It is known that organometallic compounds react with benzyne.[11] Wittig[12] has shown that benzyne generated from *o*-bromofluorobenzene adds to cyclopentadiene in Diels–Alder fashion to give 1,4-dihydro-1,4-methanonaphthalene. Indene is thought to add 1,3 to maleic anhydride *via* the reactive entity, isoindene (6).[13] However, since this occurs only at temperatures in the vicinity of 200°,[14] the reaction of benzyne with indene at 65° would not appear to be of this nature.

Experimental Section[15]

9,10-Dihydro-9,10-methanoanthracene (1) and 9,10-Dihydro-9,10-methanoanthracen-11-ol (2).—To a mixture of 4.56 g of magnesium turnings and 5 g of indene in 140 ml of tetrahydrofuran in a nitrogen atmosphere was added a solution of 30.2 g of *o*-bromofluorobenzene in 90 ml of tetrahydrofuran. After refluxing for 3 hr, the reaction mixture was hydrolyzed by the cautious addition of 50 ml of water. The precipitated inorganic salts were filtered, and the filtrate was dried over magnesium sulfate and evaporated. Vacuum distillation of the residue yielded three fractions. Fractions one (bp 100–115° (0.15 mm)) and two (bp 120–135° (0.15 mm)) which contained some solid material were combined (2.5 g) and a 100-mg sample was separated by thin layer chromatography on silica gel plates developed with hexane. The products were eluted with chloroform–methanol (1:1). A yield of 70 mg (22%) of the hydrocarbon 1 of R_f 0.65 was obtained as crystals. The mp 155–165° did not change on recrystallization from benzene–petroleum ether (30–60°): $\lambda_{max}^{CH_3OH}$, 271 mμ (ε 1770), and 278 mμ (ε 2280).

Anal. Calcd for $C_{15}H_{12}$: C, 93.71; H, 6.29. Found: C, 93.91; H, 6.21.

The crystalline fraction of R_f 0.0 consisted of 32 mg (9%) of the alcohol 2. After recrystallization from methanol it melted at 184–185°: λ_{max}^{MeOH}, 213 mμ (ε 67,500), 270 (2960), and 277 (3820). The infrared spectrum was identical with that of a sample obtained from Professor Meinwald[6] and a mixture melting point was not depressed.

Anal. Calcd for $C_{15}H_{12}O$: C, 86.51; H, 5.81. Found: C, 86.35; H, 5.89.

The third distillation fraction (bp 160–200° (0.15 mm)) crystallized when triturated with petroleum ether. After recrystallization from benzene–petroleum ether it melted at 196–198°. Its melting point and ultraviolet spectrum are identical with that of triphenylene.

Anal. Calcd for $C_{18}H_{12}$: C, 94.70; H, 5.30. Found: C, 94.68; H, 5.08.

Registry No.—Benzyne, 462-80-6; indene, 95-13-6; **1**, 4448-88-8; **2**, 15924-27-3; triphenylene, 217-59-4.

Acknowledgment.—We wish to acknowledge a helpful discussion with Professor E. Wenkert and to thank Drs. E. Schlittler and G. deStevens for support.

(11) G. Wittig and W. Merkle, *ibid.*, **75**, 1491 (1942).
(12) G. Wittig and E. Knauss, *Chem. Ber.*, **91**, 895 (1958).
(13) J. A. Berson and G. B. Aspelin, *Tetrahedron*, **20**, 2697 (1964).
(14) W. R. Roth, *Tetrahedron Lett.*, 1009 (1964).
(15) Nmr spectra were recorded on a Varian A-60 instrument for deuteriochloroform solutions using tetramethylsilane as an internal standard. Melting points were determined with a Thomas–Hoover apparatus.

A Convenient General Synthesis of Amidines

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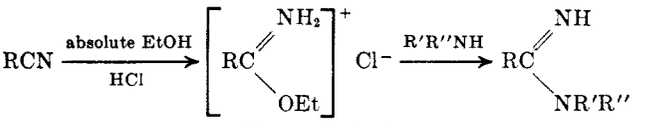
The most widely used procedure for the synthesis of amidines is the one described by Pinner at the end of the last century.[1] This method involves the preparation of an imidate salt by reaction of a nitrile and an anhydrous alcohol in the presence of an acid catalyst, usually hydrogen chloride. The imidate salt is then converted into the amidine by treatment with ammonia or an amine in absolute ethanol. Many amidines have been synthesized in excellent yield by the Pinner procedure, however, like most general methods, it has several limitations,[2] principally connected with the preparation of the imidate salts.[3] Perhaps its greatest shortcoming is that the starting nitriles are not readily available. In addition, the method has had no general application to the synthesis of *ortho*-substituted benzamidines because the necessary imidates are not formed or are obtained in very poor yield. Thus, only poor yields of *o*-chlorobenzamidine[2b] and 1-naphthamidine[2b] have been obtained and *o*-toluamidine has not yet been prepared despite several reported attempts.[2] Also, N,N′-disubstituted amidines cannot be synthesized by the Pinner procedure.



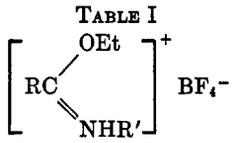
Pinner method

Amides are potentially more convenient starting materials. N-Substituted and N,N-disubstituted amidines may be prepared through intermediate imidoyl chlorides obtained by reacting secondary and tertiary amides with PCl_5, $POCl_3$, $SOCl_2$, and $COCl_2$.[2] However, these reagents dehydrate primary amides, making the procedure useless for unsubstituted amidines.

The O-alkylation of amides to produce imidate salts has been achieved with ethyl chloroformate,[4] dimethyl sulfate,[5] and triethyloxonium fluoroborate.[6] This procedure, involving electrophilic attack on the amide oxygen rather than nucleophilic attack on a sterically hindered nitrile carbon, should be superior for the preparation of *ortho*-substituted benzimidates. Bühner prepared methyl benzimidate methosulfate in good yield from benzamide and dimethyl sulfate, but he obtained only an unspecified yield of a heavy oil with N-methylbenzamide.[5] Bredereck and coworkers[7] have synthesized N,N,N′-trisubstituted and N,N,N′,N′-tetrasubstituted formamidines and acetamidines by reacting amines with the oily adducts formed from dimethyl sulfate and the appropriate secondary or tertiary formamides and acetamides. Other workers have treated the free imidate bases with amines and amino acids to prepare amidines and amidinelike compounds.[5,8] Aside from the work of Bredereck, *et al.*, there have been no reports of

(1) A. Pinner, "Die Imidoather und ihre Derivate," R. Oppenheim, Berlin, 1892.
(2) (a) For a relatively recent review of amidine synthesis, see H. Soll in Houblen-Weyl's, "Methoden der organischen Chemie," 4th ed, Vol. XI, Part 2, VEB Georg Thieme Verlag, Stuttgart, 1958, p 39. (b) For other discussions see P. Oxley and W. F. Short, *J. Chem. Soc.*, 147 (1946); F. C. Schaefer and A. P. Krapcho, *J. Org. Chem.*, **27**, 1255 (1962), and references cited therein.
(3) The chemistry of imidates has been reviewed by R. Roger and D. G. Neilson, *Chem. Rev.*, **61**, 179 (1961).
(4) W. Hechelhammer, German Patent 948,973 (1956).
(5) A. Bühner, *Ann.*, **333**, 289 (1904).
(6) H. Meerwein, E. Battenberg, H. Gold, E. Pfeil, and G. Willfang, *J. Prakt. Chem.*, **154**, 83 (1939).
(7) See H. Bredereck, F. Effenberger, and E. Henseleit, *Ber.*, **98**, 2754 (1965), and earlier papers cited therein.
(8) S. Petersen and E. Tietze, *Ann.*, **623**, 166 (1959)

TABLE I

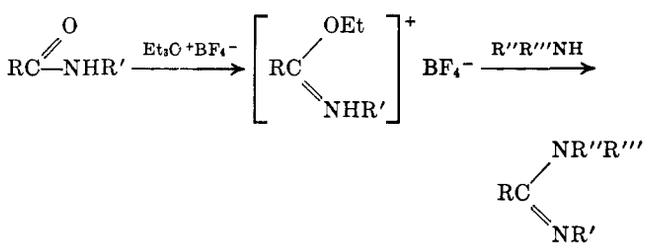


R	R′	Yield, %	Mp, °C	Anal., % Calcd C	Calcd H	Calcd N	Found C	Found H	Found N
C_6H_5	H	80.6[a]	130–131	45.60	5.11	5.91	46.23	5.41	5.82
o-$CH_3C_6H_5$	H	80.1	93–94	47.84	5.62	5.58	47.89	5.56	5.58
1-Naphthyl	H	97	88–89	54.31	4.91	4.88	53.06	5.34	4.92
o-$C_2H_5OC_6H_5$	H	90[b]	139–141	47.00	5.74	4.98	47.44	5.57	4.85
o-ClC_6H_5	H	78	101.5–103	39.82	4.08	5.16	39.65	4.22	5.15
CH_3	H	[c]							
C_6H_5	CH_3	90.1	73–74	47.84	5.62	5.58	47.48	5.49	5.56

[a] Most of the product precipitated from the CH_2Cl_2 solution during the reaction. [b] The starting o-ethoxybenzamide was soluble in CH_2Cl_2. [c] The crude imidate was converted into the amidine without isolation. Triethyloxonium fluoroborate was added to acetamide below 5° and the mixture was allowed to warm to room temperature overnight. The solvent was removed completely *in vacuo* and the residue was treated with absolute alcoholic ammonia.

the direct utilization of imidate methosulfates or fluoroborates for the synthesis of amidines.

We report here that these imidate salts can readily be converted into amidines. We find that triethyloxonium fluoroborate[9] is distinctly superior to dimethyl sulfate for the O-alkylation of amides. For this reason we report in the Experimental Section only on the preparation of imidate fluoroborates and their conversion into amidines. Yields are excellent in both steps with triethyloxonium fluoroborate. By comparison, yields of the imidate methosulfates and amidines were good with benzamide and o-toluamide and fair with o-chlorobenzamide (56% yield of o-chlorobenzimidate methosulfate and 71% yield of amidine). With N-methylbenzamide we, like Bühner,[5] were unable to obtain a crystalline imidate methosulfate and isolated only an oil with a maximum possible yield of 23%. When N,N′-dimethylbenzamidine hydrochloride was prepared without isolation of the imidate methosulfate,[10] the over-all yield was 15% as compared to 90% yields in each step with triethyloxonium fluoroborate. In view of these results, triethyloxonium fluoroborate is the preferred reagent for the preparation of the imidate salt.



The imidate fluoroborates are crystalline solids which are decomposed by moisture, but are considerably more stable than triethyloxonium fluoroborate. KBr pellets of these salts exhibit a characteristic strong broad absorption from 1020 to 1120 cm^{-1} which is due to BF_4^-[11] and a sharp peak in the region of 1600–1700 cm^{-1} due to C=N stretching.[12]

(9) For a description of current procedures for preparation and storage of triethyloxonium fluoroborate, see H. Meerwein, *Org. Syn.*, **46**, 113 (1966).

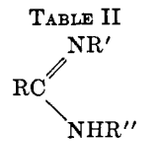
(10) See ref c in Table I.

(11) N. B. Colthup, L. H. Daly, and S. E. Wiberly, "Introduction to Infrared and Raman Spectroscopy," Academic Press Inc., New York, N. Y., 1964, p 361.

(12) Reference 11, p 283.

In the Experimental Section we describe general procedures for the preparation of the imidate fluoroborates and the amidines. No attempt has been made to optimize the conditions. The imidates and amidines are listed in Tables I and II, respectively, and variations of individual preparations from the general procedures are described in the footnotes to the tables.

TABLE II



R	R′	R″	Yield, %	Mp, °C Base	Mp, °C HCl	Mp, °C Picrate
C_6H_5	H	H	71.5[a]		166–168[b]	
o-$CH_3C_6H_5$	H	H	90[c]	104–105[d,e]	258–258.5[f]	235–236[g]
1-Naphthyl	H	H	75[c]	153–154.5[b,h]		226.5[b]
o-$C_2H_5OC_6H_5$	H	H	91[a]		195–196[i,k]	213–215[l]
o-ClC_6H_5	H	H	90[a]		280–282[m]	218–220[n]
CH_3	H	H	78[p]			249–251[b]
C_6H_5	CH_3	CH_3	90[a]		255–256[b]	171–172[b]

[a] Calculated as the hydrochloride. [b] Value agrees with literature. [c] Calcd as the free base. [d] Purified by sublimation at 80° (0.5 mm). [e] Calcd for $C_8H_{10}N_2$: C, 71.61; H, 7.51; N, 20.88. Found: C, 71.58; H, 7.50; N, 20.81. [f] Calcd for $C_8H_{11}N_2Cl$: C, 56.31; H, 6.50; N, 16.42. Found: C, 56.51; H, 6.48; N, 16.54. [g] Calcd for $C_{14}H_{13}N_5O_7$: C, 46.28; H, 3.61; N, 19.28. Found: C, 46.43; H, 3.70; N, 19.37. [h] Sublimed at 130° (0.5 mm). [i] Melting point reported by A. Pinner [*Ber.*, **23**, 2942 (1890)] is 218°. [k] Calcd for $C_9H_{13}ClN_2O$: C, 53.87; H, 6.53; N, 13.96. Found: C, 54.15; H, 6.82; N, 13.47. [l] Calcd for $C_{15}H_{15}N_5O_8$: C, 45.81; H, 3.84; N, 17.80. Found: C, 45.84; H, 4.05; N, 17.75. [m] Calcd for $C_7H_3N_2Cl_2$: C, 44.01; H, 4.22; N, 14.66. Found: C, 44.13; H, 4.35; N, 14.63. [n] Calcd for $C_{13}H_{10}N_5O_7Cl$: C, 40.69; H, 2.63; N, 18.25. Found: C, 41.21; H, 2.78; N, 18.21. [p] Over-all yield of amidine picrate based on acetamide.

Experimental Section

A solution of 0.1 mol of triethyloxonium fluoroborate in 50 ml of dry CH_2Cl_2 (reagent grade distilled from anhydrous $CaCl_2$) was added over 5 min at room temperature to a suspension of 0.1 mol of the amide in 200 ml of dry CH_2Cl_2. The mixture was stirred overnight at room temperature during which time a clear solution resulted. The solution was evaporated *in vacuo* to one-third volume and treated with five volumes of anhydrous ether. The precipitated imidate fluoroborate was filtered and dried *in vacuo*. The salts could be recrystallized for analysis from dichloromethane or dichloromethane–ether. The crude salts were used in all cases for the amidine preparation.

The amidines were prepared by the procedure described by Dox.[13] The imidate fluoroborate was stirred at room tempera-

(13) A. W. Dox, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1951, p 5.

ture in a tightly stoppered flask with an 8–9% solution of ammonia or methylamine in absolute ethanol containing approximately a 40% excess of amine. After 3 days the mixture was evaporated to dryness *in vacuo* and treated with a small volume of water. The mixture was made strongly basic with 5 *N* NaOH and the insoluble oil was extracted into ethyl acetate or ether. The oil which remained after evaporation *in vacuo* of the organic solvent was either crystallized and purified or converted into the hydrochloride. A portion was also converted into the picrate.

Stereospecific Vinyl Halide Substitution. III. *cis*- and *trans*-Vinylenebis(diphenylarsines) and Their Rhodium Complexes

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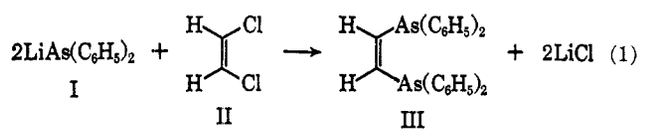
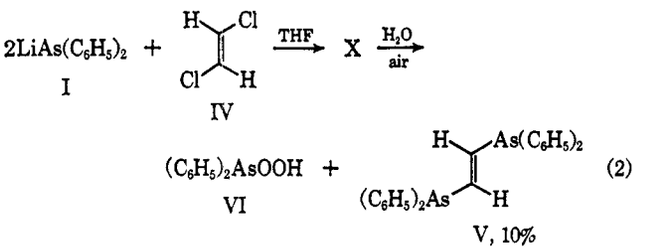
During a study of vinylarsines we reported the stereospecific replacement of the vinyl bromides in the β-bromostyrenes by lithium diphenylarsenide (I).[2] This replacement occurred with retention of configuration.

We wish to report that lithium diphenylarsenide (I) (prepared from triphenylarsine and lithium)[2] reacts with *cis*-1,2-dichloroethene (II), in tetrahydrofuran solution, to give *cis*-vinylenebis(diphenylarsine) (III) in 61% yield (eq 1).



$$2LiAs(C_6H_5)_2 \ (I) + \underset{II}{\text{H(Cl)C=C(Cl)H}} \longrightarrow \underset{III}{\text{H(As(C}_6\text{H}_5)_2\text{)C=C(As(C}_6\text{H}_5)_2\text{)H}} + 2LiCl \quad (1)$$

Treatment of I with *trans*-1,2-dichloroethene (IV) under the same conditions produced only 10% of *trans*-vinylenebis(diphenylarsine) (V). The major product isolated was diphenylarsinic acid (VI) (eq 2).

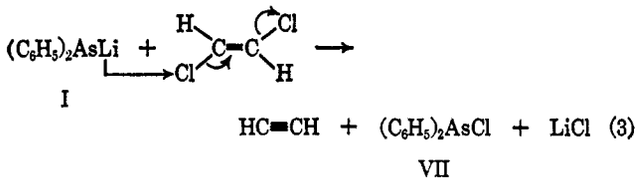


$$2LiAs(C_6H_5)_2 \ (I) + \underset{IV}{\text{H(Cl)C=C(Cl)H}} \xrightarrow{THF} X \xrightarrow[air]{H_2O} (C_6H_5)_2AsOOH \ (VI) + \underset{V,\ 10\%}{\text{H(As(C}_6\text{H}_5)_2\text{)C=C(As(C}_6\text{H}_5)_2\text{)H}} \quad (2)$$

This is in contrast to the reaction of lithium diphenylphosphide with *cis*- and *trans*-1,2-dichloroethene which leads to *cis*- and *trans*-vinylenebis(diphenylphosphine), respectively, both in excellent yields.[3] Changing the order of addition of reactants did not greatly alter the yields of V and VI.

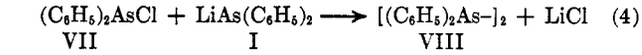
No *trans*-diarsine (V) was obtained from the reaction of *cis* dichloride (II), and no *cis*-diarsine (III) was obtained from the *trans* dichloride (IV). Therefore an elimination–addition sequence can be excluded since a common intermediate such as acetylene or chloroacetylene would lead to the same product(s) from both isomeric dichlorides. Evidence has been obtained supporting the idea that *trans*-diarsine (V) is stable under the conditions employed. This has been shown by vpc analysis on a 3% SE-30 column at 250° using a flame ionization detector.

It seems that a reaction path lower in activation energy than the halide replacement and leading to diphenylarsenic acid (VI) (or precursor) is possible in the reaction of I with IV. A possible explanation could be halogen–metal interchange, which seems to occur more readily with lithium arsenides than with lithium phosphides. This would be favored with IV (over II) due to the *trans* coplanarity of the halogens in IV and consequent ease of elimination (eq 3).



$$(C_6H_5)_2AsLi \ (I) + \text{H(Cl)C=C(Cl)H} \longrightarrow HC{\equiv}CH + (C_6H_5)_2AsCl \ (VII) + LiCl \quad (3)$$

Depending on the order of addition of reagents, chlorodiphenylarsine (VII) may or may not react with excess I to give tetraphenyldiarsine (VIII) (eq 4).



$$(C_6H_5)_2AsCl \ (VII) + LiAs(C_6H_5)_2 \ (I) \longrightarrow [(C_6H_5)_2As-]_2 \ (VIII) + LiCl \quad (4)$$

Both VII and VIII will react with water and air to produce VI and work is now in progress in an attempt to elucidate the actual pathway by which VI is produced.

An elimination–addition sequence would involve a common intermediate (chloroacetylene) for both the *cis*- and *trans*-dichloroethenes and therefore both reactions would be expected to produce the same or a mixture of isomers. In fact, however, gas chromatographic analysis of the crude reaction mixtures shows that only *one* diarsine is produced from the *cis*-dichloroethene and that it has a distinctly different retention time from the *one* diarsine produced from the *trans*-dichloroethene. Thus the two reactions give different, single products with no mixtures of the two diarsines being found in the same reaction mixture.

Support for the structure assignments III and V as the *cis* and *trans* isomers, respectively, comes from elemental analysis, infrared and proton nmr spectra, and dipole moment measurements. These moments are given in Table I along with those of *cis*- and *trans*-vinylenebis(diphenylphosphine) whose structures have previously been established.[3] From these data, it is clear that the structure assignments made above are the correct ones.

TABLE I

DIPOLE MOMENTS OF *cis*- AND *trans*-$((C_6H_5)_2M{-}CH{=}CH{-}M(C_6H_5)_2)$

Isomer	M = P	M = As
cis	1.96 D ± 0.21	1.37 D ± 0.09
trans	0.99 D ± 0.09	0.97 D ± 0.09

Further support for these structure assignments comes from the differing behavior of III and V when allowed to react with rhodium dicarbonyl chloride dimer (IX). The reaction of III produces an orange

(1) (a) NASA Predoctoral Fellow, 1964–1967; (b) NDEA Predoctoral Fellow, 1966–1968.

(2) A. M. Aguiar and T. G. Archibald, *J. Org. Chem.*, **32**, 2627 (1967).

(3) A. M. Aguiar and D. J. Daigle, *J. Amer. Chem. Soc.*, **86**, 2299 (1964).