ing frequency. Werner and O'Brien and Bell have assigned the boron–oxygen valence vibration to the strong 7.5 μ band.[9,11] The alkyl carbon–oxygen band ranges from 8.64 to 8.92 μ which is well within the generally accepted range of 8.70 to 9.40 for alkyl ethers. The phenyl carbon–oxygen absorption appears at a shorter wave length being reported[12] generally as 7.87 to 8.14 μ and more specifically as 8.22 in phenyl borate.[11] These compare favorably with the strong peak at 7.95 μ in N-trimethyl-B-triphenoxyborazene.

The only major differences between the spectra of the borate esters and the alkoxy- and phenoxyborazenes are the strong peak at 6.91 μ and the very strong peak at 8.46 μ, which are present in the borazenes and absent in the borate esters. These probably correspond to borazene ring vibrations. Borazene itself has a ring vibration at 6.83 μ, while N-trimethylborazene has ring vibrations at 7.02, 7.45 and 7.73.[13]

Acknowledgment.—The support of this work by the Koppers Company through a research contract with the University of Florida is gratefully acknowledged.

[12] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 100.

[13] W. C. Price, R. D. B. Fraser, T. S. Robinson and H. C. Longuet-Higgins, *Disc. Faraday Soc.*, **9**, 131 (1950).

GAINESVILLE, FLORIDA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF SOUTHERN CALIFORNIA]

The Sodium Salts of Tri-α-naphthylboron[1]

BY CARL W. MOELLER[2] AND W. K. WILMARTH

RECEIVED SEPTEMBER 5, 1958

Tri-α-naphthylboron reacts with an equivalent of sodium in tetrahydrofuran to form the paramagnetic tri-α-naphthylboron radical anion. Magnetic susceptibility measurements and molecular weight determinations indicate that the diamagnetic dimer forms in ethyl ether. The solid monosodium salt is also diamagnetic, as is the disodium salt in ether and tetrahydrofuran. The effect of solvent is discussed.

The reactions of the alkali metals with triarylboron compounds were first described by Krause[3] who showed by analyses that the one electron reduction product could be obtained

$$\mathrm{Na} + \mathrm{B(aryl)_3} \rightleftarrows \mathrm{NaB(aryl)_3} \qquad (1)$$

The reversibility of reaction 1 and the conductance of the sodium salts in ether were investigated by Bent and Dorfman.[4] They found that the preparation of the salt of tri-α-naphthylboron, TNB, was complicated by the formation of the disodium salt

$$2\mathrm{Na} + \mathrm{TNB} \rightleftarrows \mathrm{Na_2TNB} \qquad (2)$$

The compounds are colored, and they react rapidly, with loss of color, upon exposure to air.

If the monosodium salts of triarylboron compounds are monomeric or only partially associated, they should be paramagnetic and isoelectronic to the triarylmethyl radicals. The study of the extent of association of some of the triarylboron anions has been reported recently.[5] The results indicate that sodium triphenylboron is completely associated and diamagnetic,[6] while the sodium salts of trimesitylboron and tri-β-methylnaphthylboron are almost completely unassociated in tetrahydrofuran, THF, solutions. The investigation reported here shows that, while sodium tri-α-naphthylboron is dimeric in ethyl ether, it is paramagnetic and unassociated in THF.

Results

In THF solution tri-α-naphthylboron reacts with sodium to form a dark green solution of the monosodium salt and, with excess sodium, a black solution of the disodium salt. In ether solution the monosodium salt is orange and the disodium salt is black. In benzene the disodium salt does not form; the solution remains orange after prolonged shaking with excess sodium. The differences in color exhibited by NaTNB in the two solvents become understandable upon examination of the magnetic data in Table I. In THF solution the green NaTNB is paramagnetic, and a large fraction of the salt must exist as a monomer. By contrast, in the orange ether solution the monosodium salt is diamagnetic, indicating extensive association of the monomeric unit. The black solutions of $\mathrm{Na_2TNB}$ are diamagnetic, as anticipated.

A red solvated form of NaTNB is obtained by recrystallization from ether. Both this and the desolvated orange powder are diamagnetic. Either material forms a green paramagnetic solution in THF and an orange diamagnetic solid upon evaporation of the solvent. These latter results differ markedly from the behavior of sodium trimesitylboron, NaTMB, as reported by Chu and Weismann.[5b] In their studies NaTMB was found to be paramagnetic when prepared directly in THF, but recrystallization and thorough drying of the salt

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[1] Abstracted in part from the dissertation presented by C. W. Moeller to the Graduate School of the University of Southern California in partial fulfillment of the requirements for the Ph.D. degree, 1954. This work was supported in part by the Office of Naval Research.

[2] Department of Chemistry, The University of Connecticut Storrs, Conn.

[3] E. Krause, *Ber.*, **57**, 216 (1924); E. Krause and H. Polack, *ibid.*, **59**, 777 (1926).

[4] H. Bent and M. Dorfman, THIS JOURNAL, **54**, 2133 (1932); **57**, 1259 (1935); **57**, 1924 (1935).

[5] (a) T. L. Chu, *ibid.*, **75**, 1730 (1953); (b) T. L. Chu and T. J. Weismann, *ibid.*, **78**, 23 (1956); (c) **78**, 3610 (1956).

[6] Our results confirm the diamagnetism of sodium triphenylboron and are in agreement with those reported in 5a except that only a single peak was found in the absorption spectrum rather than the two reported to Chu. In ether the peak is at 400 mμ and in tetrahydrofuran it is at 420 mμ. The second peak reported by Chu appears when mercury is in the system.

TABLE I

MAGNETIC SUSCEPTIBILITY DATA

Solvent	Substance	Concn., M	$\chi_g \times 10^6$	$\chi_M \times 10^6$	$A \times 10^6$[a]	$(\chi_M - A) \times 10^6$
Ether	Na_2TNB	0.027	−0.63	−247	−286	39
Ether	$(NaTNB)_2$	.024	− .72	−597	−554	−43
THF	NaTNB	.026	.76	298	−440[b]	738
THF	NaTNB	.072	.73	286	−584[b]	870
THF	NaTNB	.115	1.05	420	−480[b]	900
THF	Na_2TNB	.022	− .57	−230	−286	56
Solid	TNB		− .610	−239	−268	29
Solid	$(NaTNB)_2$		− .660	−547	−554	10

[a] Diamagnetic contribution calculated from Pascal's constants. [b] Excess TNB present in these measurements.

yielded a diamagnetic polymer which remained diamagnetic when redissolved in THF.

The molecular weight data for the various compounds have been summarized in Table II. In these solvents of relatively low dielectric constant the metal salts might be expected to exist as ion pairs, at least in the concentration range under consideration.[7] The results for NaTNB and Na_2TNB serve to confirm this expectation, since the observed molecular weight corresponds to the expected monomeric unit. In ether at the single concentration studied NaTNB proved to be dimeric, presumably because of the formation of a hexaphenylethane type unit.

TABLE II

MOLECULAR WEIGHT OF THE METAL SALTS IN ETHER AND THF

Solute	Solvent	Mole fraction	ΔR, ohms	Mol. wt. Found	Calcd.
$(NaTNB)_2$	Ether	0.0025	60	800 ± 140	830
TNB	Ether	.0017	40	350 ± 90	392
Azobenzene	Ether	.0056	130	180 ± 15	182
Azobenzene	Ether	.0065	150	160 ± 10	182
Benzil[a]	Ether	.0034	70		
Benzil[a]	Ether	.0072	170		
Benzil[a]	Ether	.0114	270		
Benzil[a]	Ether	.0132	310		
NaTNB	THF	.0060	150	460 ± 30	415
Na_2TNB	THF	.0060	150	460 ± 30	438
Benzil[a]	THF	.0033	80		
Benzil[a]	THF	.0072	185		
Benzil[a]	THF	.0127	310		

[a] Standard used in calibration of the apparatus.

The absorption spectra of Na_2TNB in both ether and THF are described in the Experimental section. The rather surprising shift of absorption maxima to longer wave lengths may indicate stronger solvation in the more basic THF. Also in the Experimental section the results for NaTNB in both solvents are compared with the spectra of sodium naphthalenide.[7,8] No similarity was noted for the three absorption curves. Further quantitative studies were carried out with NaTNB in both solvents in the concentration range 10^{-4}–10^{-5} M. No deviation from the Beer–Lambert law was observed in either solvent. At these relatively low concentrations the results indicate that not more than 2% of the dimer is present in THF, whereas approximately 98% of the material is associated in ether.

Discussion

At the higher concentrations employed in the magnetic studies some dimerization of NaTNB may occur in THF since, after correction for the diamagnetic component, the molal susceptibilities fall well below either the theoretical values for one unpaired electron or the experimental values for other monosodium salts. Because of the considerable uncertainty involved in the use of Pascal's constants for solutes of the present sort, no great reliance can be placed upon an equilibrium constant calculated from magnetic data, but a dissociation constant of about 0.5 would be consistent with both the magnetic and spectral data.

Upon comparison of the data now available, it appears that the relative decrease in association of the triarylboron anions is in the order: triphenylboron > tri-α-naphthylboron > tri-β-methylnaphthylboron > trimesitylboron. This order is probably due to the relative steric requirements of the aryl groups. Further, it is clear that quite generally the solvent plays an important role in governing the extent of association, with the monomer being more stable in the more polar solvents.

The present work represents a particularly clean-cut example of the stabilization of the monomer relative to the dimer as the monosodium salt is transferred from ether to THF. From the physical viewpoint it would seem likely that both monomer and dimer should have a greater solvation energy in the more polar and more basic THF; if true, the data require that the increase in solvation energy be relatively greater for the monomer in the transfer process. Although the question of solvation energies in this system is a complicated one, at least one possible explanation for the enhanced relative stability of the monomer is of interest. In THF the monomer stability might be increased considerably if a covalent bond were formed between the boron atom and the oxygen atom of the solvent. Such bonding, presumably not possible in the dimer, would require that the odd electron be in a delocalized molecular orbital of an aryl group as in the naphthalenide ion. Chu and Yu have shown that dimerization does not occur with sodium naphthylenide[8]; thus dimerization may be less favorable in THF than in ether because the electron is forced out of the boron orbital. That the electron is in a delocalized orbital of a naphthyl group could in principle be detected by a comparison of the spectrum of NaTNB and sodium naphthalenide, although in the absence of a quantitative theoretical treatment there is some uncertainty as to the degree of similarity to be expected. The two spectra are not markedly similar.

Experimental

Preparations.—Tri-α-naphthylboron was prepared by the method of Brown and Sujishi.[9] The product from benzene contained one mole of benzene per mole of TNB. The benzene was removed by evacuating at 150°. The melting point of the white crystals was 204–206° (uncor.) in evacuated capillaries.

The sodium salts were prepared and studied in an all-glass vacuum apparatus, the design of which depended somewhat

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[7] The conductivity data of D. E. Paul, D. Lipkin and S. I. Weissman, THIS JOURNAL, **78**, 116 (1956), indicate that sodium naphthalenide is a weak electrolyte in THF solution.

[8] T. L. Chu and S. C. Yu, *ibid.*, **76**, 3367 (1954), have shown that disodium naphthalenide is not formed in THF.

[9] H. C. Brown and S. Sujishi, *ibid.*, **70**, 2800 (1948).

on the experiment under consideration. However, basically it consisted of several interconnected glass bulbs, one of which had a glass inlet tube and is referred to as the reaction chamber. In addition, burets or volumetric flasks, spectrophotometer cells, magnetic susceptibility tubes and break-off seals were sealed on to the apparatus when they were required. At the beginning of an experiment the glass surfaces were degassed by flaming and evacuation, reagents then were added to the reaction chamber through an inlet tube with a slow stream of nitrogen passing through the apparatus, finally the inlet tube was sealed, the apparatus was re-evacuated, and the connection to vacuum sealed off. The reagents usually consisted of solvent, TNB in known amounts contained in sealed glass ampules, sodium and triphenylboron (TPB) which was later converted to NaTPB and used as a wash solution. The sodium was sometimes added directly from a sodium press, with care being taken to minimize surface oxidation; on other occasions it was added in known amounts in sealed, evacuated glass ampules which could be broken either with a magnetic hammer or merely by shaking the entire unit. In general, before breaking the sealed capsule containing the TNB, it was necessary to remove residual water and oxygen from the glass by thoroughly rinsing it with a solution of NaTPB.[10] After use as a rinse the NaTPB solution was poured into one of the storage bulbs. Pure dry solvent, obtained by distillation from the NaTPB solution, was used to rinse the apparatus and then added in the amounts required for the particular experiment. After sealing off the NaTPB storage bulb, a solution of Na_2TNB was prepared by breaking the TNB storage bulb in the reaction chamber containing solvent and excess clean metallic sodium. The Na_2TNB solution sometimes was used in the preparation of NaTNB by allowing it to react with the calculated amount of TNB introduced into the apparatus through a break off seal. The green paramagnetic solutions of NaTNB in THF were made in this way or by dissolving solid NaTNB which had been prepared and recrystallized in ether. The reaction between Na_2TNB and TNB was found to be very rapid.

The THF used in the above measurements was purified in a preliminary way by storage over NaOH and distillation. Then it and the other solvents as well were stored over $LiAlH_4$ and distilled *in vacuo* as needed; only the middle fraction was used.

Analyses.—The triarylboron compounds were checked for purity by boron analyses and melting point determinations. The salts were analyzed for alkali metal and boron. The boron was volatilized as the methyl borate and, after hydrolysis, titrated with standard base. Mannitol was added and the phenolphthalein end-point was used.[11] The residue of the material being analyzed was evaporated to dryness in concentrated H_2SO_4 and weighed as the alkali metal sulfate. Analyses for sodium using the flame photometer attachment on a Beckman model DU spectrophotometer agreed well with those made gravimetrically. In a typical analysis of Na_2TNB 0.442 mmole of TNB reacted with sodium and the analysis showed 0.437 mmole of boron and 0.880 mmole of sodium in the product. Cumulative errors in the last two numbers are about 1%.

Magnetic Susceptibility Measurements.—Magnetic susceptibility measurements using the Gouy method were performed on an apparatus similar to that described by Selwood,[12] with field strengths variable to 15,000 oersted. Apparent changes in sample weight with the field off and on were measured to 0.01 mg. on an Ainsworth balance (Type TCX). The field strengths were calibrated using degassed water in sealed tubes, ferrous ammonium sulfate and pentaaquo cupric sulfate. The diamagnetic corrections to the susceptibility, listed as *A* values in column six of Table I, have been calculated in the usual manner.[12] The molal susceptibility values given in the last column of the table represent experimental values corrected for the diamagnetic component. In calculating the susceptibility of the solutes in the solutions it was assumed that the Wiedemann additivity rule was valid. The solutions were prepared as described above and sealed off in the magnetic sample tube. The solid samples of NaTNB were prepared and packed in the tube inside the vacuum system. After the sample had been prepared and dried by distilling off solvent, the part of the system containing the solid and the magnetic sample tube was sealed from the rest of the vacuum system. A small amount of the solid then was added to the tube by gentle tapping, and this was packed down by tamping with a glass rod which was sealed to a glass-enclosed bar magnet and could be manipulated with a magnet outside of the apparatus. More solid then was added and packed until the sample height was about 10 cm. After the tube was filled to the desired height, it was sealed and removed from the rest of the apparatus. This technique proved to be a more reliable method of packing solid samples of these very sensitive substances than was the use of a vacuum drybox filled with inert gas. When the solid samples were exposed to air they reacted rapidly with great evolution of heat and subsequent charring.

Absorption Spectra.—The samples were sealed in Corex cells and studied with a Beckman model DU spectrophotometer. To avoid the sealing of individual cells in the quantitative measurements a sealed dilution apparatus was used; this was a modification of one previously described.[13] An extra tube between cell and flask was added to facilitate washing of the cell. Using this apparatus made it possible to seal off larger volumes of more concentrated solutions, and less than 10% of the salt was destroyed by the water which escapes from the glass when it is fused. This estimate is based on calculations made using the results of a study of the loss of optical density during the sealing of individual cells containing different concentrations of solution. Dilutions with known solutions, as well as repeated runs with unknowns, showed that the concentrations could be duplicated to ±1% in the dilution apparatus. This illustrates the advantage of the device compared to the sealing-off of a number of cells containing various concentrations of solute, whereby in each sealing a different amount of water might react with the solute. Although one does not know the concentration of the initial solution to better than ±10%, one can still check the adherence of the solution to the Beer–Lambert law upon dilution.

In ether the disodium salt of tri-α-naphthylboron, Na_2-TNB, has absorption peaks at 390 mμ (ϵ 6 $\times$ 10^3), at 555 mμ (ϵ 5 $\times$ 10^3) and a large absorption peak below 350 mμ which was not measured quantitatively; in tetrahydrofuran the absorption peaks were at 435 mμ (ϵ 6 $\times$ 10^3), at 595 mμ (ϵ 3 $\times$ 10^3), and again a large peak below 350 mμ.

The dimer of the monosodium salt, $(NaTNB)_2$, in ether has an absorption maximum at 290 mμ (ϵ 1.4 $\times$ 10^4), a shoulder at 360 mμ (ϵ 5 $\times$ 10^3) and a small peak at 420 mμ. In THF the paramagnetic NaTNB has an absorption maximum at 445 mμ (ϵ 5 $\times$ 10^3), a second maximum at 470 mμ (ϵ 4 $\times$ 10^3), and a third small absorption at 630 mμ (ϵ 7 $\times$ 10^2). Sodium naphthalenide in THF was examined for comparison and the results were similar to those since reported in reference 7. There is a maximum at 365 mμ (ϵ 5 $\times$ 10^3), a shoulder at about 440 mμ (ϵ 3 $\times$ 10^3) and two peaks at 770 mμ and 820 mμ (ϵ 3 $\times$ 10^3).

Due to the difficulties involved in determining the concentration of the absorbing species in these systems, the values listed for the molar extinction coefficients may be in error by as much as 20%.

Molecular Weight Measurements.—Since it was desired to check the monomer–dimer equilibrium at various temperatures in a particular solvent, boiling point elevation studies were not satisfactory and the initial attempts to study the molecular weights were made using isothermal distillation techniques.[14] These proved to be unsatisfactory due to decomposition of the substances in the lengthy time required to reach equilibrium in the systems, particularly with the solvent THF. A thermoelectric molecular weight apparatus incorporating some of the features of those previously described[15] was designed and built. Because of the reactivity of the solutes it was necessary to design a completely sealed apparatus for preparing the solutions and de-

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[10] This precaution was particularly important when handling the dilute solutions employed in absorption spectra measurements. The efficiency of the procedure has been demonstrated by H. E. Bent and G. J. Lesnich, THIS JOURNAL, **57**, 1246 (1935), and H. E. Bent and H. M. Irwin, *ibid.*, **58**, 2072 (1936).

[11] D. Fowler and C. Kraus, *ibid.*, **62**, 1143 (1940).

[12] P. W. Selwood, "Magnetochemistry," Interscience Publishers, New York, N. Y., 1956, chapter I. The routine use of Pascal's constants is outlined in chapter VI, and the special uncertainties involved in free radical studies are emphasized on pages 258–263.

[13] H. E. Bent and A. J. Harrison, THIS JOURNAL, **66**, 969 (1944).

[14] R. Signer, *Ann.*, **478**, 246 (1930).

[15] S. B. Kulkarni, *Nature*, **171**, 219 (1953); and R. H. Muller and H. J. Stolten, *Anal. Chem.*, **25**, 1103 (1953).

termining the molecular weights. Within the apparatus two small cups, one filled with solvent and the other with solution, are exposed to the vapor of the solvent. A steady state temperature difference results since the vapor condenses on the surface of the solution and the temperature of that cup rises. This temperature rise counteracts the lowering of the vapor pressure by the solute, and, therefore, it depends on the colligative properties of the solution. The difference between the temperatures of the cups is measured by two thermistors, which have high negative temperature coefficients of resistance; the thermistors used were Western Electric type 14A. A null method was used in the measurements. The bridge was first balanced with the two thermistors dipping into the solvent, and then with one thermistor still in the solvent the other was placed in the solution. The instrument could be balanced to about ±10 ohms. A detailed description of the design and operation of the apparatus is to be submitted to *Anal. Chem.*

The apparatus was calibrated using benzil as the solute in ether and in tetrahydrofuran. The former has been shown to form ideal solutions.[16] The calibrations were checked with azobenzene. It was found that the results could be expressed as $\Delta R = kN$, where ΔR is the resistance change when one thermistor is in solvent and the other is in solution, N is the mole fraction, and k is a constant which is found experimentally in the calibration and which varies with solvent. For the apparatus used, k is 23,500 for ether and 25,000 for THF. The molecular weight of the solute can be determined by using the value of N determined experimentally and the equation

$$W = w(1 - N)/Nm$$

where W is the gram molecular weight of the solute, w is the weight of the solute used and m is the number of moles of solvent used. At concentrations above $N = 2.5 \times 10^{-2}$ the calibrations were not satisfactory, and no unknown solutions were studied at these relatively high concentrations. The data are in Table II.

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[16] E. Beckmann, *Z. physik. Chem.*, **63**, 197 (1908).

LOS ANGELES, CAL.

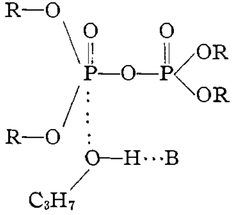
[CONTRIBUTION FROM THE MALLINCKRODT LABORATORIES OF HARVARD UNIVERSITY]

The Solvolysis of Tetrabenzylpyrophosphate

BY GERALD O. DUDEK[1] AND F. H. WESTHEIMER

RECEIVED DECEMBER 12, 1958

Tetrabenzylpyrophosphate reacts with 1-propanol in the presence of certain sterically hindered tertiary amines with carbon–oxygen cleavage, to yield (mostly) benzyl propyl ether and salts of tribenzylpyrophosphate. On the other hand, 2,6-lutidine and *sym*-collidine catalyze the solvolysis of tetrabenzylpyrophosphate with phosphorus–oxygen cleavage to yield dibenzyl propyl phosphate and salts of dibenzyl phosphoric acid. The solvolysis is also catalyzed by various cations, including those of lithium, magnesium and calcium. The catalysis by lutidine and collidine is only about a third as great in C_3H_7OD as it is in C_3H_7OH; presumably therefore the transfer of a hydrogen atom from the alcohol to the nitrogen base is part of the rate controlling step in P–O cleavage. These facts suggest that the activated complex for P–O cleavage is



in which R is $C_6H_5CH_2$ and B is collidine or lutidine.

The solvolysis of tetra-substituted pyrophosphates proceeds readily at moderate temperatures. A study of the reaction therefore can elucidate the mechanism of cleavage of the pyrophosphate bond[2] and supplement the findings concerned with the reactions of other phosphate esters.[3] The present investigation was undertaken with tetrabenzylpyrophosphate, since this compound is easily purified, and (in comparison to the tetraalkyl pyrophosphates of low molecular weight) is of low toxicity. However, the chemistry is complicated by the fact that the benzyl groups are easily removed by C–O cleavage. In the present work, the solvolyses were carried out in 1-propanol as solvent; both reactions 1 and 2 were observed. The experimental results allow reasonable mechanisms to be presented for these processes.

Experimental

Materials. 1-Propanol.—Eastman Kodak White label propanol was dried over sodium hydroxide, distilled, dried with calcium hydride and then fractionated through a 100 cm. column packed with glass helices; it boiled at 97.16–97.20° at 760 mm. A Karl Fischer titration indicated less than 1 part of water in 2000. One batch was dried by azeotropic distillation; no differences in results were noted.

Ethanol.—Commercial Solvents Corporation absolute alcohol was used without purification.

2,6-Lutidine was purified by distillation from the BF_3-etherate.[4] A vapor phase chromatogram showed only a single peak.

2,4,6-Collidine was similarly[4] purified and fractionated through a 24 cm. column packed with glass helices; it boiled at 90° at 57 mm.

Tribenzylamine.—Eastman tribenzylamine, after recrystallization from alcohol, melted at 93.2–94.4°.[5] No NH bond was observed in its infrared spectrum.

2,6,N,N-Tetramethylaniline was prepared by methylating 2,6-dimethylaniline.[6] It was distilled through a 24 cm. column packed with glass helices, and boiled at 90.8° (23 mm.).

Triethylamine was purified by distillation from acetic anhydride and finally from solid potassium hydroxide through a 100 cm. column packed with glass helices. It boiled at 89.8–90.0°.

Cyclohexylamine was purified by distillation from potassium hydroxide through a 100 cm. column packed with glass helices. It boiled at 134.5–135.0°.

Triethanolamine (Eastman) was used without purification. 2,4-Dinitrophenol, 2,4,6-tribromophenol, *p*-nitro-

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[1] Predoctoral Fellow, National Institutes of Health, 1957–1958.

[2] A preliminary report of some of this work was presented by F. H. Westheimer, *Special Publ. Chem. Soc.*, No. 8, 1 (1957).

[3] For a review of phosphate ester chemistry, see *ibid.*, No. 8, 17 ff. (1957).

[4] H. C. Brown, S. Johnson and H. Podall, THIS JOURNAL, **76**, 5556 (1954).

[5] H. Limpricht, *Ann.*, **144**, 305 (1867).

[6] H. C. Brown and M. Grayson, THIS JOURNAL, **75**, 20 (1953).