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Attempts Of Arsirane Synthesis By Addition Of Diazocompounds With Arsaalkenes

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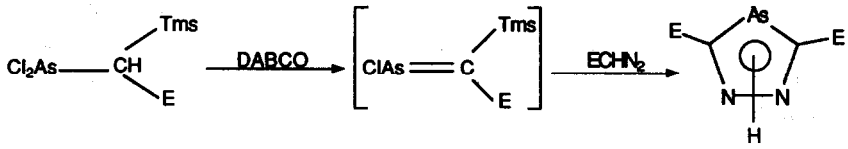
Key - words : dichloroarsines, arsaalkenes, diazaarsoles, diazocompounds, arsiranes.

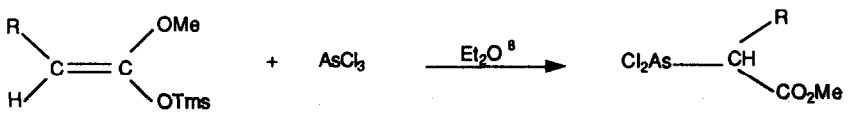
Abstract : *The reaction of ethyl diazoacetate with arsaalkenes 8 and 9, leads to diazaarsole 3 and diazocompounds 10 and 11. Diphenyldiazomethane addition follows a different course leading to alkenes 23 and 24, possibly through a transient arsirane.*

Arsiranes are scarce in the literature [1-3]. We recently described the synthesis of stable bicyclic arsiranes by addition of sulfur ylides with diazaarsoles [4], but the reaction failed with acyclic arsaalkenes. Another route to arsirane is the addition of diazocompounds to C=As [2,3] to give according to the reaction conditions,either a 1- pyrazoline which decomposes with nitrogen extrusion, or an arsirane by carbene addition. We have previously reported [5] that the addition of ethyl diazoacetate with arsaalkene **2** leads to the diazaarsole **3** after spontaneous aromatization of the primary 1-pyrazoline according to the following scheme :



1 E = CO_2Et **2** **3**

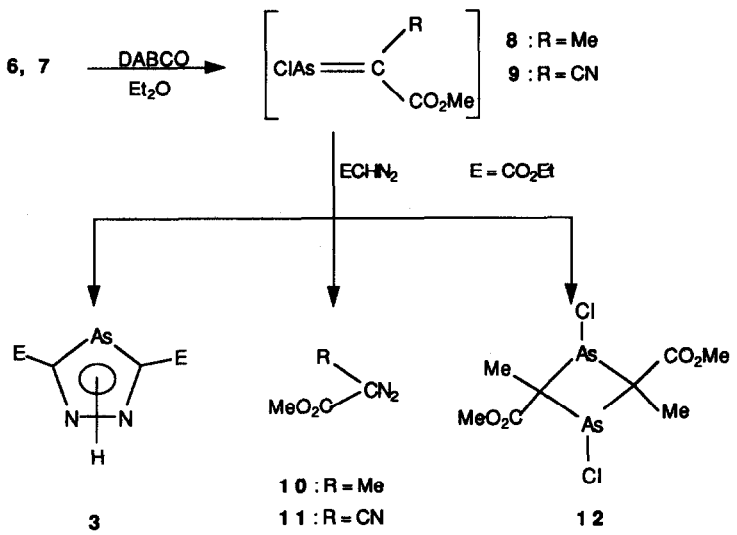
In order to avoid this aromatization without nitrogen extrusion, we have now studied the reaction either with arsaalkenes bearing on the carbon atom substituents unable to eliminate with chloride, or with disubstituted diazocompounds.
For this purpose we prepared the dichloroarsines **6** and **7**, starting from silyl ketene acetals **4** and **5** readily obtained according to literature procedures [6,7].



4 : R = Me
5 : R = CN

6 : R = Me
7: R = CN

The dichloroarsines **6** and **7** are then dehydrochlorinated to arsaalkenes **8** or **9** with DABCO in ether at -40°C and after 10 min, ethyl diazoacetate is added and the reaction mixture is left 12 hrs at room temperature. After filtration under nitrogen and evaporation of the solvent under vacum the ^{1}H NMR spectrum shows the formation of diazocompounds **10** or **11**, diazaarsole **3** and, in the case of **8**, the dimer **12**.



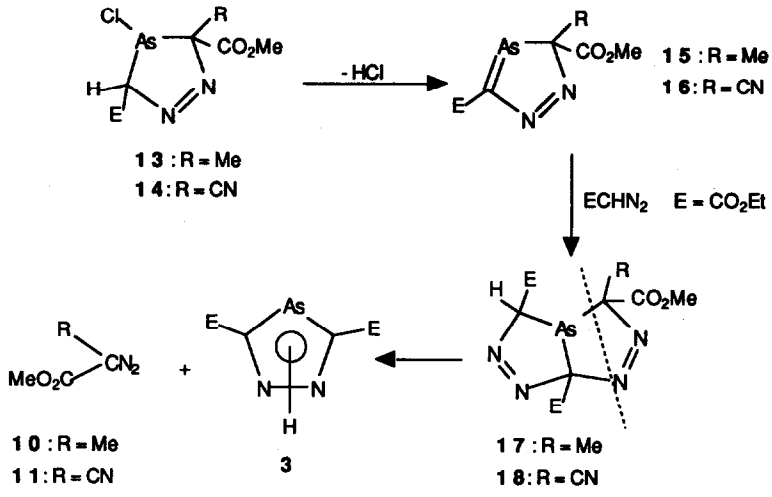
3

10 : R = Me
11 : R = CN

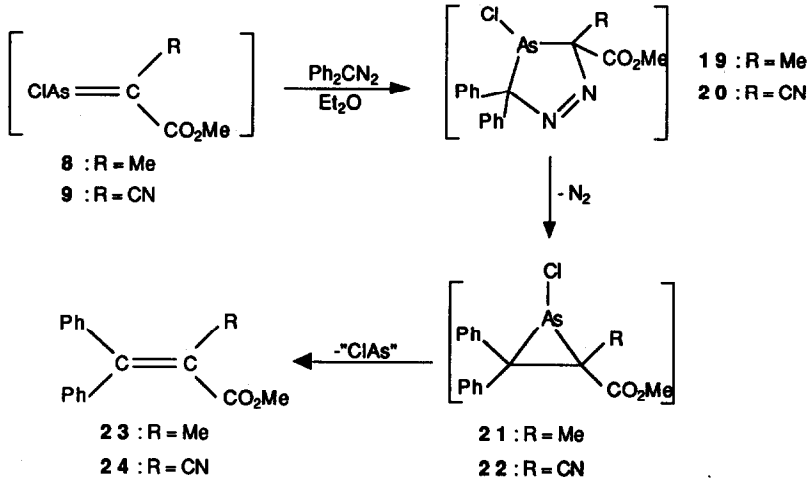
12

3 and **12** are identified by comparison with authentic samples [5,9], diazocompounds **10** and **11** are characterized by their ^{1}H NMR and IR spectra [10].

The mechanism of the formation of **3** and **10** or **11** is not established but the reaction may be rationalized in the following way. Ethyl diazoacetate reacts with the arsaalkene to give an unstable 1-arsapyrazoline **13** or **14** which loses HCl to give **15** or **16** which cannot aromatize. These compounds add ethyl diazoacetate, giving rise to the bicyclic adducts **17** or **18** which aromatize by retrocycloaddition of diazocompounds **10** or **11** and formation of **3**.



To prevent HCl elimination, we used diphenyldiazomethane instead of ethyl diazoacetate. In this case the reaction follows a different course : the primary product should be a 1-pyrazoline **19** or **20** which this time evolves nitrogen leading to the corresponding unstable arsiranes **21, 22** which decomposes to the alkenes **23** or **24** and the chloroarsinidene which is neither trapped nor characterized. In the case of **8** the dimer **12** is also formed (**23** : **12** = 60/40). Starting from **9**, the alkene **24** is formed in a nearly quantitative yield.



23 is characterized by ^1H NMR ($CDCl_3$, lock CH_2Cl_2) : 2.06 (s, 3H, R = Me) ; 3,47 (s, 3H, OMe) ; 7.25 (m, 10H, Ph_2) and mass spectrometry : $C_{17}H_{16}O_2$; calculated : 252.115 ; found : 252.114.
24 is identified by ^1H NMR and comparison vith an authentic sample (F = 113°C, ^1H NMR : 3.71 (s, 3H, OMe) ; 7.45 (m, 10H, Ph_2)).

An analogous fragmentation of phosphiranes in alkenes and chlorophosphinidene is already mentionned in the literature[11,12]. Thus functionalized As chloroarsiranes seem to be rather unstable.

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8. **6** : Et_2O, catalytic amount of $ZnCl_2$, RT, 24 hrs. ^1H NMR ($CDCl_3$, lock CH_2Cl_2) : 1.61 (d, 3H, MeC) ; 3.36 (q, 1H, As-CH) ; 3.72 (s, 3H, MeO).

   7 : Et_2O, 30 min at 0°C then 2 hrs at RT. ^1H NMR ($CDCl_3$, lock CH_2Cl_2) : 3.95 (s, 3H, MeO) ; 4.55 (s, 1H, As-CH).
9. Dimer **12** has been synthetized by two independant ways : dehydrohalogenation of **6** with DABCO or starting from Tms (Me) C = C(OMe) O Tms addition of $AsCl_3$ giving Cl_2As-C(Me) (CO_2Me) Tms and heating at 100°C. **12** : ^1H NMR : 1.87 (s, 6H, 2Me) ; 3.77 (s, 6H, MeO). Mass spectrometry : $C_8H_{12}O_4As_2\ ^{35}Cl_2$: calculated : 391.854 ; found : 391.857.
10. Diazocompound **10** : ^1H NMR : 2.25 (s, 3H, Me) ; 3.6 (s, 3H, OMe) **11** : ^1H NMR : 3.87 (s, 3H, OMe). IR : 2140 cm^{-1} (υ N=N) and 2240 cm^{-1} (υ C≡N).
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