in a minimum of acetone or nitromethane and filtered, and the filtrate was added dropwise to a large volume (100–200 ml) of ether with scratching to afford the complexes as yellow, air-stable precipitates. Purification was accomplished by reprecipitation from nitromethane–ether or acetone–ether.

Complex **7** was conveniently separated from a small amount (12%) of 1-6 bis-Fp$^+$ complex **16** by trituration of the reaction residue with several small portions of CH_2Cl_2. This bis complex was identified by its NMR spectrum (CD_3NO_2): δ 6.4–7.0 (m, 2 H, olefinic), 5.7 (s, 5 H, Cp), 5.6 (s, 5 H, Cp), 4.8–5.5 (m, 2 H, coordinated $CH{=}CH_2$), 3.5–4.2 (m, 4 H, coordinated $CH{=}CH_2$), 2.5 (bm, 2 H, allylic).

All new complexes exhibited prominent infrared absorptions (CH_3COCH_3) at 2055, 2020 (M–C≡O), and 1025 cm^{-1} (BF_4^-). NMR spectral data are presented in Table I. Satisfactory C and H analyses were obtained for all new compounds except **11** and **15**.

Hydrogenation of Fp(vinylcyclohexene)$^+$BF$_4^-$ (9). Complex **9** (0.186 g, 0.50 mol), 10 mg of 5% Pd/C, and 5 ml of trifluoroacetic acid were stirred at 25° under 1 atm of hydrogen until gas uptake ceased (ca. 15 min). The catalyst was removed by filtration and the filtrate was added dropwise to 100 ml of ether. The NMR spectrum of the resulting yellow precipitate (0.140 g, 75%) was identical with that produced from the reaction of **1** with vinylcyclohexane: δ (CD_3NO_2) 5.7 (s, 5 H, Cp), 5.1 (m, 1 H, $CH{=}CH_2$), 3.8 (d, J = 9 Hz, 1 H, $CH{=}CH_2$ cis), 3.5 (d, J = 16 Hz, 1 H, $CH{=}CH_2$ trans), 1.0–2.2 (6 m, 1 H, ring H).

Anal. Calcd for $C_{15}H_{19}BF_4FeO_2$: C, 48.18; H, 5.12. Found: C, 48.11; H, 5.09.

Fp(*cis*-2-octene)$^+$BF$_4^-$ (17). The reaction of **1** with *cis*-2-octene according to the general method (above) gave **17** (68%): NMR (acetone-d_6) δ 5.80 (s, 5 H, Cp), 5.3 (bm, 2 H, complexed $CH{=}CH$), 2.5–0.8 (bm, 14 H, CH_2, CH_3).

Anal. Calcd for $C_{15}H_{21}BF_4FeO_2$: C, 47.91; H, 5.64. Found: C, 47.89; H, 5.48.

$C_5H_5Fe(CO)_2$(h^2-*trans*-2-octene)$^+$BF$_4^-$ (18). *trans*-2-Octene and **1** gave **18** (66%); NMR (acetone-d_6) δ 5.85 (s, 5 H, Cp), 4.9 (bm, 2 H, complexed $CH{=}CH$), 2.5–0.7 (bm, 14 H, CH_2, CH_3).

Anal. Calcd for $C_{15}H_{21}BF_4FeO_2$: C, 47.91; H, 5.64. Found: C, 47.75; H, 5.46.

Monitored Competitive Reaction of 1 with *cis*- and *trans*-2-Octene. *cis*-2-Octene (30 mmol), *trans*-2-octene (30 mmol), **1** (6 mmol), and 60 ml of dichloroethane were heated in the usual fashion. Aliquots (10 ml) were withdrawn by syringe after 2.5, 5, 8, 12, and 15 min once the temperature reached 55° and transferred to separate flasks. The individual aliquots were filtered, the filtrates were added to ether, and the resulting precipitates were analyzed by NMR. Integration of the complexed olefinic proton absorptions indicated that the ratio of cis/trans complex, 2.5:1, was unchanged during the course of the reaction.

Reaction of $C_5H_5Fe(CO)_2$(*trans*-2-octene)$^+$BF$_4^-$ (18) with *cis*-2-Octene. *cis*-2-Octene (5.3 mmol), **18** (0.53 mmol), and 40 ml of dichloroethane were heated at 65–70° for 10 min and allowed to cool. The reaction mixture was filtered and the filtrate was added to 200 ml of ether. The resulting yellow precipitate (0.06 g, 30%) was found by NMR to be composed to ca. 67% trans complex **18** and 33% cis complex **17**.

Acknowledgment. The authors thank Professor M. Rosenblum for helpful discussions. Financial support provided by Boston College is also gratefully acknowledged.

Registry No.—**1**, 41707-16-8; **2**, 100-40-3; **3**, 2004-70-8; **4**, 4049-81-4; **5**, 24612-83-7; **6**, 1755-01-7; *cis*-**7**, 55758-72-0; *trans*-**7**, 44607-51-4; *exo*-**8**, 23890-32-6; *endo*-**8**, 25093-48-5; **9**, 55758-75-3; **10**, 55758-77-5; **11**, 55822-54-3; **12**, 55758-79-7; **13**, 55758-81-1; *cis*-**14**, 55758-83-3; *trans*-**14**, 55820-95-6; *exo*-**15a**, 55758-85-5; *endo*-**15a**, 55820-97-8; *exo*-**15b**, 55758-87-7; *endo*-**15b**, 55820-99-0; *cis*-**16**, 55758-89-9; *trans*-**16**, 55821-01-7; **17**, 55758-91-3; **18**, 55821-03-9; Fp(vinylcyclohexane)$^+$BF$_4^-$, 55758-93-5; *cis*-2-octene, 7642-04-8; *trans*-2-octene, 13389-42-9.

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(6) From triene **7** a 1,6-bis-Fp$^+$ complex (**16**) also formed (12%).

(7) For example, the protons syn and anti to Fp$^+$ in **13** absorb at δ −0.2 (d, J = 12 Hz) and 0.7 (d, J = 12 Hz) while the corresponding proton absorptions for Fp (h^2-norbornadiene)$^+$BF$_4^{-5}$ are at δ −0.1 (d, J = 12 Hz) and 1.0 (d, J = 12 Hz) (ref 8). Also, hydrogenation of **9** (19% Pd/C, TFA solvent) gave Fp(vinylcyclohexane)$^+$BF$_4^-$ which had a ^{1}H NMR spectrum identical with that prepared from Fp(isobutylene)$^+$BF$_4$ and vinylcyclohexane.

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(10) Since back-bonding in the Fp(olefin)$^+$ complexes may not be extensive, coordination at the 8,9 position of dicyclopentadiene could be due to stronger forward (olefin–metal) donation. Since the energy of $\pi_{8,9}$ is higher than that of $\pi_{3,4}$, $\pi_{8,9}$ would interact with relatively high energy empty metal orbitals to form a lower energy bonding MO.

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Some Observations on the Interaction of Diarylamines and Arsenic Trichloride[1]

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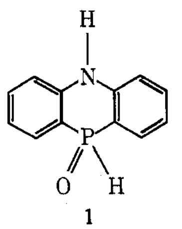
The reaction of diarylamines with phosphorus trichloride followed by treatment of the reaction mixtures with water has been found[2] to yield not only the expected heterocyclic phosphine oxides (i.e., **1** and its ring-substituted derivatives) but also the spirophosphonium chloride **2** and its derivatives. It seemed of interest to determine whether the analogous spiroarsonium chlorides could be obtained via the interaction of diarylamines and arsenic trichloride. Wieland and Rheinheimer[3] reported in 1921 that the chloroarsine **3** (now often known as Adamsite) is formed in high yield by refluxing a mixture of diphenylamine and arsenic trichloride for about 4 hr; and various ring-substituted derivatives of **3** have been prepared in a similar manner by a



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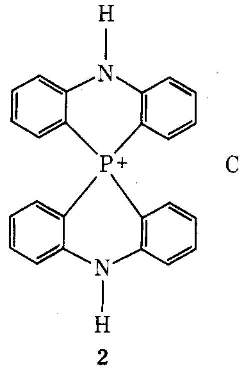

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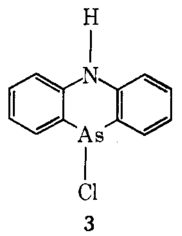

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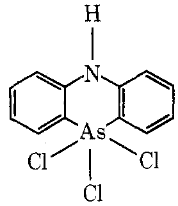
number of investigators.[4] Although spiroarsonium halides have not been isolated from any of these reactions, it seemed possible to us that such compounds had been formed as by-products and had been missed. Accordingly, we have allowed several diarylamines (diphenylamine, di-*p*-tolylamine, and *N*-phenyl-1-naphthylamine) to react with arsenic trichloride under a variety of conditions. In every case we obtained a good yield of the expected heterocyclic chloroarsine (e.g., 89% of **3**). Attempts to isolate spiroarsonium chlorides by the methods previously used for the corresponding phosphorus compounds[2c] were, however, uniformly unsuccessful. Accordingly, we have concluded that spiroarsonium chlorides analogous to **2** are not produced in appreciable amounts (i.e., >0.5%) by the interaction of diarylamines and arsenic trichloride.

We have also tried to prepare a spiroarsonium chloride by the reaction of diphenylamine and the trichloride **4**. The latter substance, obtained as a red powder by allowing the arsinic acid **5** to react with thionyl chloride as described by Gibson and coworkers,[5] was not purified but immediately after isolation was treated with a benzene solution of diphenylamine. The resulting reaction did not produce the desired spiroarsonium chloride but instead gave a green solid[6] that yielded on treatment with aqueous sodium hydroxide the trivalent arsenical **6**. It seems possible that the primary product of the reduction[7] was the amide **7**, which was hydrolyzed by the aqueous base to **6**. The hydrolysis of compounds containing the As–N bond to yield oxides of the type $(R_2As)_2O$ has been observed by Sommer.[8]



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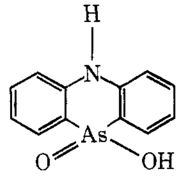

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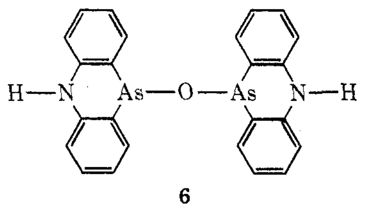

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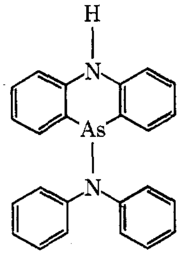

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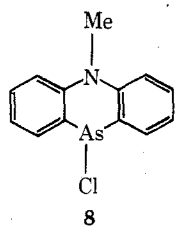
In addition to our attempts to obtain the spiroarsonium compounds discussed above, we have tried to clear up some puzzling reports in the literature dealing with the interaction of *N*-methyldiphenylamine and arsenic trichloride. Wieland and Rheinheimer[3] claimed that the reaction of these substances yielded the expected *N*-methyl compound **8** (0.75 g from 20 g of amine and 20 g of $AsCl_3$). In contrast, Burton and Gibson[9] reported that the product was the unmethylated chloroarsine **3**, and they were unable to prepare **8** by a number of indirect methods. We have allowed *N*-methyldiphenylamine to react with arsenic trichloride at 150–170° without solvent (as described by Wieland and Rheinheimer[3]) or in refluxing *o*-dichlorobenzene (as described by Burton and Gibson[9]). Under both sets of conditions we obtained a low yield (~2%) of a chloroarsine that was shown by its ir spectrum to be the unmethylated compound **3**. A larger yield of arsenical could be isolated by subjecting the reaction mixture obtained by the method of Wieland and Rheinheimer[3] to alkaline peroxide oxidation and subsequent acidification. In this way a 19% yield of the unmethylated arsinic acid **5** was obtained. As previously noted,[3] the major product formed by the interaction of *N*-methyldiphenylamine and arsenic trichloride is a dark blue-black resinous material that has not been further identified.



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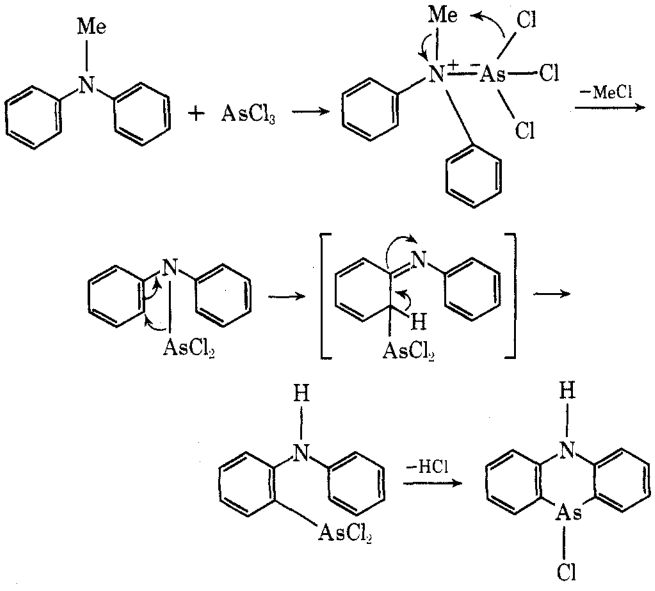
Although commercial *N*-methyldiphenylamine exhibits a weak N–H stretching vibration at 3400 cm^{-1}, the amount of diphenylamine present in this material was shown by GLC analysis to be only 0.1%. It is clear, therefore, that the unmethylated arsenicals **3** and **5** cannot arise solely from this impurity and that Burton and Gibson[9] were correct in concluding that demethylation must occur during the course of the interaction of *N*-methyldiphenylamine and arsenic trichloride. The following mechanism is suggested.



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The above mechanism (somewhat similar to the one proposed[2c] for the reaction of diphenylamine with phosphorus trichloride) rationalizes the cleavage of the methyl group and the fact that only substitution ortho to the nitrogen is observed.

Ultraviolet Spectra. Earley and Gallagher[10] have reported that the electronic spectra of several trivalent dihydrophenarsazine derivatives have one or two moderately intense bands above 300 nm. Quaternization of the arsenic atom produced no profound changes in the spectra. In particular, the bands above 300 nm were still present; and, in some cases, there were small bathochromic shifts and slight increases in intensity. The results obtained on quaternization and the fact that diphenylamine and 5,10-dihydroacridine do not exhibit absorption bands above 300 nm prompted the authors[10] to suggest that the long-wavelength bands in the spectra of the arsenic compounds should be attributed to d_π–p_π bonding involving the lone pair of electrons on the nitrogen atom and empty d orbitals of arsenic. PMR data obtained by Earley and Gallagher appear to be consistent with this conclusion. It will be noted

Table I
Ultraviolet Absorption Maxima of Arsinic and Phosphinic Acids

Compd	λ_{max}, nm	ϵ_{max}
5,10-Dihydro-10-hydroxyphenarsazine 10-oxide (**5**)	216	30,900
	238^a	9,050
	273	19,600
	307	13,000
	330	6,500
5,10-Dihydro-10-hydroxyphenophosphazine 10-oxide (**11**)	216	34,200
	238^a	11,500
	274	21,800
	304	11,800
	330	6,440
5,10-Dihydro-2,8-dimethyl-10-hydroxyphenarsazine 10-oxide (**9**)	218	29,800
	240^a	10,500
	277	23,900
	315	12,500
	342	6,300
5,10-Dihydro-2,8-dimethyl-10-hydroxyphenophosphazine 10-oxide (**12**)	218	28,600
	240^a	11,300
	277	24,900
	312	9,050
	340	5,350
7,12-Dihydro-7-hydroxybenzo[*c*]phenarsazine 7-oxide (**10**)	225	51,000
	252	31,700
	266^a	8,330
	288^a	3,850
	300	6,630
	328^a	16,900
	336	18,300
	353^a	8,500
7,12-Dihydro-7-hydroxybenzo[*c*]phenophosphazine 7-oxide (**13**)	223	54,500
	252	29,600
	268^a	10,500
	290^a	3,830
	302^a	5,920
	327^a	15,300
	337	16,900
	352^a	9,230

^{a} Shoulder.

in Table I that the spectra of the arsinic acids **5**, **9**, and **10** also contain moderately intense bands above 300 nm. The spectra of the phosphinic acids **11**, **12**, and **13** exhibit similar bands and are indeed almost identical with the spectra of the corresponding arsenic compounds.[11] Presumably, then, these arsinic and phosphinic acids also exhibit conjugative interaction between the arsenic or phosphorus atom and the π-electron system of the aromatic rings. Extensive electron delocalization in the heterocyclic rings of the spirophosphonium chloride **2** has been suggested by an X-ray and ^{31}P NMR study of this compound.[2b]

Experimental Section

General. Melting points were determined with a Mel-Temp capillary melting point apparatus and are uncorrected. Ir spectra were obtained with a Perkin-Elmer Model 521 spectrophotometer. Uv spectra were determined in 95% ethanol with a Cary 14 Model 50 recording spectrophotometer with matched 1.0-cm silica cells. Analyses for carbon and hydrogen were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.; arsenic analyses were performed by Mrs. Dolores E. Knight through the courtesy of Dr. G. G. Long of this department. Authentic samples of the chloroarsine **3**,[3,9] the arsinic acids **5**,[3] **9**,[12] and **10**,[13] the oxide **6**,[3] and the phosphinic acids[2c] **11**, **12**, and **13** were prepared by methods described in the literature. The identity and purity of these compounds were confirmed by melting point, ir, and elemental analysis.

Reaction of Diphenylamine with 5,10-Dihydro-10,10,10-trichlorophenarsazine (4). The arsinic acid **5** (3.19 g, 0.012 mol) and 4.9 ml of thionyl chloride were allowed to react in 8.5 ml of dry benzene by the procedure of Gibson and coworkers.[5] Evaporation of the solvent and the excess thionyl chloride yielded a red powder, which was assumed to be the trichloride **4**. A solution of diphenylamine (11.6 g, 0.069 mol) in 25 ml of dry benzene was added to the red powder, whereupon a green reaction mixture was quickly formed. The green solid obtained by evaporation of the benzene was dissolved in about 250 ml of boiling acetone. Addition of 4 *N* aqueous NaOH to the acetone solution precipitated a yellow solid that was removed by filtration, washed with acetone, and then dried in vacuo, yield 2.86 g. The ir spectrum, which exhibited a strong peak at 740 cm^{-1} attributable to the As–O–As linkage,[14] indicated that the yellow solid was crude 10,10′-(5*H*,5′*H*-oxydiphenarsazine) (**6**). Recrystallization from pyridine gave greenish-white crystals, mp 349–350° (lit.[3] mp 350), shown by mixture melting point and ir to be identical with an authentic sample of **6**.[3]

Reaction of *N*-Methyldiphenylamine with Arsenic Trichloride. A mixture of *N*-methyldiphenylamine (20 g, 0.11 mol) and arsenic trichloride (20 g, 0.11 mol) was heated at 150–170° for 4 hr as described by Wieland and Rheinheimer.[3] The resulting blue-black resinous material was mixed with 100 ml of xylene and heated until the mixture was homogeneous. Addition of ether precipitated a dark solid, which was removed by filtration. The filtrate was then evaporated to 25 ml and cooled, whereupon yellow crystals separated from the solution. Recrystallization from CCl_4 gave 0.61 g (2%) of pure 10-chloro-5,10-dihydrophenarsazine (**3**) as shown by melting point, mixture melting point, and ir.

In another experiment, the reaction mixture obtained from *N*-methyldiphenylamine (18.3 g, 0.100 mol) and arsenic trichloride (18.1 g, 0.100 mol) was refluxed gently for 15 hr with a mixture of 200 ml of 2 *N* NaOH and 50 ml of 30% H_2O_2. The resulting mixture was extracted with two 100-ml portions of ether to remove an oily material, and the aqueous layer was added slowly with good stirring to an excess of 10% hydrochloric acid. The blue solid that precipitated was shown by its ir spectrum to be essentially pure 5,10-dihydro-10-hydroxyphenarsazine 10-oxide (**5**), yield 5.3 g (19%).

The above experiments were performed with unpurified *N*-methyldiphenylamine (Eastman Kodak No. 2098). Similar results were obtained, however, with *N*-methyldiphenylamine purified by distillation through a spinning band column and shown by ir and GLC to be free of diphenylamine.

Registry No.—**3**, 578-94-9; **4**, 55712-32-8; **5**, 4733-19-1; **6**, 4095-45-8; **9**, 55712-33-9; **10**, 5657-43-2; **11**, 472-43-5; **12**, 53798-60-0; **13**, 53798-62-2; diphenylamine, 122-39-4; thionyl chloride, 7719-09-7; *N*-methyldiphenylamine, 552-82-9; arsenic trichloride, 7784-34-1.

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(2) (a) R. N. Jenkins, L. D. Freedman, and J. Bordner, *Chem. Commun.*, 1213 (1971); (b) *J. Cryst. Mol. Struct.*, **3**, 103 (1973); (c) R. N. Jenkins and L. D. Freedman, *J. Org. Chem.*, **40**, 766 (1975).

(3) H. Wieland and W. Rheinheimer, *Justus Liebigs Ann. Chem.*, **423**, 1 (1921).

(4) Cf. F. G. Mann, "The Heterocyclic Derivatives of Phosphorus, Arsenic, Antimony and Bismuth", Wiley-Interscience, New York, N.Y., 1970, pp 506–522.

(5) C. S. Gibson, J. D. A. Johnson, and D. C. Vining, *Recl. Trav. Chim. Pays-Bas*, **49**, 1006 (1930).

(6) The arsenic-containing substance in the green solid could not be extracted with boiling CCl_4 and therefore could not have been the chloroarsine **3**, which is moderately soluble in hot CCl_4.

(7) Since W. Steinkopf and S. Schmidt, *Ber.*, **61**, 675 (1928), have reported that thionyl chloride can reduce certain arsonic acids and since the trichloride **4** has not been adequately characterized, we felt it was necessary to show that reduction had not occurred during the course of the reaction between thionyl chloride and the arsinic acid **5**. Accordingly, we allowed a sample of the trichloride **4** to react with water and found that a virtually quantitative yield of **5** was obtained.

(8) K. Sommer, *Z. Anorg. Allg. Chem.*, **383**, 136 (1971).

(9) H. Burton and C. S. Gibson, *J. Chem. Soc.*, 450 (1926).

(10) R. A. Earley and M. J. Gallagher, *J. Organomet. Chem.*, **20**, 117 (1969).

(11) The close resemblance of the uv spectra of corresponding organoarsenic and -phosphorus compounds has often been noted; cf. G. O. Doak, L. D. Freedman, and J. B. Levy, *J. Org. Chem.*, **29**, 2382 (1964), and references cited therein.

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