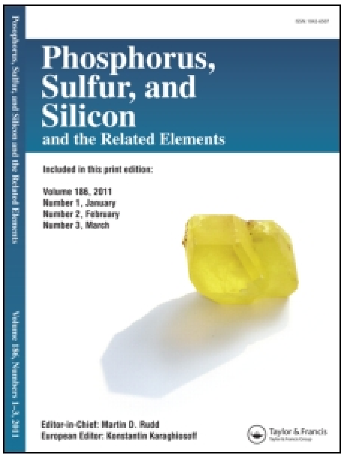

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C-(N,N-DIALKYLAMINO)-SUBSTITUTED ARSAALKENES: A SIMPLE METHOD FOR THE PREPARATION AND EXAMPLES OF THEIR REACTIVITY

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C-(N,N-DIALKYLAMINO)-SUBSTITUTED ARSAALKENES: A SIMPLE METHOD FOR THE PREPARATION AND EXAMPLES OF THEIR REACTIVITY

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A simple method for the preparation of C-(N,N-dialkylamino)-substituted arsaalkenes **4a, b** is suggested. The —As=C< bond in this kind of compounds is shown to react with sulfur to yield dithioarsaranes, which are dimeric in the solid phase and monomeric in the gas phase.

Key words: Arsine; amidacetals; arsaalkenes; dithioarsaranes.

INTRODUCTION

At present the chemistry of compounds with double element-carbon bonds has been studied more extensively for phosphorus rather than for other 15 Group elements (As, Sb, Bi). Nevertheless, there are known several methods for the synthesis arsaalkenes, including interaction of disilylarsines with dimethylformamide[1] and acyl chlorides[2–4] as well as β-elimination of HCl from the corresponding chloroarsine.[5]

Here we are reporting on a novel simple method for obtaining arsaalkenes from arsines and amidacetals. The latter are well known to be convenient reagents for the formation of multiple bonds in reactions with compounds containing a H_2Z-group with relatively acidic hydrogen atoms, that can be exemplified by the syntheses of alkenes,[6] azomethines[7] and phoshaalkenes.[8–10]

RESULTS AND DISCUSSION

The first step of the method proposed implies the formation of 2,4-di-*tert*-butyl-6-methylphenylarsine **2** quite analogously to that of the corresponding phosphine.[11]

$$\text{Ar-Mg-Br} + \text{AsCl}_3 \xrightarrow[-\text{ClMgBr}]{-78^\circ\text{C}} \underset{\mathbf{1}}{\text{Ar-AsCl}_2}$$

$$\mathbf{1} \xrightarrow[-78^\circ\text{C}]{+\text{LiAlH}_4} \underset{\mathbf{2}}{\text{Ar-AsH}_2}$$

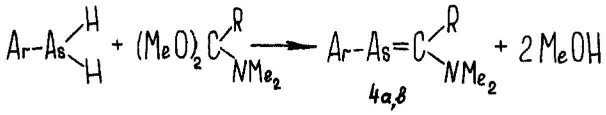
Compound **2**, however, appeared to be rather unstable and tends to decompose to 3,5-di-*tert*-butyltoluene on heating above 150°C in vacuo. The arsenic-containing residue, which could be presumably a compound **3** represents a reddish-brown solid substance insoluble in common organic solvents. In its IR spectrum there is present a band at 2100 cm^{-1}, which is characteristic of the As—H bond.[12] A substance with the formula $(As_2H)_x$ had been already mentioned in the literature.[13,14] Therefore, it seems quite reasonable to assume that compound **3** really exists, the more so as the ratio As/H in **3** is 1:0.48. In any case, the fact of such an original decomposition of **2** prompted us to carry out the reaction of **2** with amidacetals by boiling their equimolar mixtures in benzene for 5 hours with subsequent distillation of the reaction products.

$$Ar{-}AsH_2 \xrightarrow{150^\circ C} Ar{-}H + [AsH]$$

$$[AsH] \longrightarrow \underset{3}{[As_2H]} + \tfrac{1}{2} H_2$$

Ar = 2,4-di-tert-butyl-6-metylphenyl

Structures of the arsaalkenes **4a, b** thus obtained were deduced from ^1H, ^{13}C NMR, mass-spectral data as well as from results of the determination of their molecular masses. In the PMR spectrum of **4a** there is a signal with a chemical shift of 9.83 ppm, which is characteristic of a proton at the double —As=C< bond.[1] In the ^{13}C NMR spectrum of **4b** a carbon atom of the similar —As=C< bond has a chemical shift of 205.42 ppm which proves its sp^2-hybridization. In the EI mass-spectra of **4a** and **4b** there are peaks of molecular ions with M/z 335 and 349.



4a,b

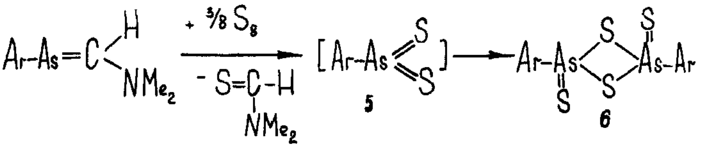
$$Ar{-}AsH_2 + (MeO)_2C(R)NMe_2 \longrightarrow \underset{4a,b}{Ar{-}As{=}C(R)NMe_2} + 2\,MeOH$$

Ar = 2,4-di-tert.-butyl-6-metylphenyl

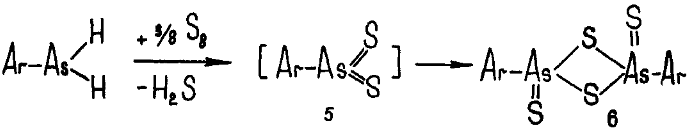
R=H(4a), R=Me(4b)

C-(N,N-Dialkylamino)-substituted phosphaalkenes are known to react with sulfur with cleavage of —P=C< bond and the formation of dithiophosphoranes.[15-17] We have found that the same occurs with C-(N,N-dialkylamino)-substituted arsaalkenes.

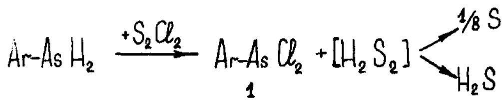
The dithioarsarane formed exists as a dimer **6** in the solid phase (ebullioscopic measurements) and as a monomer **5** in the gas phase (mass-spectrum).



A compound **6** may also be obtained from arsine and sulfur, though, however, phenylarsine was previously shown to react with sulfur adding only a single sulfur atom.[18]



While S_2Cl_2 is known to react with phenylphosphine to yield a dimeric dithiodiphosphetane disulfide,[19] we have found that arsine **2** reacts with S_2Cl_2 otherwise:



In the EI mass-spectra of reaction mixture of **2** and S_2Cl_2 there are present only peaks of molecular ions **1** and S_8. Analogous regiochemistry for the reaction of S_2Cl_2 with Ph_2AsH was also observed.[18]

CONCLUSION

The above said allows to deduce that unlike dithiophosphoranes [Ar—P(=S)$_2$][20] their As-containing analogs, dithioarsaranes [Ar—As(=S)$_2$], are less stable and do not exist as monomers under the ambient conditions.

EXPERIMENTAL

PMR spectra were recorded on a Varian T-60 spectrometer. IR spectra were measured on a spectrophotometer UR-20. The electron impact mass-spectra were recorded on a MX-1310 spectrometer at 60 V. All experiments were carried out under dry argon in anhydrous THF.

2,4-Di-tert-butyl-6-methylphenyl-dichloroarsine **1**. To a stirred solution of 78.0 g (430 mmol) of $AsCl_3$ in 200 ml of Et_2O was added at −78°C a solution of 48.2 g (150 mmol) 2,4-di-*tert*-butyl-6-methylphenylmagnesium bromide in 180 ml of THF. The temperature of the reaction mixture was allowed to rise to room temperature and then 250 ml of pentane was added. The precipitated solid was filtered. After removing the solvent from the filtrate, the residue was recrystallized from MeOH. Yield of **1** 45.2 g (87%); m.p. 107°C. PMR δ ($CDCl_3$) 1.06 (s, 9H, t-Bu), 1.46 (s, 9H, t-Bu), 2.36 (s, 3H, o-Me), 7.43 (m, 2H, C_6H_2). M/z 348. Found: C 50.7%, H 6.7%, $C_{15}H_{25}AsCl_2$. Calc.: C 51.2%, H 6.6%.

2,4-Di-tert-butyl-6-methylphenylarsine **2**. To a stirred suspension of 4.0 g (105 mmol) of $LiAlH_4$ in 100 ml of Et_2O was added at −78°C a solution of 53.6 g (134 mmol) of dichloroarsine **1** in 200 ml of THF. The reaction mixture was warmed to room temperature and then boiled for 15 minutes. The reaction mixture obtained was hydrolized by 20% solution HCl at 0°C and the organic phase was dried ($MgSO_4$) and evaporated. Distillation of the residue yielded **2** (30.3 g, 63%), b.p. 94–97°C/10^{-4} mm. PMR δ ($CDCl_3$) 1.26 (s, 9H, t-Bu), 1.66 (s, 9H, t-Bu), 2.58 (s, 3H, o-Me), 3.82 (s, 2H, AsH_2), 7.66 (m, 2H, C_6H_2). M/z 280. In the IR spectrum of **2** a band at 2090 cm^{-1} was observed which is characteristic of the As—H bond.

Thermal decomposition of **2**. Compound **2** (10 g) was boiled at 150°C for 2 hours. The precipitated reddish-brown solid was filtered. On subliming **3** (360°C) elemental arsenic was obtained. In the IR spectrum of **3** a band of 2100 cm^{-1} was observed, which is characteristic of the As—H bond. The filtrate was distillated to give 6.2 g (85%) 3,5-di-*tert*-butyltoluene with b.p. 98°C/5.4 mm, m.p. 31–32°C (lit.[21] m.p. 31–32°C). Found: C 88.1, H 11.9. $C_{15}H_{24}$. Calc.: C 88.16, H 11.84.

(N,N-Dimethylaminomethylidene)-2,4-di-tert-butyl-6-methyl-phenylarsine **4a**. A mixture of 1.7 g (7.5 mmol) of **2** and 1.33 g (11.1 mmol) of dimethyl acetal dimethylformamide in 10 ml of C_6H_6 was boiled for 5 hours and distilled to give 2.0 g (80%) of **4a** with b.p. 112–115°C/10^{-4} mmol. Found: C 63.88, H 9.2, N 8.7. $C_{18}H_{30}AsN$. Calc.: C 63.7, H 8.9, N 9.0. PMR δ ($CDCl_3$) 1.8 (s, 9H, t-Bu), 2.09 (s, 9H, t-Bu), 2.6 (s, 3H, o-Me), 3.43 (s, 6H, NMe_2), 7.43 (m, C_6H_2), 9.83 (s, —As═C—H); m/e 335.

(N,N-Dimethylaminoethylidene)-2,4-di-tert-butyl-6-methyl-phenylarsine **4b**. A mixture of 11.42 g (40 mmol) **2** and 10.5 g (80 mmol) of dimethyl acetal dimethylacetamide in 10 ml of C_6H_6 was boiled for 5 hours and distilled to give 10.2 g (70%) of **4b** with b.p. 131–137°C/10^{-4} mmol. Found: C 63.7, H 8.9, N 7.6. $C_{19}H_{32}AsN$. Calc.: C 63.3, H 8.82, N 7.4. PMR δ (C_6H_6) 1.06 (s, 9H, t-Bu), 1.47 (s, 9H, t-Bu), 2.34 (s, 3H, o-Me), 2.22 (s, 3H, —As═C—CH_3), 4.16 (s, 6H, NMe_2), 7.26 (m, C_6H_2); m/e 349. NMR ^{13}C δ ($CDCl_3$) 205.42 (s, —As═C<). The ebullioscopic measurements in benzene gave a value of 380 (the calculated molecular mass for a monomer is 349).

2,4-Bis(2,4-di-tert-butyl-6-methylphenyl)-2,4-dithio-1,3-dithia-2,4-diarsetan **6**. A mixture of 2.26 g (6.6 mmol) of arsaalkene **4a** and 1.2 g (19.8 mmol) of sulfur in 20 ml of C_6H_6 was boiled for 10 hours. The solvent was removed under vacuum of the water-pump; the residue was recrystallized from MeOH. Yield of **5**: 1.5 g (68%), m.p. 160°C. Found: C 53.0, H 6.5, S 18.2. $C_{30}H_{42}As_2S_4$. Calc.: C 52.9, H 6.2, S 18.8. PMR δ ($CDCl_3$) 1.7 (s, 9H, t-Bu), 2.97 (s, 9H, t-Bu), 2.86 (s, 3H, o-Me), 6.97 (m, C_6H_2); M/z 342 (monomer). The ebullioscopic measurements in benzene gave a value of 625 (the calculated value of the molecular mass for a dimer is 684).

2,4-Bis(2,4-di-tert-butyl-6-methylphenyl)-2,4-dithio-1,3-dithia-2,4-diarsetan **6** *(on the reaction of* **2** *with sulfur)*. A mixture of 3.7 g (13 mmol) of arsine **2** and 1.3 g (39 mmol) of sulfur in 20 ml of C_6H_6 was boiled for 10 hours. The solvent was removed under vacuum of the water-pump, the residue was recrystallized from MeOH. Yield of **5**: 2.9 g (78%), m.p. 160°C. Spectral data for **5** are identical to those described above.

Interaction of arsine **2** *with* S_2Cl_2. To 1.0 g (3.5 mmol) of arsine **2** in 20 ml of C_6H_6, 0.47 g (3.5 mmol) of S_2Cl_2 was added dropwise, with an exothermal reaction being observed. The solvent was then removed and the residue was recrystallized from MeOH. Yield of **1**: 1.25 g (76%). Spectral data for **1** are identical to those described above.

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