and e; General Procedure:

A mixture of the activated nitrile **1** (0.43 g of **1a**, 0.42 g of **1b**, or 1.0 g of **1e**[7], 3 mmol) and triphenylarsine oxide (**2**; 0.96 g, 3 mmol) in dry acetonitrile (30 ml) is stirred at room temperature for 20 min. The solvent is then evaporated under reduced pressure whereupon the arsorane **3** crystallises.

Cyanodibromoacetyliminotriphenylarsorane (3c):

A mixture of the 1:1 complex of potassium bromide/dibromomalodinitrile[4] (1.0 g, 3 mmol) and triphenylarsine oxide (**2**; 0.96 g, 3 mmol) in dry acetonitrile is heated at 30–40 °C for 15 min. The solvent is removed under reduced pressure whereupon the product crystallises.

Triphenylarsoranes 3d, 3f, and 6; General Procedure:

A mixture of the nitrile (0.76 g of **1d**, 0.84 g of **1f**, or 0.76 g of **5**[8], 3.1 mmol) and triphenylarsine oxide (**2**; 1.0 g, 3.1 mmol) is heated under reflux in dry benzene (60 ml) for 20 h. The solvent is evaporated under reduced pressure, the residue is washed with ether (50 ml), and recrystallised.

2-Aminocarbonyl-2-cyano-1,3-diphenylpropane (4d):

The arsorane **3d** (0.5 g) in 95% ethanol (10 ml) is heated under reflux for 5 min, the mixture is allowed to cool and the product is filtered; yield: 0.2 g (90%); m.p. 161 °C (from ethanol); Lit.[6] m.p. 162 °C.

Table. Iminotriphenylarsoranes **3a–f**, **6**, and **9** prepared

Product No.	R^1	R^2	X	Yield [%][a]	m.p. [°C] (solvent)	Molecular formula[b]	I.R. (nujol) ν [cm⁻¹]
3a	Cl	Cl	Cl	80	216° (benzene)	$C_{20}H_{15}AsCl_3NO$ (466.6)	1609
3b	Cl	Cl	CN	45	194° (acetonitrile)	$C_{21}H_{15}AsCl_2N_2O$ (457.2)	2240; 1636
3c	Br	Br	CN	80	214° (acetonitrile)	$C_{21}H_{15}AsBr_2N_2O$ (546.0)	2232; 1628
3d	$C_6H_5CH_2$	$C_6H_5CH_2$	CN	50	140° (benzene)	—[c]	2238; 1587; 1558
3e	$(C_6H_5)_2(NC)C$	Br	CN	88	235° (acetonitrile)	$C_{35}H_{25}AsBrN_3O$ (658.4)	2240; 1629
3f	$(C_6H_5)_2(NC)C$	CH_3	CN	75	238° (methanol)	$C_{36}H_{28}AsN_3O$ (593.4)	2230; 1608
6				86	190° (benzene)	—[c]	2333; 1616
9				—	160° (ether)	—[c]	2239; 1775; 1704; 1583; 1565

[a] Yield based on **1**.
[b] Satisfactory microanalyses obtained unless otherwise stated: C ±0.43, H ±0.24, N ±0.36.
[c] Not completely free of the corresponding amide.

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$C_{17}H_{16}N_2O$	calc.	C 77.24	H 6.10	N 10.60
(264.3)	found	77.32	6.26	10.59

I.R. (nujol): $\nu = 3423$; 3225; 1680 cm^{-1}.

2-Aminocarbonyl-2-cyano-3,3-diphenyloxirane (7):
The triphenylarsorane **6** (1.0 g) is heated under reflux in 95% ethanol (20 ml) for 3 min. The mixture is allowed to cool and the amide **7** is filtered; yield: 0.4 g (85%); m.p. 141 °C (from ethanol).

$C_{16}H_{12}N_2O_2$	calc.	C 72.72	H 4.57	N 10.60
(264.2)	found	72.51	4.43	10.39

I.R. (nujol): $\nu = 3373$; 3150; 1646 cm^{-1}.

Arsorane 9 and Amide 10:
A mixture of the nitrile **8**[7] (1.3 g, 5 mmol) and triphenylarsine oxide (**2**; 4.8 g, 5 mmol) in dry toluene is heated under reflux for 17 h. The solvent is evaporated under reduced pressure and the residue recrystallised from diethyl ether to give *5-cyano-3,6-dimethyl-2,4-dioxo-6-phenyl-1-triphenylarsiniminocarbonyl-3-azabicyclo[3.1.0]hexane* (**9**) which is used directly in the next step.

The arsorane **9** (1.3 g) in 95% ethanol (20 ml) is heated under reflux for 3 min, the mixture is allowed to cool and the product, *1-aminocarbonyl-5-cyano-3,6-dimethyl-2,4-dioxo-6-phenyl-3-azabicyclo[3.1.0]hexane* (**10**) is filtered; yield: 0.4 g (60%); m.p. 198 °C (from ethanol).

$C_{15}H_{13}N_3O_3$	calc.	C 63.59	H 4.62	N 14.83
(283.3)	found	63.71	4.77	14.57

^{1}H-N.M.R. (CDCl$_3$): $\delta = 1.92$ (s, 3H, CH$_3$); 2.37 (s, 3H, CH$_3$); 7.5 (m, 10H$_{\text{arom}}$); 7.66 (s, 1H, NH$_2$); 8.35 ppm (s, 1H, NH$_2$).

M.S. $m/e = 283.0949$ (calc. for $C_{15}H_{13}N_3O_3$: 283.09568).

I.R. (nujol): $\nu = 3430$; 3300; 2246; 1780; 1702; 1664 cm^{-1}.

Dimethyl 2-Oxo-3-triphenylarsoranylidenebutanedioate (11) from 3e:
The arsorane **3e** (2.0 g, 3 mmol) and dimethyl acetylenedicarboxylate (0.43 g, 3 mmol) in dry acetonitrile (25 ml) is heated under reflux for 5 min. The mixture is allowed to cool and the product **11** is filtered; yield: 0.56 g (40%); m.p. 213–214 °C; Lit.[1], m.p. 214 °C. The I.R. spectrum is identical to that reported[1]. The nitrile **1e** can be obtained by evaporation of the filtrate; yield: 0.4 g (40%).

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