THE SYNTHESIS OF VICINAL BIS(DIMETHYLARSINO) COMPOUNDS

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SUMMARY

The reaction between $NaAs(CH_3)_2$ and $o\text{-}Cl_2(C_6H_4)$ has been studied and the following products identified: $(CH_3)_2AsH$, $o\text{-}[(CH_3)_2As]_2[C_6H_4]$, $(CH_3)_3As$, $(CH_3)_2As(C_6H_5)$, 5,10-dimethyl-5,10-dihydroarsanthren and methylbis[o-(dimethylarsino)phenyl]arsine. The reaction between $NaAs(CH_3)_2$ and *cis*-1,2-dichloroethylene gives a mixture of *cis*- and *trans*-1,2-bis(dimethylarsino)ethylene, while 1,2-dibromoethylene yields bis(dimethylarsino)acetylene, and 1-bromo-1,2-bis(dimethylarsino)ethylene. $NaAs(C_6H_5)_2$, and $NaP(C_6H_5)_2$ react with 8-chloroquinoline to give 8-(diphenylarsino)quinoline and 8-(diphenylphosphino)quinoline, respectively. An improved synthesis of *cis*-1,2-bis(dimethylarsino)ethylene by hydroboration of bis(dimethylarsino)acetylene is also reported. The proton NMR and mass spectra of these novel arsine compounds are discussed.

INTRODUCTION

The synthesis of polydentate ligands of tertiary arsines and tertiary phosphines has been a research problem of considerable practical importance. Chelating tertiary phosphines and arsines have been of value for stabilizing transition metals in both high and low oxidation states, and for stabilizing otherwise unstable metal–ligand systems. There are several general synthetic routes which can be utilized for the preparation of tertiary arsines and phosphines[1,2]. One of the more important routes for the synthesis of polyfunctional arsines is the reaction of an alkali metal derivative of secondary arsines with an organic halide with the desired structure. When the secondary arsine is diphenylarsine, then the substitution reactions with organic halides proceed in good yield with retention of configuration. Thus, $NaAs(C_6H_5)_2$ reacts with *cis*- or *trans*-1,2-dichloroethylene producing *cis*- or *trans*-1,2-bis(diphenylarsino)ethylene in 61 % yield[3]. However, the reactions of the corresponding salts of dimethylarsine with o-dichlorobenzene[4], and *cis*-1,2-dichloroethylene[5,6] give significantly smaller yields of the substitution products, (30%–50%), and in the case of *cis*-1,2-dichloroethylene, proceed with loss of configuration. For these reasons, the reactions of $NaAs(CH_3)_2$ with organic halides have been examined in some detail.

EXPERIMENTAL

All experiments were carried out under nitrogen in an efficient hood since the compounds are both noxious and toxic. Chemicals were used as obtained from J. T. Baker, Mallinckrodt, and M and T Chemicals, when further purification is not specified. Diglyme was dried before use by distillation under reduced pressure from lithium aluminum hydride, and sodium borohydride was recrystallized from dry diglyme before use. The compounds were analyzed by Huffman Laboratories, Wheatridge, Colorado. The IR spectra were obtained by use of a Perkin-Elmer Model 337 spectrophotometer. The mass spectra were obtained using a double focusing Perkin–Elmer–Hitachi model RMU-6e spectrometer, and the NMR spectra were recorded on a Varian HA-100 or model A-60. Dimethyliodoarsine and dimethylarsine were prepared as described previously[4].

The reaction of NaAs(CH₃)₂ with o-dichlorobenzene

A three-necked round bottom flask equipped with a mechanical stirrer, dropping funnel, and nitrogen inlet and outlet was charged with 50 g of sodium, 800 ml of tetrahydrofuran, and 230 g of $(CH_3)_2AsI$ was added slowly over a 2 h period with cooling by a CO_2/ligroin bath. After stirring the mixture for an additional hour, 80 g of o-dichlorobenzene was added slowly with cooling. After the reaction was complete, 25 ml of methanol was added to destroy the residual sodium, and $NaAs(CH_3)_2$. The tetrahydrofuran/methanol fraction was removed by distillation, collected, and examined for volatile arsenic-containing products. The less volatile residue containing most of the arsenic compounds, and all of the sodium salts was isolated by adding 100 ml of water and separating the two liquid layers. The water insoluble layer was fractionated under reduced pressure. The isolation of the arsenic compounds from this reaction and their characterization are described below.

Dimethylarsinic acid. The tetrahydrofuran distillate was slowly air-oxidized, resulting in the precipitation of an insoluble white solid (5 g). The white compound was collected, recrystallized from acetone, m.p. 189–190° (lit. m.p. 200°). (Found: C, 17.4; H, 5.1. $C_2H_7AsO_2$ calcd.: C, 17.3; H, 5.1%.)

Dimethylphenylarsine. Fractionation of the water-insoluble layer gave a fraction boiling between 30° and 90° at 0.1 mm. Redistillation of this fraction (b.p. 120°/ 100 mm, lit. b.p. 180°/760 mm) gave 5.0 g of dimethylphenylarsine. (Found: mol.wt., 182. $C_8H_{11}As$ calcd.: mol. wt., 182.)

o-Bis(dimethylarsino)benzene. The second arsenic-containing fraction distilled at 97°/0.7 mm and represented 40% (55.8 g) of the arsenic compounds recovered from this reaction. The compound (Das) was characterized by its mass spectrum (Found: mol.wt., 286. $C_{10}H_{16}As_2$ calcd.: mol.wt., 286), and by the numerous transition metal derivatives prepared from this material and reported elsewhere[7].

5,10-Dimethyl-5,10-dihydroarsanthren. The remainder of the water insoluble oil could not be distilled. This non-volatile oil was dissolved in acetone, set aside, and allowed to crystallize under nitrogen (1 y). An off-white crystalline solid was then removed by filtration, and recrystallized from acetone, m.p. 191.5–192.0° (lit. m.p. 191.0–192.5°). (Found: C, 51.1; H, 4.4; As, 44.5; mol.wt., 332. $C_{14}H_{14}As_2$ calcd.: C, 50.7; H, 4.2; As, 45.1%; mol.wt., 332.) These were the only arsenic-containing products which could be isolated from the reaction, and with two exceptions discussed below, were the only arsenic compounds which could be identified from this reaction.

The reaction of NaAs(CH₃)₂ with cis-1,2-dichloroethylene

A three-necked flask equipped as described above was charged with 25 g of sodium, 400 ml of tetrahydrofuran, and 115 g of $(CH_3)_2AsI$ was added dropwise with cooling over a 1 h period. Next, a total of 25 g of *cis*-1,2-dichloroethylene was added dropwise at a rate such that the temperature of the reaction mixture was maintained at 40°. Tetrahydrofuran was removed by distillation, and the reaction mixture was then hydrolyzed with water. The oil which is pyrophoric was separated from the aqueous layer in a separatory funnel provided with a nitrogen inlet. After several water washes, the oil was transferred to a Schlenk tube, diatomaceous earth was added and the oil, which contained a large amount of finely divided solid, was finally filtered under nitrogen. Distillation of this oil resulted in a yield of 20 g [35% based on $(CH_3)_2AsI$] of 1,2-bis(dimethylarsino)ethylene. Due to the large amounts of suspended solids in the water-insoluble fraction, and to the very pyrophoric nature of this oil, it proved impossible to obtain a materials balance. However, the only volatile arsenic containing compounds identified in this reaction were the *cis*- and *trans*-1,2-bis(dimethylarsino)ethylenes (Edas).

cis-1,2-Bis(dimethylarsino)ethylene. The NMR spectrum of the distilled oil from this reaction indicated that there were two components present in a ratio of 10/90. These compounds were identified as the *cis* (10%) and *trans* (90%) isomers. This mixture of *cis*- and *trans*-1,2-bis(dimethylarsino)ethylene was separated[8] by preparation of the tetrachloroferrate(III) salt $[FeCl_2(Edas)_2][FeCl_4]$. The pure *cis* isomer was obtained in small amounts from this iron complex by a ligand displacement reaction. Larger amounts of this compound were prepared by an alternate route described below.

The reaction of NaAs(CH₃)₂ with 1,2-dibromoethylene

A 1 liter flask equipped as described above, containing 1 mole of $NaAs(CH_3)_2$ in 400 ml of tetrahydrofuran was allowed to react with 100 g of 1,2-dibromoethylene over a 1 h period. After removal of tetrahydrofuran by distillation, the reaction mixture was hydrolyzed with water and the insoluble oil was distilled (caution: pyrophoric).

Bis(dimethylarsino)ethyne. The first fraction consisting of 8.8 g of 1,2-bis(dimethylarsino) ethyne was collected at 90°/20 mm. (Found: C, 30.3; H, 5.1. $C_6H_{12}As_2$ calcd.: C, 30.8; H, 5.1%.) This compound was also prepared by an alternative route described below.

1-Bromo-1,2-cis-bis(dimethylarsino)ethylene. The second fraction of 7.1 g distilled at 125°/6 mm. The compound itself was not analyzed, but it readily formed a complex with $FeCl_3$ analogous to the complexes between iron(III) and *cis*-1,2-bis-(dimethylarsino)ethylene, $\{FeCl_2\{HBrC_2[As(CH_3)_2]_2\}\}Cl$. (Found: C, 18.1; H, 4.0; Br, 18.4; Cl, 13.4. $C_{12}H_{26}As_4Br_2Cl_3Fe$ calcd.: C, 18.1; H, 3.3; Br, 20.8; Cl, 13.4%.)

cis-1,2-Bis(dimethylarsino)ethylene (Method II)

$[(CH_3)_2As]_2C_2$. A three-necked round bottom flask (2 l) fitted with a gas inlet and outlet, mechanical stirrer, and a reflux condenser was purged with nitrogen, and charged with 1 mole of C_2H_5MgBr in 700 ml of tetrahydrofuran. Acetylene, 14 l, measured by use of a Parkinson–Cowan gas meter, was then dried by passing it through a cold trap (−77°), and finally through two sulfuric acid traps and passed

into the solution of the Grignard reagent over a period of 1 h. During the addition of acetylene, the solution became blue grey in color. After the addition of acetylene was complete, the solution was refluxed for 1 h. Next, 1 mole of $(CH_3)_2AsI$ was added dropwise over a period of 1 h. The tetrahydrofuran was removed by distillation, and the residue hydrolyzed with water. The water insoluble oil which was obtained was washed with several portions of water, and distilled under reduced pressure to yield 85 g [75% based on $(CH_3)_2AsI$] of product, b.p. 95°/25 mm (lit. 84.5°/14 mm). (Found: C, 31.1; H, 5.1; As, 63.6; mol.wt., 234. $C_6H_{12}As_2$ calcd.: C, 30.8; H, 5.1; As, 64.1%; mol.wt., 234.) A methiodide was also prepared and analyzed. (Found: C, 22.3; H, 4.1. $C_7H_{15}As_2I$ calcd.: C, 22.4; H, 4.0%.)

 cis-1,2-$[(CH_3)_2As]C_2H_2$. A 200 ml flask fitted with a thermometer, a gas inlet, dropping funnel, reflux condenser, and a magnetic stirrer was charged with 5 g of bis(dimethylarsino)ethyne, and 1 g of recrystallized $NaBH_4$ in 7 ml of dry diglyme. The flask was cooled to $-10°$, and 6 g of freshly distilled $BF_3 \cdot (C_2H_5)_2O$ was added dropwise with stirring while the temperature was maintained between $-10°$ and $-20°$. After 30 min, the reaction mixture was solvolyzed with 10 ml of glacial acetic acid, and stirred for 12 h. The mixture was flooded with 200 ml of water, and 4 g of a water-insoluble oil was collected. The oil, as well as ether washings of the aqueous layer, were added to a solution of 3 g of $FeCl_3 \cdot 6 H_2O$ in 70 ml of ether. A red complex, $[FeCl_2(cis-Edas)_2][FeCl_4]$ precipitated, was collected by filtration, and dried in a vacuum at 100° to yield 5.0 g of complex. The ligand was stored as this iron complex until needed.

 The ligand can be regenerated by heating with triphenylphosphine. A 50 ml flask was charged with 5 g of the iron complex, and 10 g of triphenylphosphine. After careful evacuation, the flask was heated to 100° for 3 h, and the distillate collected in a cold trap (−195°). The overall yield based on the bis(dimethylarsino)acetylene was 40% (2 g) However, 50% of the acetylene can be recovered and reused, if desired, giving an overall yield of 80% if the acetylene is recovered. This reaction is very sensitive to the purity of the reagents, and to the preparative scale used. The quantities listed above were found to give the best overall yields. The use of larger quantities of starting materials led to smaller quantities of product. (Found: mol.wt., 236. $C_6H_{14}As_2$ calcd.: mol.wt., 236.)

8-(Diphenylphosphino)quinoline

 It was of interest to prepare a bidentate chelating ligand which had both nitrogen and phosphorous coordination sites available. Since the 8-substituted quinolines are known to form a wide variety of complexes with transition metals, they were selected for these investigations. A 500 ml three-necked round bottom flask was equipped with a nitrogen inlet, an addition funnel, a Dry Ice condenser, and a magnetic stirrer. A total of 4.6 g of Na in 250 ml of liquid ammonia was added to the flask under nitrogen, and 24.4 g of triphenylphosphine was added over a 30 min period, during which time the solution changed color from blue to red. Next, 16.3 g of 8-chloroquinoline was added to the solution over a 1 h period. After the ammonia was allowed to boil off (16 h), the residue was hydrolyzed with 500 ml of water. The residual solid was recrystallized from ethanol/ethyl acetate to yield the final product, m.p. 193–193.5°. (Found: C, 80.9; H, 5.4; N, 4.3; P, 9.7. $C_{21}H_{16}NP$ calcd.: C, 80.5; H, 5.1; N, 4.5; P, 9.9%.)

8-(Diphenylarsino)quinoline

The reaction was carried out as described above for the phosphine compound with only minor modifications. A total of 4.6 g of Na was dissolved in 300 ml of liquid ammonia, and 30.6 g of triphenylarsine was added over a 30 min period. Next, 9.8 g of NH_4Br was added to neutralize the NaC_6H_5 formed in this reaction. Finally, 16.3 g of 8-chloroquinoline was added slowly (1 h), and the mixture stirrer for another 12 h. After the ammonia had evaporated, the residue was hydrolyzed with water. The solid residue was recrystallized from ethanol/ethyl acetate to yield the final product, m.p. 170–171°. (Found: C, 70.6; H, 4.6; As, 20.9; N, 4.0. $C_{21}H_{16}AsN$ calcd.: C, 70.6; H, 4.5; As, 21.0; N, 3.9%.)

RESULTS AND DISCUSSION

The mass spectra and NMR spectra proved particularly valuable in identifying the products obtained from these reactions. Since many of these compounds were pyrophoric and toxic, it was not always possible to separate all of the products from these reactions in pure form. However, NMR and mass spectra were routinely obtained of the crude mixtures as well as of the purified fractions. This procedure permitted the identification of the various components of these reaction mixtures. While other arsenic-containing compounds may have been formed, the NMR and mass spectra of the crude products show that there were no major products from these reactions which were not accounted for. Several attempts were made to separate these products by GLC techniques. Unfortunately, due to the ease of oxidation of these compounds, and due to their low volatility, it did not prove possible to separate these compounds by gas chromatography.

TABLE 1

NMR CHEMICAL SHIFTS[a] OF THE ORGANOARSENIC COMPOUNDS

Compound	Olefinic or phenyl protons	Methyl protons
cis-1,2-Bis(dimethylarsino)ethylene	7.00 1H	1.05 6H
trans-1,2-Bis(dimethylarsino)ethylene	6.65 1H	1.05 6H
Bis(dimethylarsino)ethyne		1.25
Bis(dimethylarsino)ethyne methiodide		2.30 3H
		1.43 2H
o-Bis(dimethylarsino)benzene	7.33 1H	1.20 3H
	A_2B_2 multiplet	
Dimethylphenylarsine	7.25 5H	1.10 6H
	A_2B_2 C multiplet	
5,10-Dimethyl-5,10-dihydroarsanthren	7.25 4H	1.70 3H
	A_2B_2 multiplet	

[a] In ppm from internal TMS (δ).

The NMR spectra of these tertiary arsines are summarized in Table 1. The NMR spectra of the tertiary arsines are relatively simple, since there is no coupling between protons of different groups attached to the arsenic. Arsenic consists of a single isotope, As^{75}, with a nuclear spin of 3/2, and a large quadrupole moment. The

TABLE 2

PROMINENT IONS IN THE MASS SPECTRA OF THE ORGANOARSENIC COMPOUNDS

cis-Edas			trans-Edas			Bis-1,2-(dimethylarsino)-acetylene			Das			5,10-Dimethyl-5,10-dihydroarsanthren		
m/e	Rel. intens.	Ions	m/e	Rel. intens.	Ions	m/e	Rel. intens.	Ions	m/e	Rel. intens.	Ions	m/e	Rel. intens.	Ions
236	96	$C_6H_{14}As_2$	236	63	$C_6H_{14}As_2$	234	100	$C_6H_{12}As_2$	286	16	$C_{10}H_{16}As_2$	332	51	$C_{14}H_{14}As_2$
221	100	$C_5H_{11}As_2$	221	89	$C_5H_{11}As_2$	219	61	$C_5H_9As_2$	271	100	$C_9H_{13}As_2$	317	49	$C_{13}H_{11}As_2$
210	9	$C_4H_{12}As_2$	210	27	$C_4H_{12}As_2$	204	15	$C_4H_6As_2$	256	57	$C_8H_{10}As_2$	302	16	$C_{12}H_8As_2$
206	2	$C_4H_8As_2$	206	2	$C_4H_8As_2$	189	63	$C_3H_3As_2$	241	7	$C_7H_7As_2$	240	17	$C_7H_6As_2$
195	76	$C_3H_9As_2$	195	100	$C_3H_9As_2$	174	17	C_2As_2	227	8	$C_6H_5As_2$	226	100	$C_6H_4As_2$
180	6	$C_2H_6As_2$	180	7	$C_2H_6As_2$	165	88	CH_3As_2	226	5	$C_6H_4As_2$	165	10	C_7H_6As
165	2	CH_3As_2	165	5	CH_3As_2	151	14	As_2H	182	8	$C_2H_8As_2$ or $C_8H_{11}As$	164	9	C_7H_5As
151	16	HAs_2	151	22	HAs_2	129	58	C_4H_6As	167	14	CH_5As_2 or C_7H_8As	152	25	C_6H_5As or As_2H_2
140	19	C_5H_5As	140		C_5H_5As	115	22	C_3H_4As	165	5	CH_3As_2 or C_7H_6As	151	28	C_6H_4As or As_2H
125	21	C_4H_2As	125		C_4H_2As	105	11	C_2H_6As	152	6	As_2H_2 or C_6H_5As	125	5	C_4H_2As
105	52	C_2H_6As	105	20	C_2H_6As	103	16	C_2H_4As	105	6	C_2H_6As	91	8	CH_4As
90	13	CH_3As	90	40	CH_3As	89	23	CH_2As	91	6	CH_4As	76	4	AsH
75	4	As	75	11	As				89	7	CH_2As	75	4	As
									77	6	AsH or C_6H_5			

quadrupole moment causes rapid relaxation of the spin systems, resulting in relatively narrow lines for protons on groups attached to the arsenic. However, the large quadrupole moment also precludes the observation of spin–spin coupling of arsenic with the attached protons. Due to the small line widths, even small chemical shifts are readily observed. These small chemical shifts can be utilized to identify different isomers[9], even though no spin–spin coupling is observed.

The mass spectra of these compounds were utilized for identifying the arsenic species. These results are summarized in Table 2. There have been few mass spectral investigations of tertiary phosphines and tertiary arsines[8,10–13]. The mass spectra of *cis*- and *trans*-1,2-bis(dimethylarsino)ethylene were particularly informative. The first notable feature of the mass spectra of these two compounds is that they are identical. The common feature of the mass spectra of all of the methyl arsine compounds is the loss of methyl groups, and the subsequent formation of As_2 fragments. The most abundant fragment from the 1,2-bis(dimethylarsino)ethylene isomers is the $(P-CH_3)^+$ ion. This $(P-CH_3)^+$ ion then fragments by the loss of an additional CH_3 group, or by the unusual loss of a C_2H_2 fragment (Fig. 1). Two metastable peaks were observed at m/e of 207.0 and 172.5 which correspond to processes I and II respectively (Fig. 1). In addition, there are a large number of fragments containing two arsenic atoms. Thus, it must be concluded that the species, $(P-CH_3)^+$ must have an As–As bond. The loss of an electron and methyl radical from the neutral compound will leave a σ bonding orbital of one of the arsenic atoms empty while there is still a lone pair of electrons available on the second arsenic for bond formation. The formation of this four-membered ring and its fragmentation, coupled with the fragmentation of the parent, account for all of the prominent features of the mass spectrum
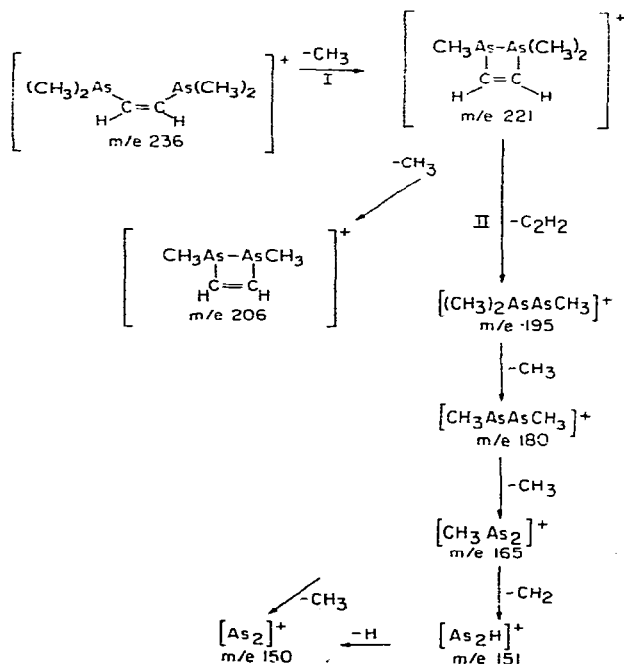

Fig. 1. The fragmentation scheme for *cis*- and *trans*-1,2-bis(dimethylarsino)ethylene.

of 1,2-bis(dimethylarsino)ethylene and also for many of the features of the other compounds discussed below.

The fragmentation pattern of bis(dimethylarsino)ethyne is closely related to those of the olefins. The mass spectrum of the acetylene shows the loss of methyl groups, and the presence of several fragments containing two arsenic atoms. Although no metastable peak was observed for the process, it proved necessary to invoke the loss of a C_2 fragment in order to explain the appearance of the As_2 species in the mass spectrum of this compound (Fig. 2).
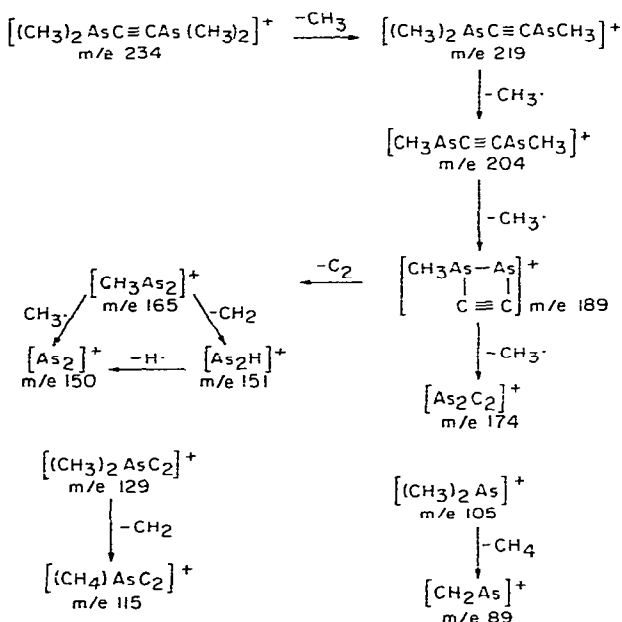

Fig. 2. Proposed mass spectral fragmentation scheme for bis(dimethylarsino)ethyne.

The mass spectra of the compounds containing benzene rings are more complicated to interpret, but the loss of CH_3 groups is again the common fragmentation pathway. As_2 fragments were not positively identified since C_6AsH_x species have similar values of m/e, and no metastable peaks were observed for those processes which would lead to the formation of As_2 fragments.

A mass spectrum was obtained of the crude oil formed after hydrolysis of the reaction of $NaAs(CH_3)_2$ with o-dichlorobenzene. There were peaks observed which could not be assigned to the major components of this mixture. Of particular importance was the presence of the fragment with m/e 120. This fragment was not observed in the mass spectra of any of the purified products from this oil, and can only be assigned to $[As(CH_3)_3]^+$. There was also a fragment observed with small relative abundance at m/e 450. This could be reasonably assigned to $\{CH_3As(C_6H_4As-[CH_3]_2)_2\}^+$, although the parent compound has not as yet been isolated from the reaction mixture.

The products either isolated or identified from the·reaction of $NaAs(CH_3)_2$ with o-dichlorobenzene other than starting materials are: $As(CH_3)_3$, $As(CH_3)_2H$,

$As(CH_3)_2(C_6H_5)$, $C_6H_4[As(CH_3)_2]_2$, 5,10-dimethyl-5,10-dihydroarsanthren, and methylbis[o-(dimethylarsino)phenyl]arsine. The presence of trimethylarsine and of derivatives of monomethylarsine, indicates that there must be some mechanisms by which methyl groups are transferred from one arsenic to another. Besides the large amounts of arsanthren which are formed, the surprising feature of this reaction is the vigor with which $NaAs(CH_3)_2$ attacks o-dichlorobenzene.

The reaction of $NaAs(CH_3)_2$ with *cis*-1,2-dichloroethylene produces the *cis* isomer in only small amounts, and the *trans* isomer in rather large amounts. This was an unexpected result, since it is well known[3,14,15] that *cis*-1,2-dichloroethylene reacts with the related nucleophiles $(C_6H_5)_2P^-$, $(C_6H_5)_2As^-$, and p-$CH_3C_6H_4S^-$ to give good yields of the substitution products with retention of configuration. Since *cis*-1,2-bis(dimethylarsino)ethylene could not be prepared in good yields from the reactions of $NaAs(CH_3)_2$, an alternative synthetic route was sought. The compound, bis(dimethylarsino)ethyne can readily be prepared in high yield from $As(CH_3)_2I$ by reaction with the di-Grignard reagent of acetylene. Reduction with diborane/diglyme gives the *cis* product in yields of 40–80%. This hydroboration reaction is very sensitive to the purity of the reagents, and to the quantities of materials used. Solvents other than diglyme were used for this reaction, but gave inferior yields. The *cis* ligand is very sensitive to oxidation and was therefore stored as the iron(III) complex, from which the ligand could be isolated easily by heating with triphenylphosphine.

The compounds, 8-(diphenylphosphino)quinoline and 8-(diphenylarsino)-quinoline were prepared from the reaction of $(C_6H_5)_2P^-$ or $(C_6H_5)_2As^-$ with 8-chloroquinoline in liquid ammonia. These reactions afforded the products in good yields, without any accompanying important side reactions.

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