Tetrahedron Letters, Vol.30, No.3, pp 349-350, 1989 0040-4039/89 $3.00 + .00
Printed in Great Britain Pergamon Press plc

EASY ACCESS TO FUNCTIONALIZED DICHLOROARSINES, SYNTHETIC EQUIVALENTS OF ARSAALKYNES

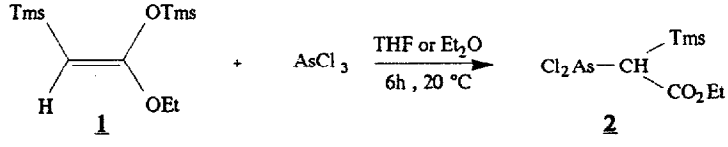
Souad HIMDI-KABBAB, Pascal PELLON and Jack HAMELIN*

Groupe de Recherche de Physicochimie Structurale, associé au C N R S,
Université de Rennes I, Campus de Beaulieu, 35042 Rennes, France

SUMMARY: An easy access to functionalized dichloroarsines **2**, **4**, is described. Dehydrochlorination with DABCO leads to arsaalkenes which are trapped in situ by a diene or a diazocompound to give arsabenzenes and diazaarsoles.

Acyclic λ^3 σ^2 As derivatives are scarce in the literature (1) and to our knowledge acyclic functionalized arsaalkenes are not known. As an extension of our previous work related to dichlorophosphines (2), we prepared in a simple way the dichloroarsines **2** and **4**.

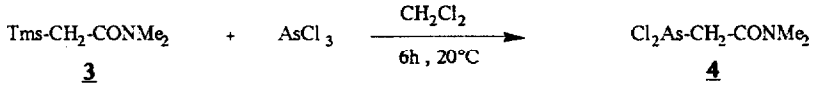
The silylated ketene acetal **1** (3) reacts with an equimolar amount of $AsCl_3$ to give **2** in a quantitative yield (NMR) after removal of the solvent under vacuum.



1 **2**

2 : ^{1}H NMR ($CDCl_3$) : 0.30 (s, 9H) ; 1.25 (t, 3H) ; 3.40 (s, 1H) ; 4.10 (q, 2H).

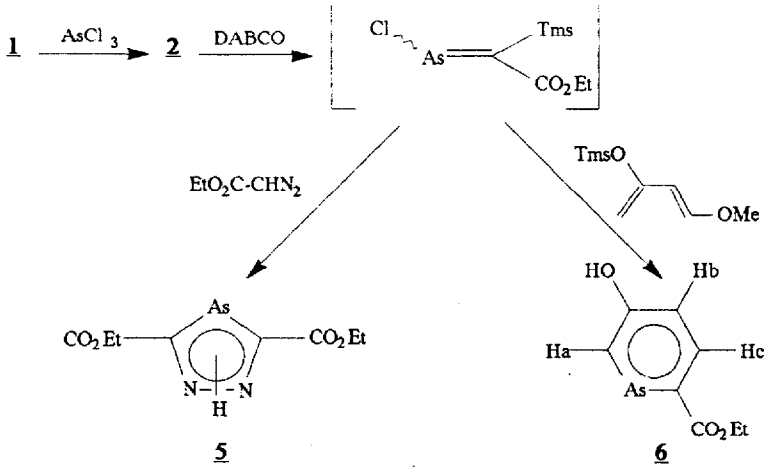
An amide group is conveniently introduced by reacting **3** with an equimolar amount of $AsCl_3$ to give **4** in a quantitative yield (NMR).



3 **4**

4 : ^{1}H NMR ($CDCl_3$) : 2.91 and 3.01 (2s, 6H) ; 3.7 (s, 2H).

Dehydrochlorination of dichloroarsine **2** was readily achieved by treatment with DABCO in Et_2O and the resulting arsaalkene was trapped "in situ" either by the Danishefsky diene (4) or by ethyl diazoacetate, to give after aqueous work up the corresponding diazaarsole **5** or arsabenzene **6** according to the following scheme.

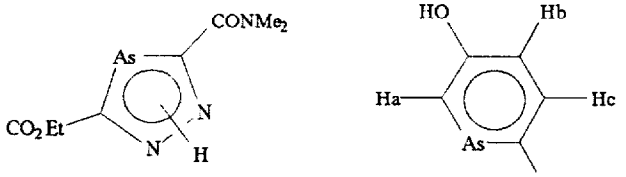


These compounds were characterized by ^1H NMR and Mass Spectrometry.

5 : mp = 126°C, 53 % isolated yield, ^1H NMR ($CDCl_3$, TMS) : 1.4 (t, 6H) ;4.45 (q, 4H) ; 8.5 to 10.5 (ws, 1H). Mass spectroscopy : $C_8H_{11}N_2O_4As$, calculated : 273.9934 ; found 273.9929.

6 : mp = 120°C, 20% isolated yield, ^1H NMR ($CDCl_3$, TMS) : 1.25 (t, 3H) ; 4.40 (q, 2H) ; 7.10 (dd, 1H, J^3_{HbHc} = 10 Hz, J^4_{HbHa} = 2.5 Hz,Hb) ; 8.60 (d, 1H, J^3_{HbHc} = 10 Hz, Hc) ; 8.90 (d, J^4_{HbHa} = 2.5 Hz, Ha).

In the same way, starting from 4 and using CH_2Cl_2 as solvent we prepared and isolated 7 but compound 8 was only characterized by ^1H NMR.



7 m p =148°C
25% isolated yield

8

7 : ^1H NMR : 1.40 (t, 3H) ; 3.2 and 3.32 (2s, 6H) ; 4.41 (q, 2H) ; 9.43 to 11.38 (ws, 1H, NH). Mass spectrometry : $C_8H_{12}N_3AsO_3$ calculated: 273.0094 ; found: 273.0079.

8 : ^1H NMR : 2.96 and 2.91 (2s, 6H) ; 7.2 (dd, 1H, J^3_{HbHc}= 10 Hz, J^4_{HbHa}= 2.0 Hz,Hb); 8,5 (d, 1H, J^3_{HbHc}= 10 Hz,Hc) ; 8,92 (d, 1H, J^4_{HbHa}= 2,0 Hz,Ha).

These results show that 2 and 4 behave formally like synthetic equivalents of the unknown functionalized arsaalkynes.

REFERENCES:

1. B.A. Arbuzov and E.N. Dianova, Phosphorus and Sulfur, 1986, 26, 203.
2. P.Pellon and J. Hamelin, Tetrahedron Letters, 1986, 27, 5611.
3. C. Ainsworth and Yu Neng Kuo, J. Organomet. Chem., 1972, 46, 59 and 73.
4. S. Danishefsky and T. Kitahara, J. Am. Chem. Soc., 1974, 96, 7807.

(Received in France 20 October 1988)