bromo-cymene with (1) itself, (2) aniline and (3) p-nitro-aniline in two ways.

4. Conversion of the amino-bromo-cymene into a hitherto unknown amino-bromo-toluic acid suggests that the bromine atom occupies Position 3.

5. A new toluic acid, 2-amino-3-bromo-p-toluic acid, was prepared; also its hydrochloride and acetyl derivative.

CHAPEL HILL, NORTH CAROLINA.

SOME COMPOUNDS OF PIPERIDINE WITH HALIDES.

BY CLIFFORD S. LEONARD.

I. Inorganic Halides.[1]

A series of new halide compounds may be prepared from piperidine by reaction with halides of trivalent arsenic, antimony, and phosphorus and of tetravalent silicon, tin, and titanium. The solvent used is normal heptane. The complete miscibility of most of the halides employed and of the piperidine with heptane, together with the inert nature of the latter, favor its use. In each case the reaction takes place with as many piperidine molecules as there are halogen atoms available (with the exception of tin chloride, of which two chlorine atoms are inactive).

The reaction appears to be an addition like the formation of ammonium halides from ammonia and hydrogen halides. In general, if M is the metalloid, n its valence and X the halogen, the reaction may be written

$$n C_5H_{10}NH + MX_n \longrightarrow M(C_5H_{10}NH)_n \ X_n.$$

The behaviors of the complexes formed are like those of ammonium compounds, i. e., they appear to be piperidinium compounds. We may write the equation and the structural formula in the following way, taking $AsCl_3$ as the example:[2]

[1] This work comprises part of a thesis presented in June, 1920, to the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy. See the preliminary note, read by Prof. Edward Kremers before the American Chemical Society, in *Science*, **53**, 145 (1920). The formula given in this note is incorrect; a typographical error adds an extra arsenic atom.

[2] Whether the mechanism is direct addition or a substitution followed by addition of freed HCl does not matter as to resultant product. It has been the habit to beg the question of the nature of organic amino-halides; thus aniline and HCl give aniline "hydrochloride." Since this work was completed, Schmidt at the University of Wisconsin has studied similar products from $AsCl_3$ and aniline. He has named them as substituted aniline hydrochlorides, as is conventional. Obviously their nature must be similar, however, to the compounds here described. (See Schmidt, THIS JOURNAL, **43**, 2449 (1921).)

$$3C_5H_{10}NH + AsCl_3 \longrightarrow C_5H_{10}:N \underset{\underset{C_5H_{10}}{\overset{Cl \quad H\cdot N\cdot Cl \quad Cl}{}}}{\overset{H \quad\quad\quad\quad\quad H}{\diagup\quad\quad As\quad\quad\diagdown}} N:C_5H_{10}.$$
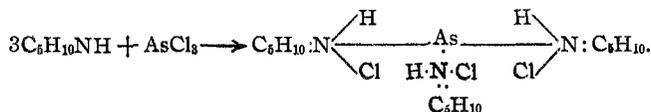
With tetravalent elements such as silicon the fourth halogen carries a fourth imino nitrogen to pentavalence in the same way. These salts may be expected to resemble any known addition products of ammonia itself to the various halides used. Such is borne out by the case of tin tetrachloride. This is described[3] as forming a complex with 2 mols of ammonia instead of 4 as might be expected. The complex with 4 mols is known but is much less stable than the one with 2 mols. So, with piperidine, the complex with tin tetrachloride, which forms even though 4 mols of piperidine are supplied, is the dipiperidyl compound.

If the above is the correct structure, complexes of the following formulas have been studied. (1) $(C_5H_{10}N.HCl)_3As$, which, if named in accordance with the organic "piperidinium" compound described below, is: arsine-tri-1-piperidinium chloride; (2) $(C_5H_{10}N.HCl)_3Sb$, stibine-tri-1-piperidinium chloride; (3) $(C_5H_{10}N.HCl)_4Si$, silicane-tetra-1-piperidinium chloride; (4) $(C_5H_{10}N.HCl)_2SnCl_2$, dichlorostannane-di-1-piperidinium chloride; (5) $(C_5H_{10}N.HCl)_4Ti$, titanane-tetra-1-piperidinium chloride. The phosphorus complex was too unstable for accurate analysis, but qualitative tests show the presence of both phosphorus and chlorine as well as piperidine, and if it is analogous to the arsenic salt it is (6) $(C_5H_{10}N.HCl)_3P$, phosphine-tri-1-piperidinium chloride. It is possible that similar compounds will form with the same readiness from lead tetrachloride, boron trichloride, germanium tetrachloride and vanadium tetrachloride, providing these are soluble in the heptane. These chlorides were not available for the present investigation.

Many halide compounds of piperidine have been prepared but none from these liquid halides of Groups IV and V. The compounds previously made have always been labeled as double salts. The writer believes that those which are made from *piperidine base* and a metallic or non-metallic halide may be likened to ammonium salts and named piperidinium compounds. The simplest would be exact analogs of ammonium chloride; thus, piperidine hydrochloride, $C_5H_{10}NH.HCl$, probably is piperidinium chloride.

Here it may be noted that another type of complex may be formed from these piperidinium salts by further addition, just as double salts may be made from ammonium salts. In the literature this latter type has never been distinguished from the former simpler type. The simpler group will be designated in this paper as Type I, resulting from the combination of piperidine base with metal, metalloid or hydrogen halide. Its prototype

[3] H. Davy, *Schweigger's J. Chem. Physik.*, **10**, 321 (1814).

is ammonium chloride, NH_4Cl (Werner's primary compounds). The other group, Type II, is formed from compounds of Type I by addition of another halide. Its prototype is ammonium zinc chloride, $2NH_4Cl.$-$ZnCl_2$, ammonium halide double salts (Werner's secondary compounds).

For Type I only the ordinary pentavalence of nitrogen need be invoked while Type II requires extra or subsidiary valences of either nitrogen or halogen to explain its structure. The writer does not intend to go into a discussion here of the valence difference between compounds such as represented by the formulas NH_4Cl and $2NH_4Cl.ZnCl_2$. Whatever that is found to be, under Werner's theory or any other theory the same differ-ence will hold between piperidinium salts and piperidinium salt addition compounds.[4]

As an example of Type II may be taken the complex formed from platinous chloride and piperidine hydrochloride and named by Cahours, piperidine chloroplatinate, $C_5H_{10}NH.HCl.PtCl_2$.[5] If he had taken, as did Williams[6] later, piperidine base and platinous chloride he would have obtained the Type I compound, $C_5H_{10}NH.PtCl_2$. For the sake of brevity a list of piperidine halide compounds in which Type I has been separated from Type II is given at the end of this paper.

The new compounds are of surprisingly high stability. All but the antimony and the phosphorus complexes (the latter was unstable and deliquesced in the air) can be recrystallized from alcohol. The arsenic compound can be recrystallized from water and the hot solution even clarified with bone charcoal. It gives a neutral water solution.[7] The tin and silicon compounds can be recrystallized from alcohol but tend to hydrolyze in the presence of water to form the hydroxides. Addition of dilute alkalies precipitates tin and silicon more completely. The antimony complex is hydrolyzed by 99% alcohol, freeing piperidine hydrochloride.

Confirmation of the belief that these complexes are related to ammonium chloride is afforded by the fact that they themselves further add metal salts as does ammonium chloride. Thus this salt yields with the highly colored lead di-iodide a nearly colorless addition compound (Type II). In an analogous manner the piperidine-arsenic compound has been found to give a crystalline addition complex with lead di-iodide. It reacts sim-ilarly with mercuric iodide giving a pale yellow-green compound, which is very different from either yellow or red iodide of mercury. So, too, does arsenious iodide lose its orange color and give a white, crystalline

[4] The newer octet atom-structure theories provide for Type I, *i. e.*, for NH_4Cl. Probably further development of these theories in connection with crystal-structure work will throw light on the Type II structure. See papers by Langmuir and Sir J. J. Thompson.

[5] Cahours, *Ann. chim. phys.*, **38**, [III] 78 (1853).

[6] Williams, *Chem. Gaz.*, **1858**, p. 346; *J. prakt. Chem.*, **76**, 251 (1859).

[7] Conductivity determinations to show the type of ion present would be of interest.

addition product with the piperidine-arsenic compound. The Type I complex adds halides to form products of Type II.

Much difficulty was experienced in the analysis of the new compounds, as might be expected from the presence together of imino nitrogen, chlorine, metalloid, carbon and hydrogen. Arsenic was determined by Ewins' method.[8] Chlorine was determined by the Stephanoff-Bacon[9] method and gave good checked results. Carbon, however, could not be determined by total combustion. Possibly a combustion in the wet way would have succeeded, but a quicker method of analysis was devised as described below.

It was found that the compounds could be hydrolyzed with dilute alkali and the freed piperidine base distilled into standard acid. The acid could be titrated back against standard alkali, and the percentage of piperidine calculated. This method had the further advantage that chlorine could be determined in the distillation residues by simply acidifying with nitric acid and determining by the Volhard method. These latter chlorine determinations checked well with the determinations by the previously cited method. Results checked well in the case of the arsenic compound, so the piperidine and chlorine determinations were considered sufficient to identify the remaining complexes.

The arsenic compound was studied most carefully because of its possible value in medicine. No previously described arsenical compound has been investigated pharmacologically in which the arsenic is bound to the nitrogen of a heterocyclic ring.[10] The findings regarding pharmacological properties of the arsenic compound will be published elsewhere.

Experimental.

The Solvent.—The solvent used in all these experiments was a purified normal heptane obtained from the oil of Jeffery pine. Purification was by the hydrochloric acid method of Sherk;[11] after drying over sodium, the heptane boiled between 97° and 98°. With these very reactive liquid halides the solvent must be dry and free from terpenes or other impurities. Fractions of heptane containing pinene give with arsenic trichloride a brown resin, very slowly precipitated on the walls of the vessel. Even with pure solvent some of the halides react to a slight extent. Clear solutions were obtained with arsenic, silicon, and phosphorus halides. Tin and titanium tetrachlorides gave small amounts of red-brown flocculent pre-

[8] Ewins, *J. Chem. Soc.*, **109**, 1356 (1916).

[9] Stephanoff, *Ber.*, **39**, 4056 (1906). Bacon, THIS JOURNAL, **31**, 49 (1909).

[10] One piperidine complex containing arsenic has recently been made by Jacobs and Heidelberger, (THIS JOURNAL, **41**, 1593 (1919)), N-phenyl-4-arsonic-glycine piperidide, but the piperidine group is not attached to arsenic and the arsenic is in the oxidized form of an arsonic acid.

[11] Sherk, *J. Am. Pharm. Assoc.*, **9**, No. 11, 1 (1921).

cipitate from which the clear solution could be decanted. Antimony trichloride (crystalline) reacts immediately with heptane to form a gummy red-brown resin. This tends to coat the crystals and prevent further solution. The antimony trichloride was shaken with solvent for from 12 to 24 hours; then the resin was allowed to settle and the clear solution decanted off.

General Procedure in the Preparation of the Compounds.—The halide was weighed out and diluted with solvent to a definite volume. Thus each cubic centimeter contained a known weight of halide. The piperidine was similarly prepared. Piperidine solution was then measured into the reaction vessel which was cooled with ice when a large quantity was employed, and the measured volume of halide solution was slowly poured in with stirring. Immediate precipitation occurred. Stirring was continued for some time, then the solution was allowed to stand and was warmed to room temperature. Refluxing at the boiling point of the heptane was not found to change the character of the material. As the precipitates were very voluminous and held much heptane either by capillarity or by adsorption, the reaction mass was usually a light yellow or white mud. The material was filtered and pressed. The precipitates were found to dry thoroughly with little decomposition on standing in the air. Final drying before analysis was in a desiccator over calcium chloride. No hydrochloric acid is given off at any stage of the preparation, which is evidence in itself that the reaction is an addition. The piperidine was commercial material. The halides were the purest obtainable reagents.

Arsenic Compound, $(C_5H_{10}N.HCl)_3As$.—By the above method arsenic trichloride was combined with piperidine. Preliminary experiments showed that the same white compound formed whether 1, 2 or 3 mols of piperidine were present, only in different amount. In the single case of this arsenic complex the heptane holds about $1/3$ of the material in solution. This could be precipitated by adding an equal volume of ether. The total yield then approximated that calculated. The arsenic compound could be recrystallized from alcohol in long needles, nearly pure white in color, melting at 238°.

The compound was very soluble in water (about 1:1). On evaporating a water solution to dryness, no change of weight of arsenic compound was found to have occurred. Consequently the material was crystallized from water thereafter. Long heating in water caused the solution to darken in color. Such solutions could be boiled with bone charcoal, then filtered and would come through light yellow in color. In this way excellent crops were obtained, melting at 240'   Whether recrystallization was from alcohol or water, on redissolving the substance ° ·   air drying, small amounts of white, insoluble material were always present. Possibly, therefore, there is a slight hydrolysis or oxidation of the complex in the air.

The arsenic compound was soluble in chloroform, pyridine and carbon disulfide; somewhat soluble in heptane, insoluble in ether, petroleum ether, acetone and carbon tetrachloride.

Piperidine was determined by the distillation method described above. A Volhard chlorine determination was run on the distillation residue. Ewins' iodometric method was used for arsenic.

Analyses. Calc. for $(C_5H_{10}N.HCl)_3As$: piperidine, 58.4; Cl, 24.35; As, 17.20. Found: piperidine, 62.1; Cl, 24.78; As, 13.09; total, 99.97.

This was further checked by Dumas nitrogen determinations and by chlorine determinations by the Stephanoff-Bacon method. Although total combustions were not successful in determination of carbon, the water, and consequently the hydrogen from these checked well, and averaged very close to the calculated results. When carbon is calculated from the piperidine figure above and the other percentages are all taken from direct determinations, the following are the results.

Analyses. Calc.: C, 41.16; H, 7.67; N, 9.62; Cl, 24.35; As, 17.20. Found: C (from piperidine), 43.8; H (comb.), 7.92; N (Dumas), 11.17; Cl (Bacon), 24.78; As (Ewins), 13.09; total, 100.76.

Piperidine results are a little higher than the calculated and arsenic low by about the same amount.[12]

Addition reactions of the arsenic compound. Just as ammonium chloride and lead di-iodide give a white, crystalline addition product,[13] so the arsenic compound and colored halides react. *With lead iodide.* One g. of orange-yellow lead di-iodide was triturated with 2 g. of the arsenic compound and with 1 cc. of water. The react on did not go to completion until the mixture was heated to boiling, but then the solution had a faint yellow color, and pale yellow needle crystals of a complex formed on cooling. The solution could be diluted to 15 cc. without decomposition and with the same crystals re-appearing after each heating and cooling. *With mercuric iodide.* One g. of red mercuric iodide was similarly triturated with the arsenic compound and on boiling gave a green solution. When cooled, pale yellow-green needle crystals formed of different color from crystals of yellow mercuric iodide. The solution could be diluted to about 5 cc. without change, but beyond this dilution red mercuric iodide precipitated and on heating, collected as yellow liquid on the bottom, solidifying as yellow mercuric iodide on cooling, and gradually changing to the red form. *With arsenic iodide.* One g. of arsenic tri-iodide was similarly triturated with the arsenic compound and while a clear solution was not obtained as in the previous cases, on heating to boiling, then cooling, rose colored to white crystals formed above the permanent precipitate (the latter probably from impurities in the tri-iodide used). On dilution to 5 cc. this white complex continued to come out on cooling after short boiling. With great dilution it did not appear, but the deep orange color of arsenic tri-iodide did not reappear.

The arsine-tri-1-piperidinium chloride does not give a precipitate with the general alkaloidal reagents except with phosphomolybdic acid, when the precipitate is of light yellow color.

Antimony Compound, $(C_5H_{10}N.HCl)_3Sb$. — Antimony trichloride dissolved in heptane (see difficulty under "solvent") was added to piperidine solution in the ratio of one mol to three. The white solid which precipitated had a melting point of 235° after air-drying. The white precipitate was recrystallized from 99% alcohol. The recrystallized product, however, analyzed not as the antimony complex expected but as piperidine hydrochloride with just enough antimony to give a qualitative test.

Analyses. (Recrystallized material). Calc. for $(C_5H_{10}N.HCl)_3Sb$: piperidine, 52.99; Cl, 22.07. Calc. for $C_5H_{10}N.HCl_3$: piperidine, 70.06; Cl, 29.1. Found: piperidine, 68.14; Cl, 29.47.

On analysis, the unrecrystallized material was found to approach the formula which had been expected.

[12] Schmidt (Ref. 2) discards Ewins' method for arsenic, as giving low results for the aniline-arsenic-chloride compound.

[13] "U. S. Pharmacopeia," **VIII,** p. 309 (1890).

Calc. for $(C_5H_{10}N.HCl)_3Sb$: piperidine, 52.99; Cl, 22.07. Found: piperidine, 49.81; Cl, 21.85.

Silicon compound, $(C_5H_{10}N.HCl)_4Si$.—This was prepared in the same manner as the arsenic compound but using 4 mols of piperidine to each mol of silicon tetrachloride. The melting point of the product recrystallized from 99% alcohol was 238°. The substance was also soluble in chloroform. A small amount of flocculent precipitate filtered from the alcohol solution, was dried and found to be wholly inorganic. Probably the percentage of water in the alcohol hydrolyzed a little of the compound to s licic acid. Possibly it may have come from oxychloride in the reagent, however.

Analyses. Calc. for $(C_5H_{10}N.HCl)_4Si$: piperidine, 66.66; Cl, 27.78. Found: piperidine, 65.97; Cl, 28.18.

Tin Compound, $(C_5H_{10}N.HCl)_2SnCl_2$.—Prepared by the general method from 4 mols of piperidine and 1 mol of tin tetrachloride. The white precipitate was recrystallized from alcohol, and melted at 201°. (On adding more stannic chloride to the heptane mother liquor a further precipitate of the material was obtained, indicating the presence of excess of piperidine). The tin compound did not analyze for $(C_5H_{10}N.HCl)_4Sn$ as had been expected in analogy with the arsenic and silicon compounds. It was found to approximate to $(C_5H_{10}N.HCl)_2SnCl_2$.

Analyses. Calc. for $(C_5H_{10}N.HCl)_4Sn$: piperidine, 56.64; Cl, 23.6. Calc. for $(C_5H_{10}N.HCl)_2SnCl_2$: piperidine, 39.54; Cl, 32.91. Found: piperidine, 36.51; Cl, 36.17.

Chlorine is thus present in greater amount, and piperidine in less amount, than calculated for the di-piperidyl compound.

Titanium compound, $(C_5H_{10}N.HCl)_4$ Ti (?).—Only a small amount of titanium tetrachloride was available for this work. On mixing 1 mol with 4 mols of piperidine in heptane a leaf-green precipitate formed. This was filtered on a Büchner funnel but began to lose color as it dried. Within a few minutes it had become white. The melting point was 238–240°. On analysis of the unrecrystallized product, the result for piperidine was found to be quite low for the formula $(C_5H_{10}N.HCl)_4Ti$, and nearer in fact to that for $(C_5H_{10}N.HCl)_2TiCl_2$. However, the chlorine result was nearer that calculated for the first formula and much lower than for either dipiperidyl or tripiperidyl complexes.

Analyses. Calc. for $(C_5H_{10}N.HCl)_4Ti$: piperidine, 64.21; Cl, 26.73. Calc. for $(C_5H_{10}N.HCl)_2TiCl_2$: piperidine, 47.38; Cl, 39.37. Found: piperidine, 51.68; Cl, 24.83.

Probably the unrecrystallized material as analyzed was more or less a mixture, but more titanium tetrachloride was not available, so that this could not be determined.

Phosphorus compound, $(C_5H_{10}N.HCl)_3P$ (?).—Phosphorus trichloride was found to give a white precipitate with 3 mols of piperidine. No hydrogen chloride came off in this reaction. The precipitate on filtering was found to be very susceptible to the moisture of the air, turning yellow and gummy. It was dried in a vacuum desiccator but had then deteriorated too much for analysis. Qualitative tests showed the presence of both phosphorus and chlorine. If the analogy with the other compounds holds the formula should be $(C_5H_{10}N.HCl)_3P$. Michaelis and Luxembourg[14] prepared in ether solution a substance of the formula $(C_5H_{10}N)_3P$, but this was by precipitating in the presence of a large excess of piperidine. Probably the addition of 3 mols' excess of piperidine would convert the hydrochloride into the free phosphine by virtue of the stronger basicity of piperidine. The phosphorus compound may be worthy of further investigation.

14 Michaelis and Luxembourg, *Ber.,* **28,** 2207 (1895).

II. 1-(α-methylamyl)piperidinium-iodide.

It was thought that piperidine should give addition compounds similar to those with inorganic halides described above, by reaction with organic halides of longer chain than the simpler carbon halides, carbon tetrabromide, and acetylene iodide, etc., which Dehn[15] had investigated. α-Methylamyl-iodide, being at hand, was tried.

The halide freshly distilled was mixed with a heptane solution containing one mol of piperidine. The mixture was refluxed for one hour. White crystals began to appear at the edge of the liquid and later a red oil was seen on the bottom. On cooling the mixture and shaking, the red oil crystallized to yellow needles. These were filtered out and dried. The yield was about $1/3$ that calculated for the monopiperidyl complex. The mother liquor was distilled and could be separated into a fraction containing heptane and piperidine, and a fraction containing α-methylamyl iodide. On remixing these and after standing, more of the yellow crystals appeared. Possibly, therefore, longer refluxing would have increased the original yield. The α-methylamyl iodide compound was very soluble in alcohol and in water. The melting point was unchanged after recrystallization with alcohol, 133°. The substance was also soluble in chloroform and slightly soluble in ether, insoluble in heptane, carbon tetrachloride or carbon disulfide.

Analysis by the piperidine distillation method described in the previous paper showed it to be a substance of the formula $(C_5H_{10}N.HI)C_6H_{13}$.

Analyses. Calc.: piperidine. 28.18; I, 42.71. Found: piperidine, 29.01; I, 43.15.

If the structure of this compound is to be explained on the same basis as that of the metalloid compounds, it is a *sec.*-hexyl-piperidonium iodide $(C_5H_{10}N(HI)$—$CH(CH_3).CH_2CH_2CH_2CH_3$. This reaction opens up possibilities in the coupling of organic halides and organic bases in heptane solution. If other aliphatic monohalides give similar addition products with piperidine, and these have sharply defined melting points, these may be useful in identification of the different aliphatic halides. There are further possibilities of preparation of various organic compounds from these piperidinium halides, for instance, by replacement of the halogen. The results of Grignard reactions might be interesting if this treatment were found not to decompose the original complex.

Summary.

A series of new edition compounds of piperidine with halides of elements of the fourth and fifth group of the periodic system have been prepared. They comprise substances of the following formulas: $(C_5H_{10}N.HCl)_3As$, $(C_5H_{10}N.HCl)_3Sb$, $(C_5H_{10}N.HCL)_4Si$, $(C_5H_{10}N.HCl)_2SnCl_2$, and titanium and phosphorus compounds which are probably of similar structure.

Reasons are advanced for assigning to these the structure of piperidinium chlorides, and known piperidine addition compounds are assigned to two groups, according to whether they are (Type I) compounds of piperidine free base and a halide or acid or salt, or (Type II) compounds of piperidine hydrohalides with halides.[16]

[15] Dehn, THIS JOURNAL, **34**, 286 (1913); **33**, 1588 (1912).

[16] Piperidine addition compounds. Type I, with AgBr, AgI, AgCl,, HgCl₂ HgBr₂, HgI₂, ZnCl₂, CdCl₂, CdBr₂, CdI₂, CBr₄, CI₃H, C₂I₄, PtCl₂, PdCl₂, AgCN, CuSO₄, HgSO₄, Hg(CN)₂, H₄FeCN₆, H₃FeCN₆, H₃CoCN₆. See Beilstein, "Handbuch der Organischen Chenie," Voss, etc.

Type II, the proper hydrohalide of piperidine with AuCl₃, AuBr₃, AgBr, AgCl, AgI, HgBr₂, TlCl₃, BiI₃, SeBr₄, PtCl₂.

α-Methylamyliodide with piperidine in heptane forms a crystalline α-methylamyl-piperidinium-iodide. This is considered to be analogous in structure to the piperidine-metalloid compounds described above.

Thanks are due to Professor Edward Kremers for guidance in this investigation.

MADISON, WISCONSIN.

TETRAPROPYL-ETHANE.

BY JEAN PICCARD AND RAY Q. BREWSTER.[1]

The number of heavier hydrocarbons with side-chained structures described in the literature is very small. Yet these hydrocarbons are of interest not only to the physical chemist in view of their surface tension and other constants, but also to the organic chemist for the identification of the carbon skeleton of unknown compounds. While in recent years many new methods have been found for the determination of characteristic groups in organic molecules, practically no progress has been made toward the determination of the carbon skeleton since Baeyer's distillation with zinc dust and its famous application to the identification of alizarin. So many good reducing agents have been found in the last few years, however, that it should be possible in most cases to reduce, in well defined successive steps, any organic compound to the corresponding saturated hydrocarbon.

Several years ago Baeyer and Piccard,[2] while working on dimethyl-pyrone, discovered an interesting violet dye of unknown constitution. The identification of its carbon skeleton was attempted by the oxidation methods in general use. A considerable number of new derivatives were thereby obtained without any progress toward the solution of the problem, since all the oxidation products obtained were unknown.

The problem was later attacked by Piccard and Edmond Wallach and still later by Piccard and McLauren, who applied successively different reduction methods with the purpose of obtaining a saturated hydrocarbon. Unfortunately this work was twice interrupted by the military obligations of the collaborators. Since there are reasons for believing that the hydrocarbon which would result from complete reduction of the violet dye would be symmetrical tetrapropyl-ethane, and since this hydrocarbon is not yet described in the chemical literature, the present work was begun parallel to the work of our collaborators Wallach and McLauren, with the

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[1] The material presented here is used by Ray Q. Brewster in his dissertation presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Chicago.

[2] Baeyer and Piccards, *Ann.*, **384**, 208 (1911); **408**, 332 (1915).