TABLE I
POSITIONAL PARAMETERS FOR 1,1,2,2-TETRACARBOMETHOXYETHANE

Atom	*X*	*Y*	*Z*
O_1	0.0167 (5[a])	−0.1817 (5)	−0.1617 (3)
O_2	0.1846 (5)	−0.3486 (4)	−0.0139 (3)
O_3	0.3568 (5)	0.1290 (4)	0.0511 (3)
O_4	0.3946 (5)	−0.0936 (4)	0.1729 (3)
C_1	0.0748 (6)	−0.0745 (6)	0.0280 (4)
C_2	0.0865 (5)	−0.2050 (5)	−0.0624 (3)
C_3	0.2102 (9)	−0.4825 (7)	−0.0928 (5)
C_4	0.2926 (6)	0.0015 (5)	0.0843 (4)
C_5	0.6058 (8)	−0.0403 (8)	0.2297 (5)

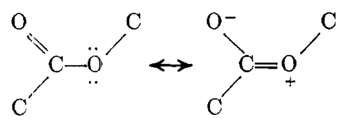
[a] Standard deviations in the least significant figures.

TABLE II
ANISOTROPIC THERMAL FACTORS[a]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{13}
O_1	5.62	3.45	3.06	0.81	0.04	0.72
O_2	5.58	2.13	3.16	0.85	0.06	0.91
O_3	3.96	3.12	4.45	−0.68	0.93	0.51
O_4	3.52	3.31	3.31	−0.08	0.85	0.23
C_1	3.28	1.88	3.14	−0.22	0.01	0.54
C_2	3.20	2.38	2.85	0.04	0.09	0.31
C_3	4.40	5.14	4.43	−0.08	1.05	−0.13
C_4	6.99	2.83	4.20	1.18	−0.74	1.71
C_5	2.99	2.25	2.38	0.33	−0.01	0.58

[a] These are of the form $\exp[-(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{23}klb^*c^* + 2B_{13}hla^*c^*)]$.

important to constrain the ester group to a planar conformation despite any unfavorable eclipsing interactions that may exist.



Registry No.—1,1,2,2 - Tetracarbomethoxyethane, 5464-22-2.

Acknowledgment.—We wish to express our gratitude to the National Science Foundation for support of C. Richard Costin during the summer as an undergraduate research participant.

The Reaction of Benzyne with Indene

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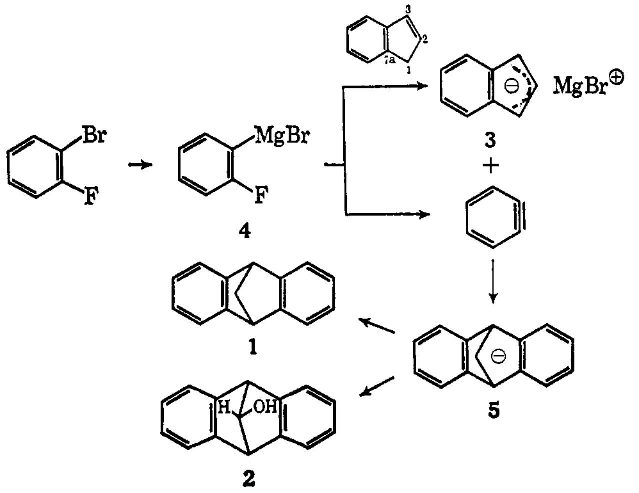
In continuation of a study on the Diels–Alder reaction of indene[1] we now wish to report on its reaction with benzyne. Indene has been shown to give various adducts in which bond formation occurs at the 2,3, at the 1,3, or at the 2,7a positions, depending on the dienophile. Benzyne reacted in the last mentioned fashion with styrene[2] and with α-methylstyrene,[3] which are formally ring-opened indenes.

When benzyne was generated *in situ* in refluxing tetrahydrofuran from *o*-bromofluorobenzene and magnesium[4] in the presence of indene, two products, a $C_{15}H_{12}$ (**1**) and a $C_{15}H_{12}O$ (**2**) species, could be isolated by thin layer chromatography. The nmr spectrum at 60 Mc of **1**, showing an A_2B_2 eight-proton signal in the aromatic region centered at 422.5 cps, a two-proton signal in the benzyl region as a very narrow triplet at 253.4 cps ($W_{1/2}$ = 4.0 cps), and a two-proton signal as a very narrow triplet at 148.7 cps ($W_{1/2}$ = 3.7 cps), indicated a symmetrical molecule. Besides the molecular ion peak of m/e 192, a feature of diagnostic value in the mass spectrum, was a major fragment at m/e 115 indicating indenyl ion (C_9H_7). These data best fit the known 9,10-dihydro-9,10-methanoanthracene (**1**)[5] whose reported melting point and ultraviolet spectrum are identical with ours. The infrared spectrum of **2** revealed the presence of a hydroxyl group at 3568 cm^{-1} and the nmr spectrum (after exchange with deuterium oxide) showed a complex eight-proton signal in the aromatic region centered at about 425, a two-proton triplet at 253, and a one-proton triplet at 262 cps. The melting point and ultraviolet spectrum of **2** are virtually identical with those reported for 9,10-dihydro-9,10-methanoanthracen-11-ol by Meinwald.[6] Identification of our substance as **2** was confirmed by comparison with an authentic sample.

A mechanism for the formation of **1** and **2** accounting for the unexpected presence of **2** could be advanced when it was found that **1** and **2** were not obtained when benzyne was generated from either benzenediazonium-2-carboxylate[7] or diphenyliodonium-*o*-carboxylate.[8] In this view, the carbanionic intermediate **3**, resulting from reaction of the acidic indene with **4**, adds to benzyne. The exact nature of this cycloaddition, whether in one or two steps, is uncertain but a carbanionic species must be involved. This is followed by reaction of the resulting **5** with water leading to **1** and with residual oxygen leading to **2**. It is generally held that organometallic compounds react with oxygen yielding alcohols *via* reduction of the intermediate hydroperoxide anion by carbanion.[9,10]



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[2] W. L. Dillon, *Tetrahedron Lett.*, 939 (1966).

[3] E. Wolthuis and W. Cady, *Angew. Chem. Intern. Ed. Engl.*, **6**, 555 (1967).

(4) N. Rabjohn, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p 965.

(5) W. R. Vaughan and M. Yoshimine, *J. Org. Chem.*, **22**, 7 (1957).

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(7) L. Friedman and F. M. Logullo, *J. Amer. Chem. Soc.*, **85**, 1549 (1963).

(8) L. F. Fieser, "Organic Experiments," D. C. Heath and Co., Boston, Mass., 1965, p 312.

(9) J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p 344.

(10) E. Müller and T. Topel, *Ber.*, **72**, 273 (1939).

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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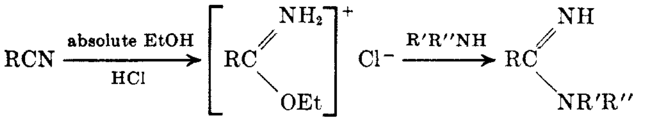
The most widely used procedure for the synthesis of amidines is the one described by Pinner at the end of the last century.[1] This method involves the preparation of an imidate salt by reaction of a nitrile and an anhydrous alcohol in the presence of an acid catalyst, usually hydrogen chloride. The 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)