coal in toluene solution but this did not remove the yellow color. However, two washings with low boiling petroleum ether did remove the color and the white crystals, m.p. 55–56°, weighed 11.5 g. Another 0.6 g. could be recovered from the petroleum ether.

*Anal.* Calcd. for $C_7H_{13}NS$: C, 58.62; H, 9.15; N, 9.77; S, 22.38. Found: C, 59.12; H, 9.13; N, 9.57.

Russell[21] prepared this thioamide from N-acetylpiperidine by the action of phosphorus pentasulfide and reported the melting point as 60–61°.

**N-*n*-Butylthioacetamide.**—In the same general manner for 12 g. of ethyl dithioacetate and 7.31 g. of *n*-butylamine, there was obtained a dark liquid which did not crystallize. On distillation there was obtained 11 g. (83.3%) of liquid boiling at 113° under 1 mm. pressure, $n^{20}\text{D}$ 1.5392.

*Anal.* Calcd. for $C_6H_{13}NS$: N, 10.67. Found: N, 10.50.

**Attempts to Prepare N-Thioacetanilide.**—Under the same general conditions no reaction was obtained between aniline and ethyl dithioacetate.

**Reaction of Piperidine and Ethyl Thiolacetate.**—When 12.75 g. of piperidine and 15.6 g. of ethyl thiolacetate were mixed at room temperature they reacted with the liberation of heat and some slight cooling was needed to keep the temperature below 60°. After about an hour at 60° the mixture was warmed to 100° to remove all of the mercaptan. The residual liquid was distilled to give 17.1 g. (89.8%) of product boiling at 224–225°, $n^{20}\text{D}$ 1.4815. Arens and Wibaut[22] report a boiling point of 220–230°.

*Anal.* Calcd. for $C_7H_{13}ON$: N, 11.00. Found: N, 11.03.

**Thiopropionamide.**—Pesina[11] has reported the preparation of this amide in 5–6% yield for the reaction of phosphorus pentasulfide on propionamide. In an attempt to convert ethyl thioimidopropionate hydrochloride to the dithioester in aqueous media we obtained the amide in 48% yield.

To an ice-cold 40% solution of potassium carbonate, 25 g. of ethyl thioimidopropionate hydrochloride was added. The free base was extracted in ether and the ether solution dried slightly over sodium sulfate and filtered. Hydrogen sulfide was passed into this solution at 0–5° for three hours. At first some solid ammonium sulfide separated and then disappeared as an aqueous layer separated. The reaction mixture was allowed to stand overnight, washed three times with water, dried over sodium sulfate and distilled. A very small amount of ethyl dithiopropionate distilled but the main portion boiled at 97° at 1–2 mm. and solidified on cooling. The yield was 7 g. (48%) of thiopropionamide, m.p. 41–42°. The literature[11] reports the melting point as 41–43°.

*Anal.* Calcd. for $C_3H_7SN$: N, 15.71. Found: N, 15.71.

This amide is soluble in water, ether, toluene and carbon tetrachloride. It is somewhat soluble in low boiling petroleum ether and cyclohexane.

**Infrared Spectra.**—The spectra were obtained employing a Perkin–Elmer model 21 double beam infrared spectrophotometer equipped with sodium chloride optics. All samples except thiopropionamide and thioacetylpiperidine were examined as liquid films; the latter were prepared by melting the solid between two sodium chloride plates and allowing the material to crystallize.

URBANA, ILLINOIS

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[21] W. F. Russell, *Proc. Chem. Soc.*, **26**, 89 (1910); *J. Chem. Soc.*, **97**, 953 (1910).

[22] J. F. Arens and J. P. Wibaut, *Rec. trav. chim.*, **61**, 452 (1942).

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS UNIVERSITY, AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CONNECTICUT]

# Triarylaminium Salt Free Radicals[1]

BY ROBERT I. WALTER

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A series of tri-*para*-substituted triarylamines has been prepared, and oxidized to the corresponding free radical triarylaminium ions. The products have been isolated as the perchlorates. Some properties of this family of stable free radicals are described.

Nearly 30 years ago, Weitz and Schwechten[2] reported the oxidation of solutions of tri-*p*-tolylamine to a deep blue product which they isolated as a perchlorate and a picrate. They also obtained a blue–green color on oxidation of tris-(*p*-aminophenyl)-amine, and a transient blue color with triphenylamine, but did not isolate reaction products in these cases. They suggested that their blue substances were free radical cations, and proposed the name aminium salt for compounds of this type. They also suggested that the blue tribromides prepared earlier by Wieland from tri-*p*-anisylamine[3a] and tri-*p*-tolylamine[3b] were aminium salt perbromides.

Their proposed structure for the blue oxidation product from tritolylamine has been verified by physical measurements. Walden and Birr[4] showed that the perchlorate in nitrobenzene has the conductivity of a strong electrolyte, with the blue ions migrating to the cathode. Katz[5] and Rumpf and Trombe[6] confirmed that the substance is a free radical by measurements of magnetic susceptibility. Finally, Granick and Michaelis[7] showed by potentiometric titration that conversion of amine to aminium ion involves loss of one electron.

More recently, the preparation of two other arylaminium perchlorates has been reported. Kuhn and Kainer[8] have made pentaphenylpyrrolium perchlorate, and Chu and Weissman[9] have prepared the triphenylaminium salt. Neither of these substances has been isolated in the pure state, and neither is stable in air. In contrast, tri-*p*-tolylaminium perchlorate was prepared using normal techniques which involved exposure to air, and was reported to be stable in the dry state "for several days." The research reported here was prompted by a need for a series of free radicals suitable for physical measurements. The available information suggested that such a series of tri-*para*-substituted amininium salts might be prepared, and might be sufficiently stable for convenient manipulation.

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[1] The major part of this work was carried out at Rutgers University with the support of the Office of Naval Research, under contract N7 onr 45403.

[2] (a) E. Weitz and H. W. Schwechten, *Ber.*, **59B**, 2307 (1926); (b) **60B**, 545 (1927).

[3] (a) H. Wieland and E. Wecker, *ibid.*, **43**, 705 (1910); (b) H. Wieland, *ibid.*, **40**, 4279 (1907).

[4] P. Walden and E. J. Birr, *Z. physik. Chem.*, **A168**, 107 (1934).

[5] H. Katz, *Z. Physik*, **87**, 238 (1934).

[6] P. Rumpf and F. Trombe, *Compt. rend.*, **206**, 671 (1938).

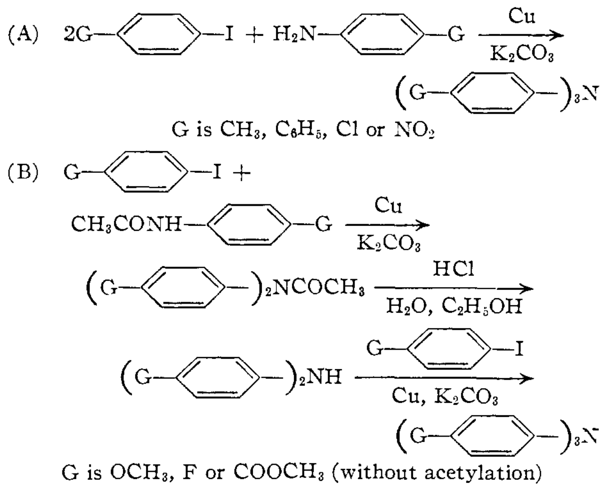
[7] S. Granick and L. Michaelis, THIS JOURNAL, **62**, 2241 (1940).

[8] R. Kuhn and H. Kainer, *Chem. Ber.*, **85**, 498 (1952).

[9] T. L. Chu and S. I. Weissman, private communication.

Two routes to the triarylamines which were explored in this research are given in Chart I.

CHART I



Method A, although apparently more direct than B, under the conditions used gave tertiary amines which were contaminated with large amounts of aryl iodide and secondary amine. Separation of these mixtures was difficult, and the tertiary amines eventually recovered were generally not as pure as those obtained by method B. The condensation, employed in both methods, of an aryl halide with an arylamine in the presence of a copper catalyst was first described by Ullmann.[10] The large substituent effects on rate and yield in this reaction have been summarized by Bunnett and Zahler.[11]

Reaction conditions for the arylamine preparations described here were initially patterned after those given by Hager[12] for making triphenylamine. It became evident while preparing this series of amines that modifications in his procedure were desirable. The earlier preparations were not repeated with the modified procedure, but presumably would be improved if this were done. The reaction need not be conducted in nitrobenzene solution. This solvent increased contamination of the amines by tarry products, and was difficult to remove completely by steam distillation. Instead, the molten reagents can be heated together in a bath maintained at 180–220°. Separation of secondary amines from tertiary by precipitation from benzene solution with dry hydrogen chloride was incomplete when the amount of secondary amine was large, and failed completely when the basicity of the secondary amine was reduced by electron-accepting substituents. Fractional sublimation was more effective. Both the secondary and tertiary amines contained tars which were not removed by recrystallization; chromatography on alumina accomplished this separation.

Oxidation of the tertiary amines to aminium salts occurred most readily for those compounds having electron-donating substituents. Tri-*p*-anisylamine was oxidized completely by silver ion. The other compounds were oxidized by a mixture of silver perchlorate and iodine in ether. Gomberg[13] believed that this mixture contained the perchlorate free radical, but no paramagnetic resonance absorption has been observed with such solutions.[9] More probably, they contain $I^+$ in some form.[14] This oxidant was sufficiently strong to convert all of the amines studied to the aminium salts except the tricarbomethoxy compound, which always contained uncharacterized diamagnetic material, and the trinitro compound, which was not oxidized by any reagent investigated. These facts indicate that amines ($p$-G–$C_6H_4$–)$_3$N in which G has a Hammett $\sigma$-value smaller than 0.5 (using the usual values, not those for the *para*-substituted primary arylamines) can be oxidized to the aminium perchlorates in the manner reported by Weitz and Schwechten,[2] except when secondary reactions intervene.

A number of attempts to oxidize triphenylamine to the radical led only to brown mixtures. These efforts were abandoned when it was learned that Chu and Weissman had prepared triphenylaminium perchlorate.[9] Their reaction was essentially that described here, with the important exception that the oxidation was carried out in a vacuum line in the absence of oxygen. Solutions of their product were instantly decolorized by oxygen, presumably by reactions involving those structures in which the unpaired electron is on a *para* carbon atom. Solutions of tribiphenylylaminium perchlorate, for which there are also contributing structures with the unpaired electron on a *para* carbon, are stable in air. Presumably the electron density on any one carbon is too low for reaction to occur with the latter compound. All of the radicals with *para* substituents other than hydrogen are stable in air.

Occasionally solid samples of aminium salts have decomposed to tarry residues. This decomposition was more rapid if the preparation was not freed of oxidizing agent by thorough washing with ether. It was also more rapid on hot days. The solid tricarbomethoxyphenyl, tribiphenylyl and trianisyl (if protected from moisture) radicals seem to be stable indefinitely, and samples of each of these aminium perchlorates have been kept for at least a year in the refrigerator.

The aminium salts are soluble in chloroform, both dichloroethanes, tetrachloroethane, bromoform, acetone and alcohol. Chloroform solutions lose color at a rate dependent upon the strength as an oxidant of the aminium ion; the tricarbomethoxyphenyl radical is colorless within an hour, but the trianisyl radical is stable for several months. Acetone and alcohol solutions are much less stable. The aminium perchlorates are deep indigo blue in solution, except for the tri-*p*-biphenylylaminium salt, which is green. Decomposition of solutions is usually accompanied by a color shift from blue to green, and finally to brown or colorless. The solutions are reduced instantly by reagents such as hydroquinone and ferrous ion. They are also decolorized, with evolution of nitrogen, by the addition of diazomethane.

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(10) F. Ullmann, *Ber.*, **36**, 2382 (1903).

(11) J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 307ff, 341ff (1951).

(12) F. D. Hager, "Organic Syntheses," Coll. Vol. I, Second Ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 544.

(13) M. Gomberg, THIS JOURNAL, **45**, 398 (1923).

(14) L. Birckenbach and J. Goubeau, *Ber.*, **65B**, 395 (1932).

## Experimental

Chromatography of the crude secondary or tertiary amines effectively removed tars. The adsorbent was Alcoa F-20 alumina which was washed with water until neutral, and activated at 500°. The solvents were benzene–chloroform mixtures; by controlling chloroform concentration, they could be adjusted to retain tar while passing colorless solutes through the column. In this manner, 50–100 g. of amine could be purified on a single column, but secondary and tertiary amines were not separated from one another.

The copper catalyst used was Venus 44 Natural Copper bronze.

Reagent grade chloroform was purified by the method described by Fieser,[15] and 0.1% absolute alcohol added as an oxidation inhibitor. Mallinckrodt anhydrous reagent grade ether was used directly.

Commercial anhydrous silver perchlorate consists of large crystals which dissolve slowly in ether. When ground in a mortar (this procedure is safe if the salt has not been recrystallized from an organic solvent), the powder rapidly absorbs water. The damp powdered salt was weighed roughly into test-tubes, dried overnight at 130–150°, the dry cake broken up, and the tubes stored over phosphorus pentoxide until used.

To avoid absorption of water from the atmosphere by the cold solutions used in most free radical preparations, all transfers were made by siphoning within closed systems which terminated in calcium chloride drying tubes. The products were filtered on medium fritted filters, and the processes of filtration, washing, and re-solution in chloroform carried out by siphoning the appropriate solutions or solvents through the filter. Careful exclusion of water during the preparations and thorough washing to remove excess oxidant, appeared to improve the stability of the free radicals obtained.

Weitz and Schwechten[2] were unable to get analytical data on their tri-*p*-tolylaminium salts. The analyses of free radicals reported here were obtained after drying in vacuum at room temperature for 24 hours by slowly bringing the samples to combustion temperature over a ten minute period. They were run by the Galbraith Microanalytical Laboratories.

All of the substances described as aminium salts have been shown to be free radicals by observation of the paramagnetic resonance absorption of solid samples. These observations are not affected by diamagnetic impurities, if present. The measurements are described elsewhere.[16]

Melting points were determined on a hot-stage microscope with calibrated thermometers. The aminium salts melt with decomposition; the melting range usually is narrow, but not easily reproducible. The highest values observed are reported.

**Preparation of Aryl Iodides.**—*p*-Iodoanisole,[17] m.p. 51–52°; *p*-iodotoluene,[18] m.p. 36–37°; *p*-iodobiphenyl,[19] m.p. 112–114°; *p*-iodofluorobenzene,[20] b.p. 65–66° on the aspirator; *p*-iodochlorobenzene,[21] m.p. 57°; and methyl *p*-iodobenzoate,[22] m.p. 112–114°; were prepared from the corresponding amines by diazotization in sulfuric acid and addition of potassium iodide. The last compound can be made without hydrolysis of the ester group. Yields ranged from 50 to 80%.

**Tri-*p*-anisylamine.**[3a]—Attempts to prepare this compound directly by method A gave a diamagnetic blue substance which was not investigated further; instead, the tertiary amine was made by method B. Di-*p*-anisylamine, m.p. 102.0–102.5°, was prepared from *p*-iodoanisole and N-acetyl-*p*-anisidine in yields of 6–14%, using Wieland's procedure.[23] The highest yield was obtained when the crude product was purified chromatographically. Wieland and Wecker's procedure[3a] gave crude trianisylamine from the secondary amine and *p*-iodoanisole. It was chromatographed and recrystallized from benzene–hexane in 28% yield, m.p. 94–96°.

**Tri-*p*-anisylaminium Perchlorate.**—To one gram of dry, powdered silver perchlorate dissolved in 250 ml. of anhydrous ether was added a solution of one gram of trianisylamine in 25 ml. of chloroform. The mixture immediately turned blue-black, and was shaken for five minutes. The precipitated silver metal and aminium salt were filtered and washed with ether, and the radical redissolved by washing chloroform through the filter. This solution was added to 250 ml. of ether, and the mixture cooled to Dry Ice temperature. Filtration and washing with ether gave a dark blue powder, yield 85–95%. The product is amorphous, and conditions have not been found which give a crystalline radical. It is also hygroscopic; samples exposed to air absorb enough water to become insoluble in chloroform. For these reasons, melting occurred over the range 108–112°, and analytical data were very poor.

*Anal.* Calcd. for $C_{21}H_{21}NO_7Cl$: C, 57.99; H, 4.84; N, 3.22. Found: C, 54.21; H, 4.74; N, 3.00.

**Tri-*p*-anisylaminium Picrate.**—Silver picrate[24] was dried in vacuum over phosphorus pentoxide. Two-tenths gram of both silver picrate and picric acid were shaken with 50 ml. of 95% ethanol. A solution of 0.2 g. of trianisylamine in 10 ml. of chloroform was added in increments during a shaking period of five minutes. The green solution was evaporated to dryness under vacuum, the residue dissolved in 15 ml. of chloroform, and the filtered chloroform solution added to 250 ml. of ether. Filtration gave a green powder which was very hygroscopic, but stable in the absence of moisture. Again, conditions were not found which would give a crystalline sample.

*Anal.* Calcd. for $C_{27}H_{23}N_4O_{10}$: C, 57.56; H, 4.11; N, 9.94. Found: C, 54.75; H, 4.18; N, 8.91.

**Tri-*p*-tolylamine.**[3b]—This compound was prepared by method A. Ninety grams of *p*-toluidine, 390 g. of *p*-iodotoluene, 140 g. of dry, powdered potassium carbonate, 4.5 g. of copper powder and 150 ml. of nitrobenzene were refluxed together for 22 hours. After nitrobenzene was removed by steam distillation, a black crystalline cake remained in the aqueous residue. This was dissolved in 1 l. of benzene, dried by distillation and saturated with dry hydrogen chloride. A tarry precipitate was discarded. The benzene solution was boiled until free of hydrogen chloride, and chromatographed to remove tars. Concentration of the eluate gave 54 g. of pale yellow crystals which melted 60–115°. Sublimation on the steam-bath in a vacuum desiccator removed about 10% of this solid; the sublimate, m.p. 83–86°, was di-*p*-tolylamine. The residue from the sublimation was recrystallized from acetic acid to give white crystals, m.p. 110–117°; yield 27 g., or 11%.

**Tri-*p*-tolylaminium Perchlorate.**—A solution of 2.9 g. of dry, powdered silver perchlorate and 2.87 g. of tritolylamine in 250 ml. of ether was cooled in Dry Ice in a flask protected with a calcium chloride drying tube. An ether solution of 2.0 g. of iodine was added over a 10-minute interval. The mixture was removed from the cooling bath and stirred with a magnetic stirrer for 45 min. while it warmed to room temperature. During this interval, the color slowly changed from brown to deep blue–green. The mixture of aminium salt and silver iodide was filtered and washed with ether, and the radical redissolved by washing chloroform through the filter. Addition of this blue solution to 250 ml. of ether, followed by cooling, gave 3.5 g. of small red–bronze crystals; yield 90%, m.p. 129–130°.

*Anal.* Calcd. for $C_{21}H_{21}NO_4Cl$: C, 65.20; H, 5.47, N, 3.62. Found: C, 65.02; H, 5.67; N, 3.66.

**Tri-*p*-biphenylylamine.**[25]—This compound was prepared from *p*-aminobiphenyl and *p*-iodobiphenyl by the procedure used for tri-*p*-tolylamine. As in that case, the reaction was incomplete after 24 hours, and fractional sublimation removed both *p*-iodobiphenyl and dibiphenylylamine from the product. The tertiary amine was recovered after recrystallization of the last sublimation fraction from benzene; m.p. 265–266°, yield 7%.

**Tri-*p*-biphenylylaminium Perchlorate.**—One gram of the amine and 1 g. of silver perchlorate in 200 ml. of ether were

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(15) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., Second Edition, 1941, p. 365.

(16) R. I. Walter, R. Codrington, A. F. D'Adamo, Jr., and H. C. Torrey, *J. Chem. Phys.*, to be published.

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(20) O. Wallach and F. Heusler, *ibid.*, **243**, 227 (1888).

(21) M. Gomberg and L. H. Cone, *Ber.*, **39**, 3281 (1906).

(22) H. Schmidt and G. Schultz, *Ann.*, **207**, 333 (1881).

(23) H. Wieland, *Ber.*, **41**, 3493 (1908).

(24) The author is indebted to Mr. Ambrose Hunsberger, Jr., of Wyeth, Inc., for a sample of silver picrate. The crystalline salt was shipped with 10% added water.

(25) W. Bulow, *Ber.*, **57B**, 1434 (1924).

treated at room temperature with 0.4 g. of iodine in ether. The mixture was stirred an hour, filtered and washed with ether. This radical was very slightly soluble in chloroform, but dissolved in 300 ml. of acetone. This solution was evaporated under vacuum to 50 ml., and added to 150 ml. of cold ether. Dark green crystals of the aminium salt were recovered in 75% yield, m.p. 240–242°.

*Anal.* Calcd. for $C_{36}H_{27}NO_4Cl$: C, 75.46; H, 4.75; N, 2.44. Found: C, 75.24; H, 4.57; N, 2.63.

**Bis-(*p*-fluorophenyl)-amine.**[26,27]—This amine was obtained in 62% yield from *p*-fluoroacetanilide[28] and *p*-iodofluorobenzene. The reagents were heated at 200° for 22 hours in the presence of potassium carbonate and copper powder, and the product hydrolyzed by refluxing for four hours with 1:1 hydrochloric acid–alcohol. The amine was recovered by extraction of the hydrolysate with benzene, and purified by chromatography and vacuum distillation; b.p. 163–166° on the aspirator.

**Tris-(*p*-fluorophenyl)-amine.**[26]—Reaction of 0.11 mole of the secondary amine with 0.13 mole of *p*-iodofluorobenzene (without a solvent), extraction with benzene, and evaporation gave 13 g. of crude crystals. These were chromatographed and the product crystallized from 50% benzene–ethanol. The resulting white crystals melted 117–124°, yield 37%. The analytical sample, m.p. 122–124°, was purified by sublimation.

*Anal.* Calcd. for $C_{18}H_{12}NF_3$: C, 72.23; H, 4.04; N, 4.64. Found: C, 72.32; H, 3.89; N, 4.66.

**Tris-(*p*-fluorophenyl)-aminium Perchlorate.**[26]—This radical was prepared in the same manner as the tolyl compound. The solid consisted of red–bronze crystals, m.p. 151–153°, yield 85%. It decomposed appreciably within a few days at room temperature. The analytical sample was shipped in Dry Ice.

*Anal.* Calcd. for $C_{18}H_{18}NF_3ClO_4$: C, 54.21; H, 3.03; N, 3.51. Found: C, 54.01; H, 3.20; N, 3.32.

**Tris-(*p*-chlorophenyl)-amine.**—Reaction of *p*-iodochlorobenzene (2 moles) with *p*-chloroaniline (1 mole) in nitrobenzene solution, followed by steam distillation to remove the solvent, recrystallization from benzene–methanol, and chromatography on alumina, gave a crystalline product, m.p. 140–149°, yield 20%. A sample prepared by reduction of the aminium salt with hydrazine hydrate, followed by sublimation, melted 148–149°.

*Anal.* Calcd. for $C_{18}H_{12}NCl_3$: C, 62.00; H, 3.47; N, 4.02; Cl, 30.51. Found: C, 62.22; H, 3.57; N, 3.96; Cl, 30.27.

**Tris-(*p*-chlorophenyl)-aminium Perchlorate.**—Preparation of this radical was carried out as described for the tolyl compound. Yields ranged from 50 to 87%, m.p. 155–157°.

*Anal.* Calcd. for $C_{18}H_{12}NO_4Cl_4$: C, 48.24; H, 2.70; N, 3.13. Found: C, 48.00; H, 2.94; N, 2.97.

**Bis-(*p*-carbomethoxyphenyl)-amine.**—A mixture of 60 g. of methyl *p*-iodobenzoate, 33 g. of methyl *p*-aminobenzoate, 35 g. of powdered anhydrous potassium carbonate and 3 g. of copper were heated together at 180–200° for 27 hours. (It is important to keep the temperature below 200°; the ester groups are converted to the free acid potassium salt above this temperature.) The crude product was recrystallized from methanol, chromatographed, and recrystallized again to give white needles, m.p. 177–178°, yield 23%.

*Anal.* Calcd. for $C_{16}H_{15}NO_4$: C, 67.36; H, 5.30; N, 4.91; mol. wt., 285. Found: C, 67.33; H, 5.35; N, 4.80; mol. wt., 272.

**Tris-(*p*-carbomethoxyphenyl)-amine.**—Four and eight-tenths grams of the secondary amine, 7.9 g. of methyl *p*-iodobenzoate, 2.8 g. of potassium carbonate and 2.0 g. of copper bronze were heated for 24 hours at 190–200°. The product was recrystallized once from methanol to give 5 g. of very long needles, m.p. 138–140°, yield 70%.

*Anal.* Calcd. for $C_{24}H_{24}NO_6$: C, 68.72; H, 5.05; N, 3.34; mol. wt., 419. Found: C, 68.69; H, 5.02; N, 3.42; mol. wt., 429.

**Tris-(*p*-carbomethoxyphenyl)-aminium Perchlorate.**—A solution of 2.1 g. of tris-(*p*-carbomethoxyphenyl)-amine and 1.5 g. of silver perchlorate in 250 ml. of ether was converted to the free radical using 0.65 g. of iodine in ether, by the procedure given for the tritolyl radical. The blue-green crystalline product appeared homogeneous under the microscope, but much less intensely colored than the other solid radicals. Furthermore, the color intensity of the indigo-blue solutions was roughly one-third that expected (by comparison with the other radicals) for any given concentration. Thus, the product appears to be a solid solution of the deep blue radical in colorless diamagnetic material. It melted at 180–182°.

Analytical results were intermediate between those calculated for the tertiary amine and the free radical.

*Anal.* Calcd. for tertiary amine: see above. Calcd. for aminium salt, $C_{24}H_{24}NO_{10}Cl$: C, 55.55; H, 4.08; N, 2.70. Found: C, 60.03; H, 4.98; N, 2.84.

**Tris-(*p*-nitrophenyl)-amine.**—The preparation of this compound has been described previously.[29] Method A is preferred in this case because the product is insoluble in acetone and can be purified readily by extraction with this solvent. The tertiary amine melts above the reaction temperature, so nitrobenzene must be used to keep the product in suspension during the heating period. None of the methods applied to the other amines gave detectable oxidation of this compound, nor did modifications involving solvents such as nitromethane, in which it is more soluble.

STORRS, CONNECTICUT

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(26) This compound was prepared at the Brookhaven National Laboratory, under contract with the Atomic Energy Commission.

(27) N. J. Leonard and L. E. Sutton, THIS JOURNAL, **70**, 1564 (1948).

(28) A. Sveinbjornsson, *et al.*, *J. Org. Chem.*, **16**, 1451 (1951).

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