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ON THE FORMATION OF THE SO-CALLED ARSANTHRENE

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Abstract—The structure of Kalb's "arsanthrene oxide" and "arsanthrene" have been reinvestigated. The "arsanthrene oxide" is monomeric and is therefore properly termed 5,10-epoxy-5,10-dihydroarsanthrene(**6**). A spectroscopic study of "arsanthrene" revealed that this compound has the dimeric structure **12** corresponding to the photodimer of anthracene. Mechanisms of formation of dimeric "arsanthrene" and the possible dissociation of dimeric "arsanthrene" into its monomer by reaction with a dienophile at elevated temperature are discussed. An attempt to synthesize arsanthrene (**7**) by dehalogenation of 5,10-dichloro-5,10-dihydroarsanthrene (**5**) was unsuccessful. The mass spectral fragmentation patterns of some 5,10-dihydroarsanthrenes are recorded.

The arsanthrene ring system was first synthesized by Kalb,[1] utilizing the series of reactions shown in Scheme 1.

Hydrolysis of 5,10-dichloro-5,10-dihydroarsanthrene (**5**) with aqueous sodium carbonate gave 5,10-epoxy-5,10-dihydroarsanthrene (**6**). Reduction of **5** with zinc and hydrochloric acid or of **6** with phenylhydrazine was reported by Kalb to give the parent arsanthrene (**7**).[1] This compound is structurally of great interest, because it is an aromatic system which contains two arsenic atoms in a two-coordinated, $p\pi$-hybridized state. However, since no molecular weight determination or other physical measurements were carried out, and also in view of our experience that tricyclic heteroatomatic phosphorus and arsenic compounds are only of limited stability,[2] it was unlikely that Kalb's compound had the simple structure **7**. The same holds for the so-called phenarsazine (**8**), synthesized at the same time by Wieland and Rheinheimer.[3] The proposed aromatic structure **8** proved to be incorrect; recently, we showed that this compound is identical with 10,10′-bis-(5,10-dihydrophenarsazinyl) (**9**).[4]

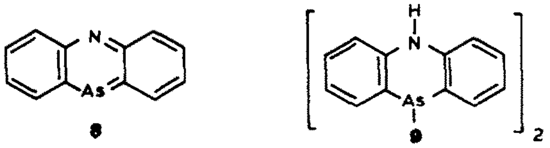


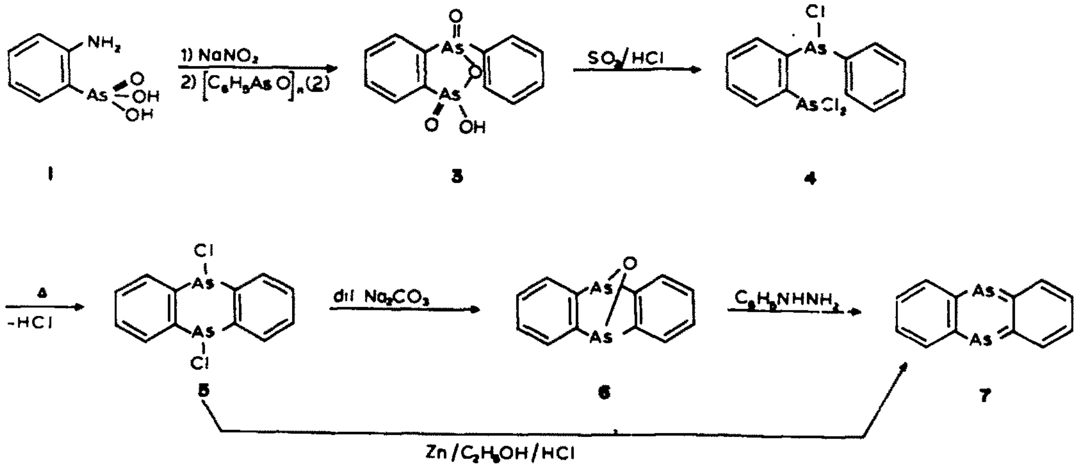
Fig. 1.

In this paper we give a full description of the formation and structure of Kalb's "arsanthrene"; some of the results have been published in preliminary form.[5,6] Further, the mass spectra of some 5,10-dihydroarsanthrenes were examined as part of our interest in the formation of heteroanthracenes upon electron impact.[2,4,7,8]

RESULTS AND DISCUSSION

Synthesis of the dihydroarsanthrene system.

Structure of "arsanthrene". According to Kalb's procedure, **7** can be obtained from **6** and we therefore synthesized this compound by the cumbersome route of Kalb[1] (Scheme 1). Oxophenylarsine [arsenosobenzene (**2**)] was prepared from phenyldichloroarsine.[9] It has been suggested[10] that **2** exists in a monomeric as well as in a polymeric form. We have found by means of vapour pressure osmometry that **2** is tetrameric in toluene (Experimental).



Scheme 1.

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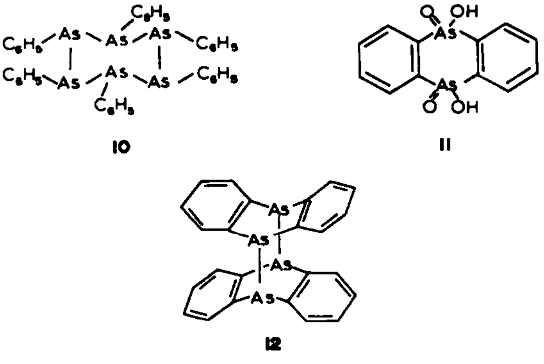
2-Aminophenylarsonic acid (1)[11] was diazotized and treated with 2 under the usual Bart reaction conditions[12] to give the anhydride of 2-arsono-diphenylarsinic acid (3) (Kalb reports for this compound the structure of the acid instead of 3[1]). This acid was converted to a mixture of 2-(dichloroarsino)diphenylarsinous chloride (4) and 5, as described by Chatt and Mann.[13]

Kalb formulated structure 6 on the basis of elemental analysis, but without determination of the molecular weight, However, the possibility of a dimer, affording relief of possible strain in 6 could not be excluded. We found that compound 6 is indeed monomeric in toluene and the mass spectrum showed the molecular ion at *m/e* 318 ($C_{12}H_8As_2O^+$, calc.: 318). 6 can therefore be regarded as the internal anhydride of 5,10-dihydroxy-5,10-dihydroarsanthrene. At our instigation MacGillavry *et al.*[14] elucidated the crystal and molecular structure of 6 by a single-crystal X-ray diffraction study which confirmed a monomeric bridged structure.

Kalb's arsanthrene, a golden-yellow, metallic bright compound, was obtained by both routes in *ca.* 80% yield. Vacuum sublimation gave the pure product with a melting point of 359–361°. The extremely low solubility of the compound prevented an osmometric determination of the molecular weight and made the spectroscopic and chemical investigation difficult. The low number of bands in the IR spectrum (KBr) indicated a very simple symmetrical structure. The UV spectrum showed maxima at 229, 278 and 328 nm ($\epsilon_{328} = 4300$), which made the proposed aromatic structure very unlikely in view of the maxima at 399, 423 and 448 nm for 9-arsaanthracene.[15] On the other hand, the absorption at 328 nm is analogous to that of arsenobenzene (10), which has been tentatively assigned to a transition involving a non-bonding electron and an As–As dπ orbital.[16] This band at 328 nm might therefore be considered as evidence for the presence of As–As bonds. The UV spectrum disappeared when air was admitted to the solution; a precipitate of the arsanthrenic acid 11[3] was formed quantitatively; 11 was also obtained upon oxidation of Kalb's compound with hydrogen peroxide in dilute sodium hydroxide. The mass spectrum showed $C_{24}H_{16}As_4^+$ (*m/e* 604, 58%) as molecular ion, which indicates that the compound is a dimer of 7.



10

11

12

Fig. 2.

The results we have discussed above, rule against the monomeric aromatic structure 7. They are in agreement with a dimeric structure 12 corresponding to that of the photodimer of anthracene.[17] To verify this conclusion an X-ray structural analysis of "arsanthrene" was performed, which actually confirmed the dimeric structure 12.[6]

The mechanism of formation of dimeric arsanthrene

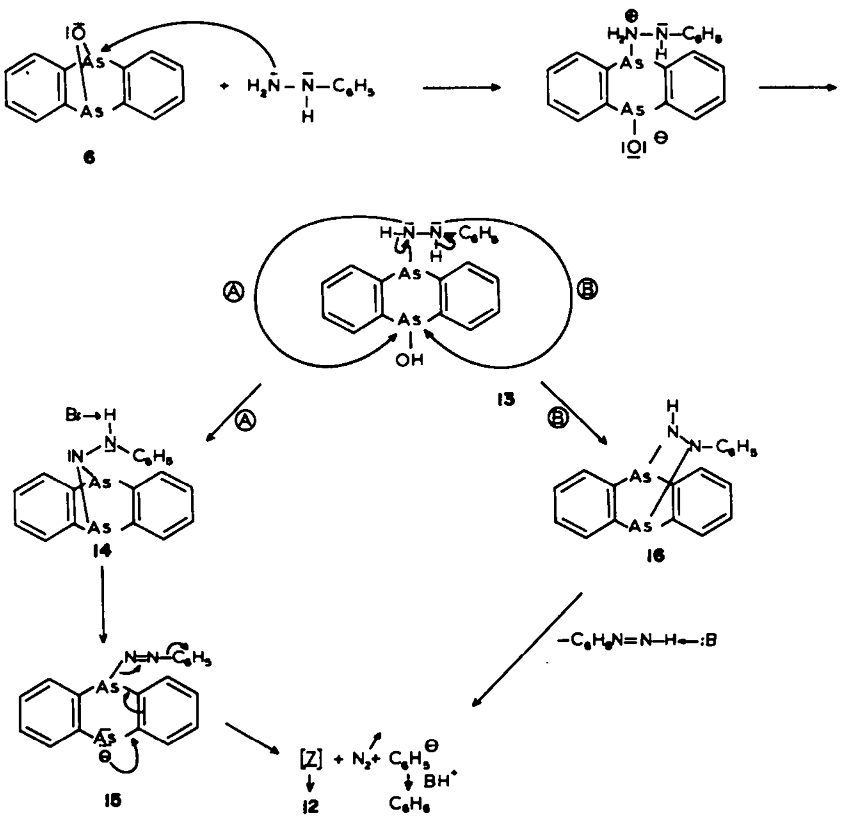
The reaction of 6 with phenylhydrazine (reactant and solvent) is accompanied by evolution of nitrogen. Furthermore, we found 95% benzene in the reaction mixture identified by UV spectroscopy and gas chromatography. A control experiment showed that benzene was not formed in the absence of 6. Therefore, we propose a reaction mechanism via route A as depicted in Scheme 2. The nucleophilic attack of the N atom on arsenic gives the intermediate 13, which is converted to species 14 by an internal attack of the same N atom on the second arsenic. Arsanthrene (7) could then possibly be formed as intermediate by elimination of nitrogen and benzene from 15 to give 12. This mechanism seems attractive because of the structural analogy between 14 and 6 or other epi-dihydroarsanthrenes.[14]

However, there is a plausible alternative pathway B starting from 13 by attack of the second nitrogen on the second arsenic to yield 16 which, in a retro Diels–Alder reaction could give 7 and phenyldiimine; the latter is known to decompose to benzene and nitrogen under the influence of base.[18] Under the reaction conditions (*ca* 135°) the aromatic system 7 reacts with itself by a formal 4+4 cycloaddition. This reaction is thermally forbidden according to the Woodward–Hoffmann rules.[19] However, the relevance of this rule in our case is questionable. Arsenic d orbitals of the appropriate energy could combine with the carbon π orbitals giving a set of molecular orbitals with symmetries that make the thermal 4+4 cycloaddition an allowed process. On the other hand, a nonconcerted course of the reaction cannot be excluded.

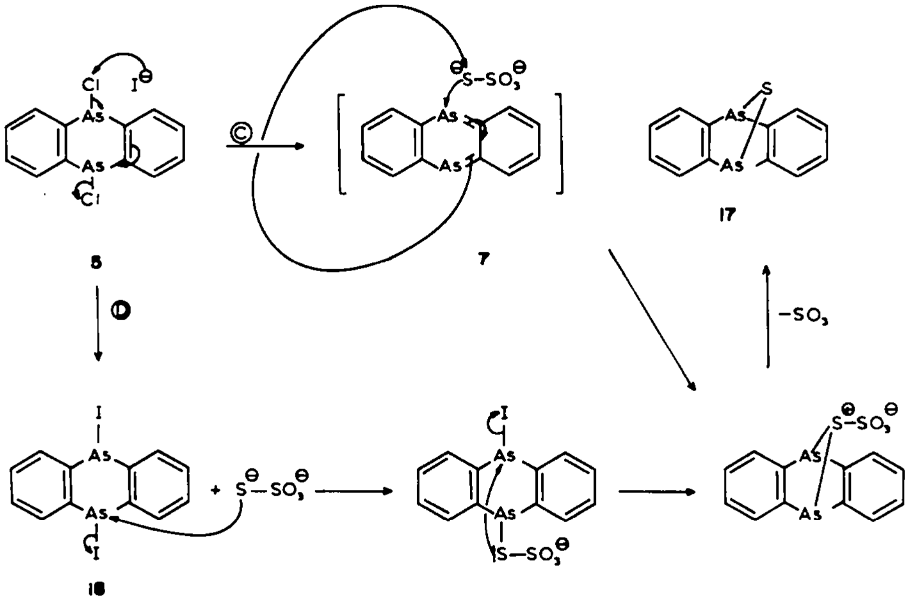
Attempted alternative synthesis of arsanthrene

A method of synthesizing alkenes is the dehydrohalogenation of dihalides. These eliminations may be brought about by a large number of dehalogenating agents.[20] Kalb's second route to 12 by reduction of 5 by zinc is an example of this approach. We attempted to dehalogenate 5 under milder conditions with potassium iodide in dimethylformamide solution at room temperature. In order to prevent any subsequent action of the iodine formed during the reaction on the presumably reactive 7, sodium thiosulfate was added. When working up the reaction mixture under nitrogen we isolated 5,10-epithio-5,10-dihydroarsanthrene (17). The structure of 17 was elucidated by elemental analysis, and by UV, ^{1}H NMR and mass spectra. The formation of 17 might have occurred by nucleophilic attack of the thiosulfate ion on 7, as depicted in Scheme 3 (Pathway C).

In order to detect 7 as a possible intermediate, the reaction was performed in the presence of maleic anhydride. An excess of this trapping agent was used in order to remove the iodine by addition. However, the Diels–Alder adduct was not formed as appears from the almost quantitative isolation of 5,10-diiodo-5,10-dihydroarsanthrene (18), identified by its elemental analysis, and by ^{1}H NMR and mass spectra. When its ethereal solution was shaken with aqueous sodium carbonate 18 was quantitatively converted to 6. Treatment of 18 with sodium thiosulfate in dimethylformamide solution afforded 17 in 98% yield. This result indicates that the formation of 7 as intermediate is not necessary and even very unlikely. Therefore, we assume that the diiodo compound 18 is formed by an attack of the iodide ion on the arsenic of 5 under extrusion of the chloride ion. The formation of 17 may occur as depicted for route D.



Scheme 2.



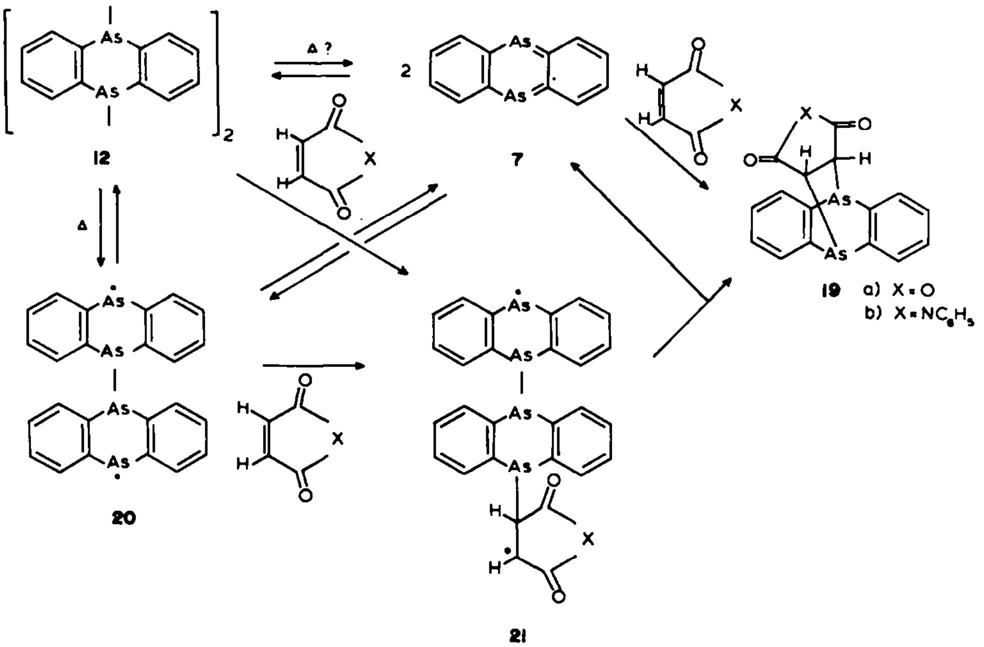
Scheme 3.

Nucleophilic substitution on arsenic is followed by an internal attack on the second arsenic. Finally, elimination of sulfur trioxide leads to 17.

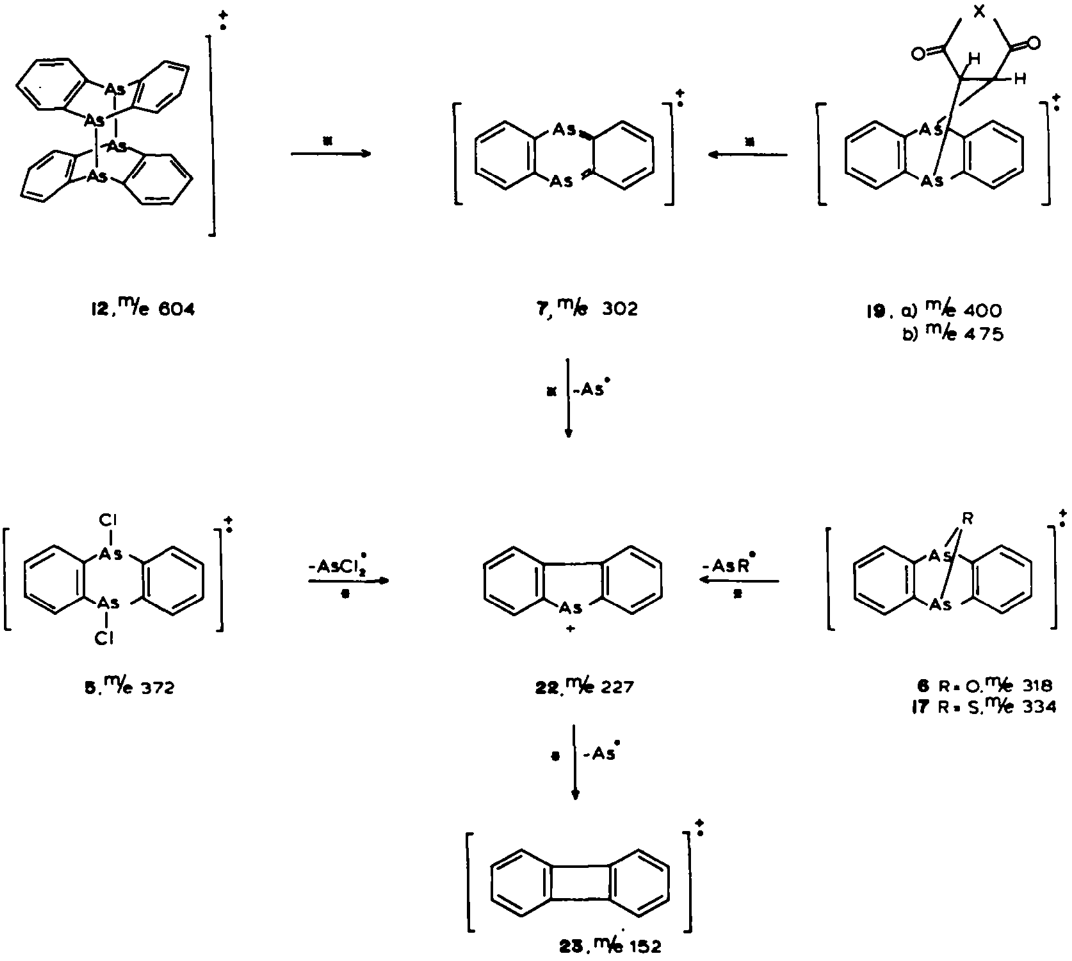
Mann *et al.*[21] reported the synthesis of 17 from the reaction of the epoxy compound 6 with hydrogen sulfide in ethanol solution. X-ray crystal analysis has established the complete structure and conformation of 17 as the 5,10-epithio compound.[14]

Reaction of dimeric arsanthrene 12 with dienophiles

Although we did not succeed to prove the existence of the monomer 7 in the elimination with thiosulfate (Scheme 3), we were able, starting from 12, to obtain the Diels–Alder adducts of 7 with maleic anhydride and N-phenylmaleimide, 19a and 19b, respectively (Scheme 4). The reaction conditions were as follows: 12 was heated together with a slight excess of the dienophile in a



Scheme 4.



The symbol * indicates a metastable peak.

Scheme 5.

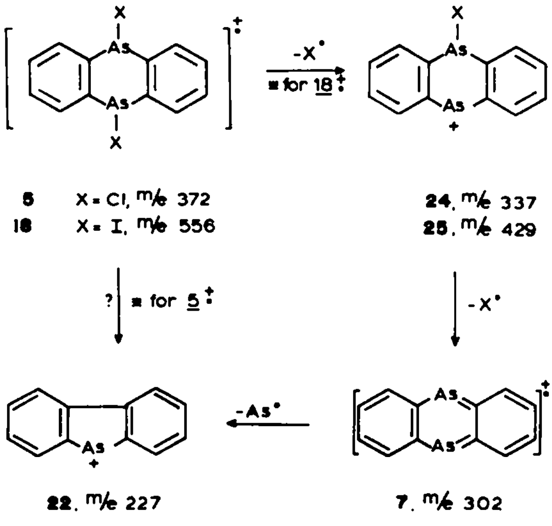
sealed vacuum tube. The lowest temperature required for reaction was estimated to be about 120°. At higher temperatures (135, 165 and 200°) the reaction proceeded more smoothly and was complete in about 1.5–2 hr as indicated by the disappearance of the golden-yellow colour of **12**. At these reaction conditions, in which the dienophile is in the vapor phase, it is tempting to speculate on a fast equilibrium between the dimer **12** and its monomer **7**, which reacts irreversibly with the dienophile to **19**. By heating **19** in vacuo a retro Diels–Alder reaction was not observed (under electron impact, retro Diels–Alder reaction of **19** occurs easily; see next section); likewise, the Diels–Alder adducts of 9-arsaanthracenes are not cleaved thermally.[22]

However, the experimental results can also be explained without postulating **7** as an intermediate. Cleavage of the As–As bond in **12**—either via the diradical **20** which is intercepted by the dienophile to form **21**, or by an induced direct reaction of **12** to **21**—followed by further reaction of **21** to **19** and **7** appears to be at least equally attractive, especially if one considers the high temperature of sublimation of **12** (230°/10^{-3} mm) (*cf* 10-phenyl-9-arsaanthracene; which sublimes at 130°/10^{-3} mm) and the low temperature (120°) at which the Diels–Alder reaction starts.

Mass spectra of some 5,10-dihydroarsanthrenes

In the course of the structural study of some dihydroarsanthrenes we examined the mass spectra of **5**, **6**, **12**, **17**, **18** and **19** (Experimental). On the strength of metastable peaks and exact mass measurement the fragmentation paths as shown in Scheme 5 and 6 were established. Alternative fragmentation pathways are of lesser importance as shown by the low relative abundance of the corresponding ions and the absence of metastable peaks.

The mass spectra, with the exception of that of **18**, show distinct molecular ions; the base peak is the same in each spectrum (*m/e* 227; except for **19b**). This is attributed to the 9-arsafluorenyl ion **22**, which again loses arsenic resulting in the *o,o*-biphenylene species **23**. For the compounds **6** and **17**, **22** arises by the simultaneous loss of arsenic and the bridging element. In the case of **5** we observed a similar fragmentation; $5^{+\cdot}$ gives **22** by loss of $AsCl_2$. Under electron impact **19a** and **b** give a retro Diels–Alder reaction to $7^{+\cdot}$ (*m/e* 302), which gives the expected fragment 22^{+} and $23^{+\cdot}$.



Scheme 6.

Our results are in good agreement with those reported by Mann *et al.*[21] for the compounds **6** and **17**; however, for the dichloro compound **5** the authors described the fragmentation pattern as depicted in Scheme 6.

This fragmentation pattern was also observed by us, but the loss of Cl˙ was not supported by metastable peaks. There are several precedents in the literature in which the presence of a metastable peak does not constitute conclusive evidence for a one-step decomposition process. It appears that metastable peaks may arise from two-step or possibly even from multi-step fragmentation reactions.[23] Therefore, the decomposition of $5^{+\cdot}$ to 22^{+} which occurs with appropriate metastable peak, is likely to correspond to a three-step process, as described in Scheme 6. Only this latter pattern was found for the diiodide compound **18**; the loss of I˙ was supported by metastable peaks.

EXPERIMENTAL

All m.ps are uncorrected; those of compounds sensitive to air and moisture were determined in sealed capillaries. The IR spectra were obtained on a Perkin–Elmer model 237 spectrophotometer, the NMR spectra with a Varian A-60 or a Bruker WH-90 spectrometer (chemical shifts relative to tetramethylsilane as an internal standard, $\delta = 0$ ppm), the UV spectra with a Perkin–Elmer 137 spectrophotometer and the mass spectra with a Varian MAT CH-5 mass spectrometer at 70 eV. The molecular weights were determined with a Hewlett-Packard 302B vapor pressure osmometer in toluene as solvent. Elemental analyses were carried out under supervision of Mr. W. J. Buis at the Analytical Department of the Institute for Organic Chemistry TNO, Utrecht, The Netherlands.

Oxophenylarsine [*Arsenosobenzene*, (**2**)]

This compound is most conveniently prepared from phenyldichloroarsine, which is readily available from phenylarsonic acid.[10,24,25] 404 g (2 mol) of phenylarsonic acid were dissolved in conc. HCl (700 ml) and treated with a stream of SO_2 for 3 hr. From time to time a trace of KI soln was added (0.2–0.5 g of KI is usually sufficient to complete the reduction). The crude phenyldichloroarsine separated as a heavy oil. This was dissolved in CS_2 (700 ml) and the soln dried with $CaCl_2$. After filtration and evaporation to dryness the residue was vacuum distilled and yielded 406.9 g (91%) of almost colourless phenyldichloroarsine (b.p. 102–105°/1 mm). This was cautiously added dropwise to a warm stirred soln of NaOH (350 g, 8.75 mol) in H_2O (800 ml). After the addition, the soln was stirred for 1 hr, then neutralized (pH = 7) with HCl, whereupon a white ppt was obtained in a yield of 88% (based on phenyldichloroarsine). Recrystallization (benzene/ether) gave pure **2**, m.p. 120–121° (lit. 144–146°,[9] 119–120°[10]). Repeated crystallization from c-C_6H_{12} did not change the m.p., which is not in keeping with the result of Steinkopf *et al.*[10] Found: C, 42.97; H, 3.04; As, 44.41. C_6H_5AsO (M = 168.03), requires; C, 42.89; H, 3.00; As, 44.59%. IR (KBr) ν max in cm^{-1}: 840–700 (s), As–O–As.[26] Molecular weight (toluene): 670; Calc. for $(C_6H_5AsO)_4$: 672.

Anhydride of 2-arsonodiphenylarsinic acid (**3**)

A soln of **1**[11] (64 g, 0.295 mol) in H_2O (600 ml), mixed with conc HCl (88 ml), was diazotized at 0° by the slow addition of a soln of $NaNO_2$ (20 g) and then poured slowly into 1 litre of vigorously stirred ice-water concurrently with a cold soln of **2** (60 g, 0.357 mol) in 5N NaOH (280 ml) and 1N Na_2CO_3 (240 ml). The pH of the soln was kept between 7 and 10 during the addition. The mixture was set aside at 5° overnight, then diluted with H_2O (1 litre) and heated to 95°. Conc. HCl was cautiously added until pH = 6. The filtered soln was heated to 95° and acidified with acid (congo-red); **3** precipitated as a light brown powder in 65% yield (based on **1**); it was purified by boiling its soln in aqueous

Na_2CO_3 (charcoal) and reprecipitation with HCl, m.p. 353° (lit.[1] 350°). Found: C, 38.99; H, 2.76; As, 40.90. $C_{12}H_{10}As_2O_4$ (M = 368.02), requires: C, 39.16; H, 2.74; As, 40.70%. IR (KBr) ν max in cm^{-1}; 3200 (s), 2330 (m), 1630 (w), AsO–H; 900 (m), As=O; 850–650 (s), As–O–As. Equivalent weight (potentiometric titration in 0.1N NaOH with 0.1N HCl): 336.

5,10-*Dichloro*-5,10-*dihydroarsanthrene* (5)

(a) Compound **5** was prepared as described by Chatt and Mann.[13] Recrystallization ($CHCl_3$) and vacuum sublimation yielded pure **5**, m.p. 183–185° (lit. 182–183°,[1] 179–184°[13]). Found: C, 38.56; H, 2.25; As, 39.59; Cl, 19.36. $C_{12}H_8As_2Cl_2$ (M = 372.92), requires: C, 38.64; H, 2.16; As, 40.19; Cl, 19.01%. NMR ($CDCl_3$): 8.23–7.96 (m, 4, aryl protons), 7.68–7.43 (m, 4, aryl protons). UV (c–C_6H_{12}), λ max in nm (log ϵ): 230 (4.57), 274 (3.83). Mass spectrum *m/e* (%): 376 (1.0), 374 (5.5), 372 (9.0), 339 (2.5), 337 (8.0), 302 (3.0), 227 (100), 152 (34.0), 151 (19.5).

(b) In an attempt to obtain direct cyclization, a stirred soln of **3** (500 mg) in polyphosphoric acid (15 g) was heated at 150° for 15 min and then poured into H_2O (150 ml), but only **3** (m.p. and m. m.p. 349–351°) separated. The IR spectrum turned out to be identical with the spectrum of the starting material.

5,10-*Epoxy*-5,10-*dihydroarsanthrene* (6)

A soln of **5** (1 g) in ether (20 ml) was vigorously shaken with 1 N Na_2CO_3 (10 ml) for 2 hr. The ether was evaporated, the precipitated product **6** (0.85 g, 100%) collected, washed with H_2O and dried. Vacuum sublimation at 110°/5.10^{-2} mm and crystallization (CH_3OH) afforded pure **6**, m.p. 196–197° (lit. 196°,[1] 197–199°[21]). Found: C, 45.29; H, 2.60; As, 46.94. $C_{12}H_8AsO$ (M = 318.00), requires: C, 45.32; H, 2.54; As; 47.11%. NMR ($CDCl_3$): 8.08–7.76 (m, 4, aryl protons), 7.40–7.06 (m, 4, aryl protons). UV (c–C_6H_{12}), λ max in nm (log ϵ): 239 sh (3.98), 278 (2.87). IR (KBr) ν max in cm^{-1}: 640 (s), As–O–As. Mass spectrum *m/e* (%): 318 (23.0), 227 (100), 152 (25.5), 151 (18.0).

Dimer of arsanthrene (12)

(a) *Preparation of* **12** *from* **6** *and phenylhydrazine.*[1] Under argon a mixture of **6** (483.8 mg, 1.52 mmol), toluene (142.9 mg) and phenylhydrazine (5 ml, freshly distilled) was heated until the temp. of the soln reached 135° and held at this temp. for 5 min. The formation of golden-yellow crystals was accompanied by evolution of N_2 (identified by mass spectroscopy). In the mixture 95% benzene was found by means of UV spectroscopy and gas chromatography. The supernatant liquid was removed by a pipet, the crystals washed with dry ether and dried *in vacuo* yielding crude **12**, (379.2 mg, 82.5%). Vacuum sublimation at 230°/10^{-3} mm afforded pure **12**, m.p. 359–361° (lit. *ca* 340°[1]). Found: C, 47.75; H, 2.92; As, 49.47. $C_{24}H_{16}As_4$ (M = 604.01), requires: C, 47.72; H, 2.67; As, 49.61%. UV (THF, because of the air-sensitiviness the measurement was performed under vacuum), λ max in nm (log (ϵ); 229 (4.79), 279 (4.57), 328 (4.02). IR (KBr) ν max in cm^{-1}: 3045 (w), 1445 (m), 1415 (m), 1260 (m), 1090 (m), 760 (m), 740 (s), 735 (s). Mass spectrum *m/e* (%): 604 (57.5), 302 (69.0), 227 (100), 152 (68.0), 151 (22.0).

(b) *Preparation of* **12** *from* **5** *by zinc and hydrochloric acid.*[1] The reaction of **5** (992 mg, 2.66 mmol) with Zn (1.6 g) and conc HCl (8 ml) in abs EtOH yielded crude **12**, (770.4 mg, 95.9%); after vacuum sublimation it was identical with pure **12**, prepared from **6**, according to m.p. and IR spectrum.

(c) *Reaction of* **12** *with hydrogen peroxide.* Addition of 30% H_2O_2 (10 ml) to **12** (98.5 mg, 0.326 mmol) and heating for 1 hr afforded after filtration **11**, (116.3 mg, 96.9%). It was purified by boiling its soln in Na_2CO_3aq (charcoal) and precipitating with HCl, m.p. above 360° (lit. above 360°[3]). Found: C, 39.45; H, 2.83; As, 40.55; O, 17.04. $C_{12}H_{10}As_2O_4$ (M = 368.02), requires: C, 39.16; H, 2.74; As, 40.71; O, 17.39%. IR (KBr) ν max in cm^{-1}: 2660 (s), 2290 (s), 1690 (s), AsO–H; 885 (s), As=O. Equiv, wt (titration with 0.1N NaOH): 191.

(d) *Reaction of* **12** *with air.* A deep yellow soln of **12** (12.1 mg, 0.040 mmol) in THF prepared under vacuum was allowed to react with air. The colour vanished and a white ppt was formed. Filtration, washing with THF and drying *in vacuo* yielded **11**, (13.9 mg, 94.3%), m.p. above 360°. The elemental analysis and IR spectrum showed the compound to be identical with **11** from the H_2O_2 oxidation.

Attempted alternative synthesis of 7 *from* 5

(a) *Preparation of* **17**. A soln of KI (201.7 mg, 1.215 mmol) in dry DMF (5 ml) was added dropwise under N_2 to a soln of **5** (112.3 mg, 0.301 mmol) and anhyd $Na_2S_2O_3$ (111.3 mg, 0.704 mmol) in dry DMF (10 ml). After stirring for 1 hr, the soln was evaporated to dryness and the residue extracted several times with dry toluene. Evaporation of the solvent yielded crude **17**, (98.3 mg, 98%). Vacuum sublimation at 90°/10^{-3} mm afforded pure **17**, m.p. 184–185° (lit. 184–185°[21]). Found: C, 43.18, H, 2.28, S, 9.65. $C_{12}H_8As_2S$ (M = 334.07), requires: C, 43.14; H, 2.41; S, 9.60%. NMR (CS_2): 8.02–7.69 (m, 4, aryl protons), 7.24–6.90 (m, 4, aryl protons). UV (c–C_6H_{12}) λ max in nm (log ϵ): 221.5 (4.40), 279 (3.25), 288 (3.16). Mass spectrum *m/e* (%): 334 (3.5), 227 (100), 184 (5.0), 152 (18.0), 151 (14.5), $C_{12}H_8As_2S^{\dagger}$, calcd. 333.8779; found 333.8777.

(b) *Preparation of* **18**. A soln of KI (909.2 mg, 5.48 mmol) in dry DMF (25 ml) was added dropwise under N_2 to a soln of **5** (500 mg, 1.34 mmol) and maleic anhydride (277.1 mg, 2.83 mmol) in dry DMF (10 ml). When the addition was accomplished the soln was stirred for 4 hr, evaporated to dryness and the residue extracted with dry $CHCl_3$. Evaporation of the solvent gave crude **18**, (698.8 mg, 94%). Recrystallization ($CHCl_3$) yielded yellow crystals of pure **18**, m.p. 202–206°. Found: C, 26.26; H, 1.63; I, 46.01. $C_{12}H_8As_2I_2$ (M = 555.80), requires: C, 25.93; H, 1.45; I, 45.66%. NMR (D_6-DMSO): 8.18–7.93 (m, 4, aryl protons), 7.42–7.13 (m, 4, aryl protons). Mass spectrum *m/e* (%): 556 (0.7), 429 (45.0), 302 (27.5), 227 (100), 152 (65.5), 151 (41.0). $C_{12}H_8As_2I_2^{\dagger}$, Calc. 555.7146; found 555.7164.

Reaction of **18** *with sodium carbonate.* A soln of **18** (50 mg) in ether (20 ml) was shake n with 1N Na_2Co_3 (5 ml) for 2 hrs. The ether was evaporated and the residue (28.2 mg, 98.6%) was identified as **6** by its m.p. and IR spectrum.

Reaction of **18** *with sodium thiosulfate.* Addition of **18** (129.2 mg, 0.232 mmol) in dry DMF (5 ml) to a soln of $Na_2S_2O_3$ (178.4 mg) in dry DMF (10 ml) and shaking for 3 min afforded a colourless soln. On working up as before, **17**, (77.7 mg, 98.3%) was obtained as identified by its m.p. and IR spectrum.

5,10-*Dihydro*-5,10-*ethanoarsanthrene*-11,12-*dicarboxylic anhydride* (19a)

Compound **12**, (604 mg, 1.00 mmol) and maleic anhydride (245 mg, 2.50 mmol) were mixed together in a sealed high vacuum tube and heated at 220° for 2 hr. After cooling, the tube was opened and the crude mixture extracted with diethyl ether (15 ml) to remove excess of maleic anhydrice. The residue was crystallized ($CHCl_3$) and yielded **19a**, (586.7 mg, 73.3%), m.p. 278–280°. Found: C, 47.88; H, 2.64; O, 12.14. $C_{16}H_{10}As_2O_3$ (M = 400.10), requires: C, 48.03; H, 2.52; O, 12.00%. NMR ($CDCl_3$): 8.13–7.84 (m, 4, aryl protons), 7.60–7.33 (m, 4, aryl protons), 3.66 (s, 2, anhydride ring protons). IR (KBr) ν max in cm^{-1}: 1830 (s), 1810 (s) and 1760 (s), anhydride. Mass spectrum *m/e* (%): 400 (<0.1), 303 (12.9), 302 (82.4), 228 (14.7), 227 (100), 152 (33.8), 151 (22.1).

5,10 - *Dihydro* - 5,10 - *ethanoarsanthrene* - 11, 12 - N - *phenylmaleimide* (19b)

Compound **12**, (253 mg, 0.420 mmol) and N-phenylmaleimide (155.9 mg, 0.900 mmol) were thoroughly mixed in a high vacuum sealed tube. After heating at 200° for 1.5 hr and cooling, the crude mixture was dissolved in $CHCl_3$ and chromatographed on a small column of silicagel using $CHCl_3$ as eluent. The eluate was concentrated to a small volume, hot MeOH added and after cooling **19b** crystallized, m.p. 262–263°, yield 314.0 mg, 78.8%. NMR ($CDCl_3$): 8.07–7.80 (m, 4, aryl protons), 7.54–7.32 (m, 4, aryl protons), 7.32–7.11 m, 3, aryl protons), 6.56–6.33 (m, 2, aryl protons), 3.58 (s, 2, imide ring protons). IR (KBr) ν max in cm^{-1}: 1755 (s) and 1690 (s), imide. Mass spectrum *m/e* (%): 475 (0.4), 302 (100), 227 (89.5), 173 (5.1), 152 (12.3). $C_{22}H_{15}As_2NO_2^{\dagger}$. Calc.: 474.9534; Found: 474.9544.

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