The solution was stirred for 1 hr. at room temperature, and after this time, 100 ml. of absolute methanol was added and the resulting solution was stirred for 2 days, again at room temperature. An equal volume of water was added and the mixture was shaken. The organic phase was washed with sodium bicarbonate solution, then twice with water. The solution was dried over magnesium sulfate and filtered, and the solvent was evaporated under reduced pressure leaving an orange oil. Upon addition of anhydrous ether and subsquent cooling at 0° for 1 day, 1.98 g. of a white crystalline material was obtained. After further evaporation of the solvent and cooling, another 0.30 g. of this material was isolated: m.p. 77–78°, 2.28 g. (50%).

Anal. Calcd. for $C_{20}H_{15}BrCl_2O_3$: C, 52.88; H, 3.32. Found: C, 52.55; H, 3.32.

The n.m.r. spectrum indicated that the product was 2,2-di-(*o*-chlorobenzoyl)-6-bromocyclohexanone. There was a multiplet at 5.1 p.p.m., corresponding to one hydrogen, and aromatic and aliphatic areas in a ratio of 8 to 6. The infrared spectrum showed a carbonyl stretch at 5.73 and 6.03 μ; $\lambda_{\max}^{\mathrm{EtOH}}$ 245 mμ (ϵ 14,700).

Polarographic Reduction of 6,6-Di(*o*-Chlorobenzoyl)-1-morpholinocyclohexene-1.—A 10^{-3} *M* solution of this dibenzoylated enamine in acetonitrile, with *t*-butylammonium iodide as supporting electrolyte, was reduced using a dropping mercury cathode and mercury pool anode. The resulting polarogram indicated a reduction of the dibenzoylated enamine ($E_{1/2}$ = −1.36 v.). A 10^{-3} *M* solution of 1-morpholinocyclohexene-1 showed no reduction under the same conditions. A Sargent Model XXI instrument was used: range, 0–2.5 v.; sensitivity, 0.100 μa./mm.; damping, 2.

The Attempted Reaction of 6,6-Di(*o*-chlorobenzoyl)-1-morpholinocyclohexene-1 with Sodium Borohydride in Ethanol.—To 0.80 g. (0.021 mole) of sodium borohydride in 250 ml. of absolute ethanol, was added 4.40 g. (0.01 mole) of the dibenzoylated enamine and the mixture was stirred for 1 day. After this time it was noticed that some of the enamine had not gone into solution. As a result, 100 ml. of anhydrous tetrahydrofuran was added to increase the solubility. The solution was then stirred for 4 days at room temperature. After this time the solvents were evaporated at reduced pressure leaving a solid residue. The solid was dissolved in anhydrous methanol, and upon cooling in an ice bath, 3.20 g. of a white solid was isolated. A mixture melting point with the starting material showed no depression (149–151°). An infrared spectrum was identical with that of the starting material. (The 3.20 g. of solid corresponds to a recovery of 72%.) An infrared spectrum of the oil which remained did not give any evidence of a reaction. As with the starting material, there was a carbonyl peak at 5.7 μ.

Monobenzoylated cyclohexanones (as the copper chelates) were isolated after hydrolysis of the oily residue remaining when the dibenzoylated enamines were crystallized and removed from the reaction of the benzoyl chlorides with 1-morpholinocyclohexene-1. After hydrolysis, the organic layer was separated from the aqueous layer and the organic solvent was evaporated. The residue was taken up in ether and shaken with sodium bicarbonate solution, washed with water, and shaken with aqueous cupric acetate solution. Upon standing for a few hours, the chelate was visible. It was washed with hot water, then ether, and dried.

All melting points are corrected. The n.m.r. spectra were measured on a Varian A-60 spectrometer. Ultraviolet spectra were obtained from the Cary Model 11 and Model 14 instruments. Infrared spectra were run on a Perkin-Elmer Model 21 and Model 347 Infracord spectrometers.

Electrophilic Substitution Reactions of Triphenylamine[1a]

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The conditions for halogenation, sulfonation, and acylation of triphenylamine have been investigated, and the *para* positions have been shown to be those attacked under the conditions used. These reactions in most cases proceed to the trisubstitution stage without formation of isolable amounts of intermediates. These facts are considered in the light of knowledge of the configuration and electronic nature of the triphenylamine molecule.

The electrophilic substitution reactions of triphenylamine afford a route to the synthesis of a number of otherwise difficultly accessible compounds necessary for the preparation of aminium salt free radicals.[2] In addition, they have some theoretical interest in connection with the transmission of substituent effects between aromatic rings through bridging atoms. We report here procedures for carrying out trisubstitution in triphenylamine by most of the usual electrophilic substitution reactions, the proofs of structure of the products, and experimental and theoretical evidence bearing on directive effects in these reactions.

Procedures for a number of trisubstitution reactions of triphenylamine are in the literature. Years ago, the preparation of a trinitrotriphenylamine was described by Heydrich,[3] a trisulfonic acid by Herz,[4] and a tribromo compound by Wieland.[5] More recently, Wilson[6] has patented a synthesis which is claimed to give triformyltriphenylamine. Fox and Johnson have just published a study of acylation reactions of triphenylamine in which trisubstitution products have been identified.[7] In all of these cases, the number of substituents introduced was determined by analysis of the products. The facts that amino groups direct electrophilic aromatic substitution to the *ortho, para* positions, that the geometry of triphenylamine is such that *ortho* substitution would be inhibited sterically, and that most reactions are observed to lead to the introduction of no more than three substituents, suggest that reaction occurs at the three *para* positions. Those trisubstitution products which have been described in the literature have been said to be 4,4′,4″-trisubstituted, usually with no experimental support for these claims. The structures

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(1) (a) This work was supported in part by U. S. Army Signal Research and Development Laboratory Contract No. DA-36-039-SC-74917, administered by the University of Pennsylvania, and in the later stages by U. S. Public Health Service Grant GM-10605 to Haverford College. Royalty-free reproduction for purposes of the United States Government is permitted. (b) Senior research participant at Haverford College. (c) Summer research participant sponsored by the National Science Foundation undergraduate research participation program. (d) Inquiries should be sent to this author.

(2) R. I. Walter, *J. Am. Chem. Soc.*, **77**, 5999 (1955).

(3) C. Heydrich, *Ber.*, **18**, 2157 (1885).

(4) R. Herz, *ibid.*, **23**, 2541 (1890).

(5) H. Wieland, *ibid.*, **40**, 4278 (1907).

(6) C. D. Wilson, U. S. Patent 2,558,285 (1951).

(7) C. J. Fox and A. L. Johnson, *J. Org. Chem.*, **29**, 3536 (1964).

of some acylation products have been inferred from the infrared band at 825 cm.$^{-1}$ characteristic of *para*-disubstituted benzene rings,[7] and that of the trinitro compound has been verified by an independent synthesis.[8] Structural determinations for the other products are given here.

Reaction conditions also are known which introduce fewer than three substituents. Acylation in the presence of zinc chloride introduces one acyl group.[7] Triphenylamine heated with N-bromosuccinimide gives a monobromo compound which is said to be the 4-substituted product.[9] The *para*-mono- and dinitro intermediates in the formation of tris(*p*-nitrophenyl)amine have been isolated.[10] A mononitroso compound results from triphenylamine treated at −5° with amyl nitrite in alcohol saturated with hydrogen chloride.[11] A dithiocyanate results from reaction of triphenylamine with thiocyanogen in ether solution.[12] Coupling with the diazonium salt from sulfanilic acid gives a diphenylaminoazobenzene-4′-sulfonic acid.[13] Metalation with butyllithium gives the *meta* lithium derivative.[14]

Thus, *para* substitution in triphenylamine is expected on theoretical grounds and has been found to occur in those few cases in which structures of the substitution products have been determined, except for the metalation with butyllithium. The *meta* orientation in this reaction is consistent with that generally observed when the strongly preferred *ortho* position is blocked.[15]

In our work, we have found that quite specific reagents are necessary to carry out trisubstitution in triphenylamine without serious side reactions. This molecule is a reactive aromatic system—qualitatively comparable to anisole—so mild conditions are adequate. Reagents which are also strong oxidizing agents convert the amine to the unstable deep blue triphenylaminium ion; this undergoes polymerization in air to products which range in texture from rubbery to very hard. The polymers are insoluble in all solvents which we tested, and are partially substituted by the electrophilic reagent used.

Triphenylamine in carbon tetrachloride, acetic acid, dimethylformamide, or tetrachloroethane reacted with chlorine, either with or without the addition of iron catalyst, beyond the trisubstitution stage. The products were sticky mixtures. A fully chlorinated product was obtained by chlorination in warm tetrachloroethane in the presence of iron. This "perchlorotriphenylamine" is referred to by Stilmar,[16] but with no data for its characterization.

The bromination of triphenylamine by Wieland's procedure[5] using bromine in chloroform solution, gave a tribromotriphenylamine. The three bromine atoms were shown to occupy the three *para* positions by treatment with butyllithium, carbonation, and esterification; the product was the known compound tris(*p*-carbomethoxyphenyl)amine.[2] Bromination stopped at this trisubstitution stage when the reaction was carried out in an organic solvent.

In one early experiment, a low yield of a triiodotriphenylamine was obtained by adding iodine chloride to triphenylamine in refluxing acetic acid. A great many subsequent trials with iodine chloride in a variety of solvents and over a wide temperature range failed to give the same product; only insoluble polymers were obtained. The reaction also was unsuccessful with silver acetate and iodine in phosphoric acid,[17] with potassium peroxydisulfate and iodine in acetic acid,[18] and with iodine and potassium carbonate in chloroform. A reproducible procedure was based upon that reported by Classen,[19] who used mercuric oxide and iodine to substitute diphenylamine.

The Friedel–Crafts acetylation of triphenylamine proceeded in a normal manner to give a triacetyl derivative which was shown to be substituted in the three *para* positions by an independent synthesis from *para*-disubstituted starting materials *via* the Ullmann reaction.[20] Attempts to prove the structure by hypohalite or chromic acid oxidation to the tricarboxylic acid failed to give homogeneous products. Evidently this was because the tricarboxylic acid formed is not stable toward these reagents, since both oxidants were consumed when they were stirred under the reaction conditions with triphenylamine-4,4′,4′′-tricarboxylic acid.

A number of attempts to prepare tris(*p*-formylphenyl)amine by Wilson's procedure[6] have given us only the monosubstitution product. The properties of this substance are similar to those reported by Wilson for his supposed trisubstitution product; we believe that he also prepared 4-formyltriphenylamine.

Herz[4] used fuming sulfuric acid in his preparation of a trisulfonic acid of triphenylamine. In our hands, both this reagent and chlorosulfonic acid gave inhomogeneous water-soluble products and in some cases insoluble rubbery polymers. A convenient reagent which gave reproducible sulfonations is sulfur trioxide in dimethylformamide.[21] The acid was recovered as its potassium salt, and this was esterified by heating with dimethyl sulfate. The positions of the three sulfonic acid groups were demonstrated by displacement with acetyl nitrate to give the known tris(*p*-nitrophenyl)amine. Attempts to carry out displacement of the sulfonate groups with iodine generated by the reaction between iodide and iodate were not successful, but the analogous reaction with "nascent" bromine formed by reaction of bromide and bromate[22,23] gave tris(*p*-bromophenyl)amine. A second product was isolated in varying amounts from this reaction mixture; it proved to be a hexabromotriphenylamine. This compound can also be prepared by the direct bromination of tris(*p*-bromophenyl)amine in the presence of an iron catalyst and water.

A few of the yields in the reactions reported here are quite low. It should be kept in mind that the yield for a reaction of a monofunctional compound is cubed

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when a single reaction is carried out simultaneously on each of three identical functional groups in one molecule. If several steps are required, this can easily reduce the yield in a quite respectable reaction sequence below 10%.

A number of instrumental methods for the determination of structure have been applied extensively during recent years. We have felt ill at ease about the use of the infrared band at *ca.* 825 cm.$^{-1}$ to determine the positions of substitution in these reactions because we have observed it to change position significantly or to overlap other bands when a series of compounds which contain a variety of substituents is considered. The n.m.r. spectra are less ambiguous: if the pattern in the aromatic proton region is that characteristic of an A_2B_2 system, all three rings of the triphenylamine must be *para*-disubstituted. All of the trisubstitution products of triphenylamine show this characteristic pattern, which affords independent confirmation of their structures. Unfortunately, this application of n.m.r. spectroscopy had not yet been generally recognized at the time when most of this chemical work was carried out. An analysis of these n.m.r. spectra will be published elsewhere.

The geometry of triphenylamine has not been fully determined. Experimental values of the dipole moment range from 0.2 to 0.7 D.[24] This is sufficiently small that it may not reflect the geometry of the molecule, but might instead result from polarization of the unshared electron pair on the nitrogen atom.[25] Electron diffraction data indicate that the molecule is a shallow pyramid, with C–N–C angles equal to 116°.[26] This is hardly significantly different from the 120° which would be found for a planar system of bonds to the nitrogen atom. Whether the system of ring-nitrogen bonds is planar or pyramidal, the three rings must be rotated some 30–45° to avoid overlap of the *ortho*-hydrogen atoms.[26,27] This decreases overlap between the nitrogen 2p and the ring π orbitals by a factor equal to the cosine of this angle in the MO approximation,[28] or by 0.87 to 0.71 times the value for the planar system. As a result, the transmission of substituent effects will not be greatly reduced by the lack of planarity.

Jaffé has studied the ultraviolet spectra of compounds in which one or more benzene rings are attached to a central atom.[29] He interpreted the very large increase in intensity of the long wave length band, and the loss of vibrational fine structure, as evidence for the conjugation of the unshared electron pair on nitrogen with the ring π systems. It seems clear, however, that the interaction between any two *para* positions in triphenylamine must be much less than that in benzene. The rates of nitration of benzene and nitrobenzene differ by a factor of the order of a million. There are no quantitative data available for triphenylamine and its derivatives, but the conditions used by Herz[10] (1 hr. at room temperature to prepare 4-nitrotriphenylamine, and 2 hr. at 28° to prepare 4,4′-dinitrotriphenylamine, with a somewhat higher concentration of nitric acid) are such that one can estimate that the relative rates of nitration of triphenylamine and 4-nitrotriphenylamine differ by a factor of 10 to 100. Clearly, the deactivating effect of the nitro group already present is diminished strongly by transmission between rings through the central nitrogen atom.

Experimental Section

Chromatography was carried out on Merck alumina. Melting points were determined on a Kofler hot-stage microscope. Analyses were run by Galbraith Laboratories, Knoxville, Tenn.

Chlorination.—Chlorine was passed into a flask containing 0.01 mole of triphenylamine, 0.3 g. of steel wool, and 50 ml. of tetrachloroethane for 30 min. without heating, and then for 1 hr. at 90°. The mixture was washed with hydrochloric acid solution to remove iron salts, and the solvent was removed by steam distillation. The residue was recrystallized first from tetrachloroethane, then from carbon tetrachloride, sublimed at *ca.* 280°, and finally recrystallized from chlorobenzene. The product of these operations retained a pale reddish color and melted sharply at 363°. The yield before the sublimation step was 58%.

Anal. Calcd. for $C_{18}Cl_{15}N$: C, 28.37; H, 0.00; Cl, 69.79. Found: C, 28.48; H, 0.22; Cl, 69.67.

Bromination.—A tribromotriphenylamine was formed by slowly adding 3 moles of bromine in chloroform solution to a stirred solution of 1 mole of triphenylamine in chloroform.[5] The product was recovered by addition of hot ethanol to the saturation point. It can be conveniently recrystallized by extraction in a Soxhlet with methanol or heptane, m.p. 144.5–146.5°. The yield exceeded 90%.

To determine the structure of this compound, 4.8 g. (0.01 mole) dissolved in 200 ml. of redistilled benzene was treated with 0.045 moles of butyllithium in ether. Addition of the reagent required 20 min., and the suspension formed was stirred for an additional 3 hr. while the temperature was slowly raised to 75°. It was then poured on 150 g. of powdered Dry Ice. After this mixture came to room temperature it was extracted with 5% sodium hydroxide, and this yellow alkaline solution was subsequently acidified. The blue-green solid which formed was refluxed for 4 hr. with 30 ml. of sulfuric acid in 130 ml. of methanol, and the ester was recovered by pouring on ice. The dried solid (*ca.* 3 g.) was dissolved in benzene and chromatographed on alumina. The material eluted by benzene was recovered by vacuum distillation and recrystallized twice from methanol and once from hexane. The product consisted of 0.3 g. (7% yield) of needles, m.p. 137–140°. Its mixture melting point with authentic tris(*p*-carbomethoxyphenyl)amine[2] was 138–141°, and the infrared spectra were identical.

Bromination of 4,4′,4′′-Tribromotriphenylamine.—A solution of 4.8 g. (0.01 mole) of the tribromo compound in 10 ml. of chloroform was shaken with 50 ml. of water, 3 ml. (0.06 mole) of bromine, and 0.5 g. of steel wool catalyst for 6 hr. Excess bromine remained in the solution at the end of this period. The organic layer and suspended solids were separated and 40 ml. of hot chloroform was added to effect complete solution. This was treated with charcoal, and hot methanol was added to produce crystallization. The product was then recrystallized by extraction in a Soxhlet with heptane; the colorless product melted at 218–220°, yield 6.4 g. (89%).

Anal. Calcd. for $C_{18}H_9Br_6N$: Br, 66.71. Found: Br, 67.63.

Iodination of Triphenylamine.—Triphenylamine (24.5 g., 0.1 mole) was dissolved in 1 l. of refluxing ethanol and 100 g. of red mercuric oxide was added. The mixture required strong stirring to keep the oxide in suspension during the gradual addition of 125 g. (0.5 mole) of iodine.[19] After the exothermic reaction had ceased, the suspension was cooled and the solids were transferred to a Soxhlet extractor. Extraction with benzene separated the product from mercuric salts, and this solution was decolorized by passing it through an alumina column. The product (crude yield over 90%) was recovered by addition of alcohol to the hot benzene solution, but good crystals were not obtained in this way. The most satisfactory method for recrystallization proved to be extraction with acetonitrile in a Soxhlet

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[24] A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman and Co., San Francisco, Calif., 1963, p. 512.

[25] See L. Paoloni, *J. Am. Chem. Soc.*, **80**, 3879 (1958), and other references given there.

[26] Y. Sasaki, K. Kimura, and M. Kubo, *J. Chem. Phys.*, **31**, 477 (1959).

[27] F. J. Adrian, *ibid.*, **28**, 608 (1958).

[28] A. Streitweiser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 105.

[29] H. H. Jaffé, *J. Chem. Phys.*, **22**, 1430 (1954).

apparatus. The product consisted of pale yellowish needles, m.p. 188–190°.

Anal. Calcd. for $C_{18}H_{12}I_3N$: I, 61.11. Found: I, 61.29.

We have not carried out a chemical determination of the structure of the iodination product. It gives a clean A_2B_2 n.m.r. spectrum in the aromatic region, so all three rings must be *para*-disubstituted.

Acetylation of Triphenylamine.—A solution of 12.3 g. (0.05 mole) of triphenylamine and 26 g. (0.25 mole) of aluminum chloride in 250 ml. of redistilled carbon disulfide was stirred in a 500-ml. flask while 22 ml. (0.3 mole) of acetyl chloride was dropped in over a period of 35 min. In order to prevent accumulation of acetyl chloride which eventually reacts uncontrollably, the addition was started with the temperature in the range 25–30°. After reaction began, the mixture was cooled to maintain the temperature in the range 25–30°. After addition of the acetyl chloride, the mixture was stirred for 1 hr. at room temperature, and then slowly heated to reflux for another hour. The tarry brown intermediate was decomposed with ice, and the solvent was removed by steam distillation. The yield of crude yellow-brown product was 85–90%. It was purified by chromatography from benzene solution on alumina. Since the product and most of the impurities were yellow to brown on the column, the separation was followed by the fluorescence of the bands and the eluted solutions under ultraviolet light. The lowest band on the column (purple fluorescence) was eluted as a benzene solution with pale violet fluorescence. It contained triphenylamine. The next band contained partially acetylated material which fluoresced yellow or yellow-green on the column and pale blue in benzene solution. The yellow band of triacetyl compound eluted very slowly with benzene and was better removed by washing with chloroform. This solution fluoresced very strongly with a pale blue color. A brown band which contained tarry material remained on the column after the chloroform wash. The solid which was recovered by evaporation of the chloroform eluate was recrystallized from alcohol. The over-all yield was about 50%, m.p. 154–156°. Evidently there is some decomposition of this compound on an alumina column: a single band eluted from one chromatogram gives several bands when it is rechromatographed under the same conditions.

Anal. Calcd. for $C_{24}H_{21}NO_3$: C, 77.60; H, 5.70; N, 3.77. Found: C, 77.67; H, 5.67; N, 3.68.

Synthesis of Bis(*p*-acetylphenyl)amine.—*p*-Iodoacetophenone was prepared by the acetylation of iodobenzene.[30] A solution in 500 ml. of xylene of 98 g. (0.4 mole) of *p*-iodoacetophenone and 63 g. (0.38 mole) of *p*-acetylacetanilide was refluxed for 44 hr. the presence of 5 g. of Fernlock copper bronze[31] and 50 g. of anhydrous potassium carbonate, with vigorous stirring. The inorganic solids were then filtered off and xylene was removed by steam distillation. The tarry residue was dissolved in 400 ml. of acetone, 100 ml. of concentrated hydrochloric acid was added, and the mixture was refluxed 2 hr. to hydrolyze the amide group. Acetone was removed by steam distillation and the organic residue was taken up in benzene. The dry solution was chromatographed on a 1 × 6 in. alumina column. The first 400 ml. of benzene eluate gave crystals on evaporation. Recrystallization twice from alcohol gave 6.3 g. of pale yellow crystals. An additional 700 ml. of darker colored eluate was concentrated and rechromatographed. The first half of the material eluted from this column was sublimed at *ca.* 180°. Recrystallization from alcohol gave 2.9 g. of crystals, total yield 9.9%. We believe the low yield is due to aldol-type reactions while the mixture is heated in the presence of the potassium carbonate. This substance acquires a very large static charge on grinding: m.p. 159–160°.

Anal. Calcd. for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.53. Found: C, 76.03; H, 6.05; N, 5.56.

Synthesis of Tris(*p*-acetylphenyl)amine.—A mixture of 2 g. (0.008 mole) of *p*-iodoacetophenone, 2 g. (0.008 mole) of bis(*p*-acetylphenyl)amine, 1.2 g. of anhydrous potassium carbonate, 0.5 g. of Fernlock copper bronze, and 5 ml. of xylene were heated together for 18 hr. (All of the solvent distilled off while the mixture was left overnight.) The residue was extracted as completely as possible into benzene, and the dry solution was chromatographed on a 1.5 × 6 in. alumina column. Elution with 50% chloroform–benzene gave a sample which was fractionally crystallized from ether and then from hexane. The solid recovered consisted of 50 mg. of pale yellow crystals, m.p. 155–159°. The mixture melting point with the acetylation product was not depressed, and infrared curves for the two preparations were identical. Since this tertiary amine has a melting point close to that of the secondary amine, the mixture melting point was checked: 120–155°.

Formylation of Triphenylamine.—Wilson's procedure[6] for formylation of triphenylamine with dimethylformamide and phosphoryl chloride was carried out a number of times as described, and also with longer reaction times and greater excess of the reagents. The crude products melted in the range 129–134°. Recrystallization from alcohol, followed by Soxhlet extraction into Skellysolve B, gave yellow crystals. The first fraction of these had the highest melting point, 132–133.5°. The n.m.r. spectra of all products showed an A_2B_2 pattern in the aromatic region, but superimposed on this was a stronger pattern characteristic of the monosubstituted rings in triphenylamine. The analysis corresponds to the monoformylation product, and the n.m.r. spectrum requires that this be 4-formyltriphenylamine.

Anal. Calcd. for $C_{19}H_{15}NO$: C, 83.49; H, 5.53; N, 5.13. Found: C, 83.16; H, 5.51; N, 4.94.

Sulfonation of Triphenylamine.—The sulfonating agent[21] was prepared by dropping 21 ml. of stabilized liquid sulfur trioxide (Sulfan B) into 500 ml. of dimethylformamide which was stirred in an ice–salt bath during the addition. This solution is 1.0 *F*. The entire system was protected by a drying tube. Triphenylamine (12.5 g., 0.05 mole) was sulfonated in 160 ml. of the sulfur trioxide solution while the temperature was gradually raised to reflux over 1 hr. and held at reflux for a second hour. About half of the solvent was removed by vacuum distillation, 150 ml. of absolute alcohol was added, and the solution was made basic with 50% potassium hydroxide. The precipitated potassium salt was recovered, washed with alcohol, dissolved in 150 ml. of water, and decolorized by treatment with charcoal. To the hot solution was added 75 ml. of hot saturated aqueous potassium acetate and the mixture was cooled. The product consisted of 30.5 g. (99%) of slightly yellowish crystals which became darker on exposure to light. The n.m.r. spectrum of this product indicated that acetate was present. This was removed by extraction of a small sample into methanol in the Soxhlet apparatus.

Anal. Calcd. for $C_{18}H_{12}K_3NO_9S_3$: C, 36.04; H, 2.02; K, 19.56; S, 16.04. Found: C, 36.16; H, 2.19; K, 19.41; S, 16.13.

Triphenylamine-4,4′,4″-trisulfonic Acid Trimethyl Ester.—Freshly redistilled dimethyl sulfate (60 ml.) and 23 g. (0.39 mole) of the potassium salt were heated in an oil bath. As the temperature rose above 70°, there was appreciable bubbling of the liquid and some refluxing. After *ca.* 20 min., the temperature was 100°, all solids had dissolved, bubbling had stopped, and the solution was blue. It was then heated for 1 hr. at 100–110°. Relatively little solid precipitated on cooling. Addition of methanol or of tetrahydrofuran increased the amount of precipitated solid a great deal, but changed the melting point: from methanol, m.p. 194–197°; from THF, m.p. 230–240°. A sample for analysis was prepared by extracting the product precipitated by THF in a Soxhlet extractor with THF: m.p. 239–242°.

Anal. Calcd. for $C_{21}H_{21}NO_9S_3$: C, 47.80; H, 4.01; S, 18.23. Found: C, 47.62; H, 3.96; S, 18.39.

The structure of the trisulfonic acid was verified by displacement of the acid groups with acetic anhydride and nitric acid in acetic acid. Presumably this reagent is the acetyl nitrate discussed by Bordwell.[32] Six grams (0.01 formula wt.) of the potassium salt was suspended in 34 ml. of acetic acid and 18 ml. of acetic anhydride. To this was added dropwise a solution of 2 ml. of concentrated nitric acid. Within 10 min. the mixture became a clear bright red solution as it was slowly heated, then held for 90 min. at 90°. The product was poured into 800 ml. of water and stirred overnight to coagulate the fine precipitate. The dry weight of this fine yellow solid was 0.4 g., yield 10.5%. The filtrate was bright yellow, indicating partial displacement. Recrystallization from nitromethane gave 0.2 g. of yellow crystals which underwent the phase changes observed for tris(*p*-nitrophenyl)-amine[8] and melted at 377°. Its infrared spectrum is identical with that of an authentic sample.

In an alternate structure proof, 2.0 g. of the trisulfonic acid salt in 30 ml. of aqueous 1.0 *F* hydrochloric acid was treated

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[30] W. Kimura, *Ber.*, **67**, 395 (1934).

[31] Available from U. S. Bronze Powder Works, New York, N. Y.

[32] F. G. Bordwell and E. W. Garbisch, Jr., *J. Am. Chem. Soc.*, **82**, 3588 (1960).

dropwise at 45° with an aqueous solution of 1.0 g. of potassium bromide and 0.28 g. of potassium bromate. After the addition, the mixture was warmed for 30 min. on a water bath. The oil which separated solidified on cooling. The product was purified by extraction into methanol twice in the Soxhlet apparatus. It had an infrared spectrum identical with that of the authentic 4,4',4''-tribromotriphenylamine, and the melting point of the mixture was not depressed. When this bromodesulfonation reaction was carried out at 60°, a substantial part of the product was the hexabromo compound already described.

Nitrogen Analogs of Ketenes. VII.[1] Reactions with Amines

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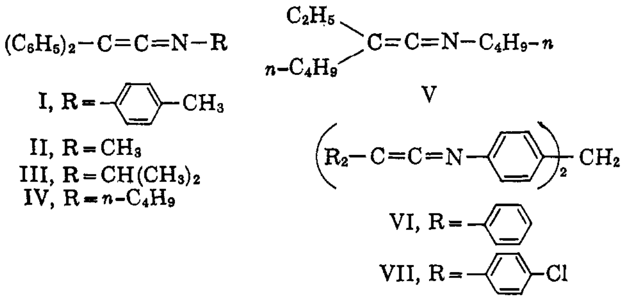
Amidines have been prepared in good yield by treating ammonia, primary and secondary aliphatic amines, and aromatic amines with ketenimines I–VII. Although aromatic amines are less reactive than aliphatic amines, good yields were obtained at elevated temperatures. Ketenimines IV and V were less reactive than other ketenimines, but yields of 84–94% were obtained by employing elevated reaction temperatures and alkali metal catalysts. Structures of amidines are assigned on the basis of both n.m.r. data and on chemical evidence provided by acid hydrolysis of the amidines. Yield data and experimental conditions provide data for discussing the relative reactivities of the amines and ketenimines.

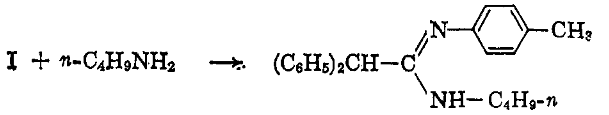
Over the past several years, this laboratory has developed three general and convenient methods for the synthesis of ketenimines.[2] This paper reports a study of the reaction of ketenimines I–VII with amines and the development of a new method for the preparation of amidines.

Amidines, in general, have been prepared most frequently by the reaction of amides, thio amides, imido esters, and nitriles with amines.[3] Amidines have also been prepared by the rearrangement of arylaldehyde hydrazones,[4] and by the reaction of amines with ortho esters,[5] amide acetals,[6] enamines,[7] and ethoxyacetylene.[8] Dijkstra and Backer have studied the reaction of amines with bis-substituted sulfonyl N-methylimines to form amidines.[9]

The scope of our new synthesis includes the reaction of ammonia, primary and secondary aliphatic amines, and aromatic amines with various ketenimines (I–VII) to give amidines in good yields (see Tables I–III). The reactivity of aromatic amines was considerably less than aliphatic amines, but the addition of the aromatic amines to the ketenimines could be successfully carried out at elevated temperatures. In general, amines added smoothly to the ketenimines under mild reaction conditions. The reactivity of ketenimines IV and V toward amines was less than the other ketenimines. However, amidines were isolated in yields of 84–94% from IV and V by using alkali metal catalysts and elevated reaction temperatures.

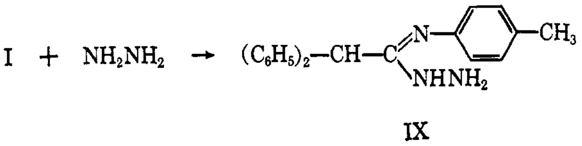


To study the scope of useful amines, ammonia, primary and secondary aliphatic amines, and aromatic amines were added to diphenylketene N-*p*-tolylimine (I) to give amidines in yields ranging from 62 to 97% (see Table I). For example, when *n*-butylamine was added to I, an exothermic reaction occurred and within 3 hr. the amidine, N-*n*-butyl-N'-(*p*-tolyl)diphenylacetamidine (VIII), was obtained in 78% yield after one recrystallization.



VIII

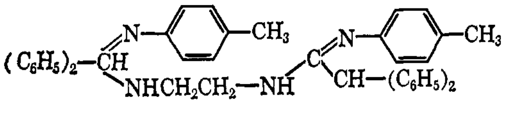
Amidrazones were isolated from the reaction of I with hydrazines. A 1:1 molar ratio of hydrazine and I gave the stable N³-(*p*-tolyl)diphenylacetamidrazone (IX), in 97% yield.



IX

Bisamidines were prepared both by the reaction of ethylenediamine with I (eq. 1) and amines with the diketenimines VI and VII. Attempts to isolate an

$2I + NH_2CH_2CH_2NH_2 \rightarrow$



(1)

X

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