Unusual Substitution in an Arsole Ring

By *Gottfried Märkl* and *Hagen Hauptmann*[*]

The less pronounced nucleophilic character of tertiary arsanes[1, 2] compared to phosphanes is further reduced in the aromatic arsole system *(1)*. The chemistry of the arsoles resembles that of pyrrole rather than the phospholes.

1,2,5-Triphenylarsole and 1-phenyl-2,5-dimethylarsole are unable to form quaternary salts and sulfides; arsole oxides are formed only in moderate yields alongside arsenic-free decomposition products on oxidation with H_2O_2.

However, these arsoles react smoothly with elemental chlorine (as phenyl iodide dichloride) to give the stable 1,1-dichloro derivatives *(2)* (Table 1), and with *tert*-butyl hypochlorite to give the 1-chloro-1-*tert*-butoxy derivatives *(3)*:

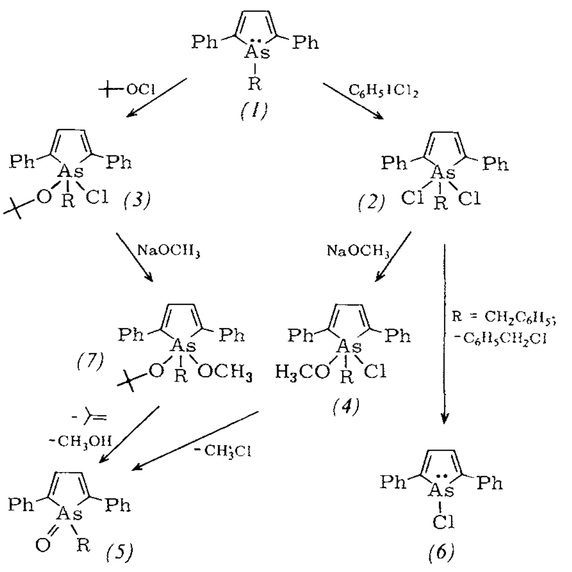

Table 1. 1,1-Dichloro derivatives *(2)* of 1,2,5-trisubstituted arsoles.

(2), R=	Yield (%)	M. p. (°C)	UV λ_{max} (nm) (log ε) (in ethanol)	^{1}H-NMR (τ) (in $CDCl_3$)
C_6H_5	96	168–169	395 (4.19) 239 (4.14) 220 (4.32)	
$CH_2C_6H_5$	88	85 (dec.)		
CH_3	83	170	400 (4.18) 237 (4.25)	—CH_3: 7.05 (s) aryl-H: 2.06–3.06 (m)

The dichlorides are thermolabile [1,1-dichloro-1-benzylarsole *(2)*, $R=C_6H_5CH_2$, decomposes at room temperature to 1-chloro-2,5-diphenylarsole *(6)*, fine red needles, m.p. 136—137°C; yield 85%; UV spectrum (in CH_2Cl_2): λ_{max} (log ε): 402 (4.07), 246 nm (4.23)] but surprisingly stable toward water and alcohols (recrystallized from ethanol). Reaction with one equivalent of Na methoxide furnishes the unstable 1-chloro-1-methoxyarsoles *(4)* which spontaneously lose methyl chloride to give the arsole oxide *(5)* in good yield ($R=C_6H_5$, yield 80%; m.p. 226—227°C. $R=CH_3$, yield 64%; m.p. 199°C. $R=CH_2C_6H_5$, yield 35%; m.p. 115°C (decomp.)).

The yellow-orange voluminous *tert*-butyl hypochlorite adducts *(3)* ($R=C_6H_5$, $CH_2C_6H_5$) resemble *(4)* in structure but do not decompose to the arsole oxides; however, they disproportionate in solution at room temperature to give *(2)*. In the case of $R=CH_2C_6H_5$ the reaction proceeds further to give the 1-chloroarsole *(6)* directly in 41% yield.

Reaction of *(3)*, $R=C_6H_5$, with $NaOCH_3$ proceeds directly to the arsole oxide *(5)*, $R=C_6H_5$, *via* the 1-methoxy-1-*tert*-butoxy derivative *(7)*.

These results suggested that the reaction of the *tert*-butyl hypochlorite adducts *(3)* with organolithium compounds should give pentacoordinate arsoles *(8)* or their reaction products. Surprisingly, the pale yellow crystalline reaction products are actually 3-substituted arsoles *(9)* (Table 2):

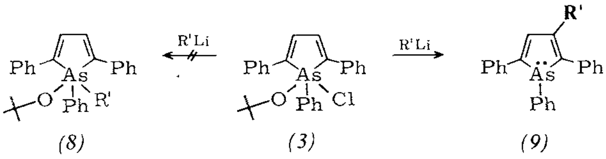

Table 2. 1,2,3,5-Tetrasubstituted arsoles *(9)*.

(9), R=	Yield (%)	M. p. (°C)	UV λ_{max} (nm) (log ε) (in ethanol)	^{1}H-NMR (τ) (in $CDCl_3$)
CH_3	36	122–124	353 (4.17) 234 (4.35)	—CH_3: 7.80 (s)
C_6H_5	40	151–152.5	370 (4.11) 265 (4.25) 240 (4.41)	aryl-H: 2.26–3.30
$C_6H_4N(CH_3)_2$	16	154–155	385 (4.00) sh 330 (4.30) 265 (4.32) 230 (4.39) sh	$N(CH_3)_2$: 7.08 (s) 6 aryl-H: 2.24–3.46

Formation of *(9)* can be rationalized mechanistically as S_N2' substitution and subsequent aromatization by elimination of *tert*-butanol.

The bulky *tert*-butyl group induces the S_N2' mechanism by blocking nucleophilic attack at the heteroatom.

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General Synthesis of Aryl-Substituted Arsabenzenes

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Both the "phenarsazine" described by *Wieland*[1] in 1921 and the "arsanthrene" of *Kalb*[2] have been shown by *Bickelhaupt et al.*[3, 4] to be dimers and therefore not arsaaromatic compounds containing —As=C$\lessgtr$ (4pπ—2pπ) double bonds.

Evidence for the existence of this bond system was first provided by the preparation of arsamethinecyanines[5].

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