NOTES

A Criterion for the Mechanism of the Reactions of Alkyl Halides with Hydroxylic Solvents. Reactions of Benzhydryl Chloride

By Leslie C. Bateman, Edward D. Hughes and Christopher K. Ingold

The two types of mechanism which we have postulated[1] for aliphatic substitutions, one involving bimolecular replacement in a single stage and the other preliminary ionic fission, have been discussed recently.[2] The point of interest is the ionization mechanism, which we term unimolecular and Hammett polymolecular; and although in the sequel we use our own label, we strongly agree with the purpose of Hammett's, which is to emphasize the role of the solvent. We ourselves have done this in discussions,[1c,3] pointing out, for instance, that only through solvation is the activation energy of an ionic fission reduced to accessible values.

In a number of well-established unimolecular substitutions the entrant group comes, not from the solvent, but from a reagent present in small and controllable concentration.[4] For these the observed reaction order determines the mechanism. In other substitutions, for instance, the hydrolysis and alcoholysis of alkyl halides in hydroxylic solvents, the reaction order is no longer diagnostic, and other, less direct, methods must be employed. Several have been suggested,[4] but we need here to refer only to one particular method.

This has been illustrated with respect to the simultaneous hydrolysis and alcoholysis of *t*-butyl chloride in aqueous alcohol. The total first order reaction was first investigated by Hughes,[5] who found that the rate was unaffected by hydroxonium and hydroxide ions, but was much increased with increasing water content of the solvent. He concluded that the reaction was unimolecular. Olson and Halford[2b] examined the applicability of an equation, in constructing which they assumed the reaction to be bimolecular. The formula is

$$\text{Rate} = (k_a p_a + k_w p_w) p_{\text{RCl}}$$

where the k's are rate constants, the p's partial vapor pressures, and the subscripts refer to alcohol, water and *t*-butyl chloride; and it may be used either to calculate the total rate, or, from the partial rates $k_a p_a p_{\text{RCl}}$ and $k_w p_w p_{\text{RCl}}$, to deduce the composition of the product (ROEt + ROH). Having computed k_a and k_w from observed total rates, the authors showed that their formula gave an accurate description of the variation of total rate with solvent composition, and concluded on this account that the reaction was indeed bimolecular. Then we pointed out[3] that the success with which the formula represents the total rate owes nothing to the assumed mechanism, the essential postulate, the participation of solvent in the transition state, being true for all reactions in solution, including the unimolecular process. We also noted, however, that the product compositions should be calculable with a corresponding success only if the reaction is bimolecular, for in that case the product is formed in the rate-measured reaction, so that its composition is fixed by measured rate constants, whereas in unimolecular substitution the product arises subsequently to the rate-measured stage, so that its composition cannot in principle be deduced from measured constants. An application of this criterion to the reactions of *t*-butyl chloride showed that they were not bimolecular as had been claimed, and we concluded that they were unimolecular in agreement with Hughes.

The main object of this note is to point to the analogy of a second reaction of an alkyl halide with a solvent, in which a similar criterion has been applied, with results pointing again to the unimolecular interpretation. This is the reaction of benzhydryl chloride with aqueous ethanol. Like the reaction of *t*-butyl chloride, its first order rate is unaffected by hydroxonium and hydroxide ions, but is much increased with increasing water content of the solvent. Total rates have been measured by Ward, by Norris and Morton, by Kny-Jones and Ward,[6] and by Farinacci and

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[1] (a) Hughes, Ingold and Patel, *J. Chem. Soc.*, 526 (1933); (b) Gleave, Hughes and Ingold, *ibid.*, 236 (1935); (c) Hughes and Ingold, *ibid.*, 244 (1935); (d) Hughes, Ingold and Shapiro, *ibid.*, 225 (1936).

[2] (a) Farinacci and Hammett, This Journal, **59**, 2544 (1937); (b) Olson and Halford, *ibid.*, **59**, 2644 (1937).

[3] Bateman, Hughes and Ingold, *J. Chem. Soc.*, 881 (1938).

[4] References are given in paper (3).

[5] Hughes, *J. Chem. Soc.*, 255 (1935).

[6] (a) Ward, *ibid.*, 2285 (1927); (b) Norris and Morton, This Journal, **50**, 1795 (1928); (c) Kny-Jones and Ward, *ibid.*, **57**, 2394 (1935).

Hammett,[2a] and product compositions by the last-named authors. This was before Olson and Halford's vapor pressure theory had become available, but Farinacci and Hammett noted that a bimolecular mechanism, interpreted with the aid of a concentration mass law, could not bring rates and product compositions into harmony, for when added water increased the reaction rate it did so chiefly, not by diverting the formation of benzhydryl ethyl ether into that of benzhydrol, but by accelerating the production of benzhydryl ethyl ether. Such a "catalytic" effect is, however, expected on the basis of the unimolecular mechanism.

Olson and Halford show, with respect to the example studied by them, that, whereas the vapor pressure formula exactly accounts for the variation of rate with solvent composition, a corresponding concentration formula fails completely. We have therefore considered the question of whether Farinacci and Hammett's inference is likely to be changed if this calculation is carried from the concentration basis of the assumed equation

$$\text{Rate} = (k'_{a}c_{a} + k'_{w}c_{w})c_{\text{RCl}}$$

to the vapor pressure basis of Olson and Halford's theory. We conclude that it could not be changed. The transformation cannot, as a matter of fact, be effected completely, because the partial vapor pressures of benzhydryl chloride are unknown and would be difficult to determine accurately. We can, however, convert to the new basis the treatment of the solvent components, and, assuming an approximate invariance in the Henry's law constants of benzhydryl chloride over the relevant range of solvent compositions, test for the effect of the incompleteness of our procedure by reference to the observed total rates. For this range, the representation of the total rates is in fact so good that we have the same empirical justification as Olson and Halford for proceeding to predict the separate parts of the total rate, or, what is equivalent, the product compositions; and this is the prediction that really distinguishes the bimolecular and unimolecular mechanisms. In view of the relatively low water concentrations used, we are not surprised to find that the predicted values differ relatively little from Farinacci and Hammett's, and that therefore, as the table indicates, they show correspondingly pronounced divergences from the experimental values. Bearing in mind also the more completely investigated case of *t*-butyl chloride, it cannot be doubted that Farinacci and Hammett's conclusions stand, *i. e.*, that the vapor pressure theory could not bring the hydrolysis and alcoholysis of benzhydryl chloride into harmony with the bimolecular mechanism.

REACTION OF BENZHYDRYL CHLORIDE WITH AQUEOUS ETHANOL AT 25°

	k(10^{-5} min.$^{-1}$)		Moles % ROH		
H_2O Moles/l.	Found	Calcd.	Found (F. and H.)	Calcd.	Calcd. (F. and H.)
0.000	343	..	..	0.0	0.0
.600	474	482	1.8	31.5	27.7
1.320	634	652	11.8	51.5	46.0
1.579	691	..	..	55.1	..

We take the opportunity to refer to four points raised by Hammett[2a,7] with reference to the detailed interpretation of the unimolecular mechanism, as the relevant experimental material is, and will be, considerably scattered. The first, relating to the incompleteness of racemization, is dealt with in papers[8] which were unavailable when he wrote. The second was that dissolved negative ions had not been found to participate in homogeneous solvolytic reactions. But they do participate if their concentration is adequate in relation to that of the reactive constituent of the solvent; thus chloroacetate ions form *t*-butyl chloroacetate without increasing the reaction rate in the hydrolysis of *t*-butyl chloride in moist formic acid, and chloride ions retard the hydrolysis of benzhydryl chlorides in moist acetone. The third point was that solvolytic reactions apparently require high concentrations of hydroxylic solvents, water having failed to react with α-phenylethyl chloride in moist acetone though it accelerated the total reaction in moist acetic acid. However, we regard the difference as one of degree, depending on the ionizing properties of the solvent as a whole, and can show that hydrolyses which are slow in moist acetone are rapid in equally moist sulfur dioxide, though sulfur dioxide, like acetone, is non-hydroxylic. Fourthly, the example of sulfur dioxide illustrates how poor an index to ionizing power is the dielectric constant, doubtless because of its very indirect connection with the short-range forces determining solvation. These, however, are points of detail: as to essentials we endorse Hammett's statement[7] that his views and ours are in harmony.

Summary.—Of the bimolecular and unimolecular mechanisms of aliphatic substitution,

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[7] Steigman and Hammett, *ibid.*, **59**, 2536 (1937).

[8] Hughes, Ingold and others, *J. Chem. Soc.*, 1196 *et seq.* (1937).

the former alone yields the product in a reaction stage whose rate can be measured; and therefore a comparison of rates and product compositions in competing reactions, such as those of an alkyl halide in aqueous alcohol, affords a criterion of mechanism. Such a criterion was applied by Farinacci and Hammett to the reactions of benzhydryl chloride but Olson and Halford have made proposals to change the quantitative basis of such comparisons. We consider whether Farinacci and Hammett's rejection of the bimolecular mechanism stands in the light of this work, which we have more fully examined with respect to the reactions of *t*-butyl chloride; and we conclude that it does stand. Thus the hydrolyses of *t*-butyl chloride and benzhydryl chloride are mutually confirmatory examples in which the application of the criterion mentioned favors the unimolecular mechanism, some details concerning which are discussed.

SIR WILLIAM RAMSAY AND
RALPH FORSTER LABORATORIES OF CHEMISTRY
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LONDON, ENGLAND
RECEIVED MAY 17, 1938

A New Method for the Preparation of 3,5-Cholestadiene

BY KENZO HATTORI

The various methods for the preparation of the so-called cholesterilene have been discussed recently by H. E. Stavely and W. Bergmann.[1] These authors also prepared 3,5-cholestadiene (I) by the Wolf–Kishner reduction of the semicarbazone of the 7-ketocholesterilene (II). Since this procedure involves prolonged heating at 180–200°, the possibility of a rearrangement of the double bonds is not excluded. In order to eliminate such possibility, 3,5-cholestadiene was prepared by the treatment of pseudocholestene dibromide (III) with silver nitrate in pyridine solution at room temperature.[2] The diene obtained by this reaction seems to be identical with the 3,5-cholestadiene described by Stavely and Bergmann.

Nine-tenths of a gram of pseudocholestene dibromide was dissolved in 20 cc. of pyridine containing 18% of silver nitrate. The reaction mixture was kept in the dark at room temperature for one month. The solution was then diluted with water, acidified with sulfuric acid and extracted with ether. The residue obtained on evaporation of the ether extract was recrystallized from a mixture of alcohol and ether. The diene crystallizes in needles, m. p. 79–80°, $[\alpha]^{15}\mathrm{D}$ −68.7°.

Anal. Calcd. for $C_{27}H_{44}$: C, 87.96; H, 12.04%. Found: C, 88.3; H, 11.7%.

The diene gave a positive reaction with Rosenheim's reagent and with antimony trichloride. Mixed with a sample of cholesterilene, prepared from cholesterol,[3] m. p. 79°, $[\alpha]^{15}\mathrm{D}$ −76.0°, it gave no depression of the melting point.

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(1) W. Bergmann, *J. Org. Chem.*, **1**, 567 (1937).

(2) E. Dane, *Z. physiol. Chem.*, **245**, 80 (1937); **248**, 1 (1937).

(3) Mauthner, *Monatsh.*, **17**, 34 (1896).

THE PHARMACEUTICAL INSTITUTE
IMPERIAL UNIVERSITY
TOKYO, JAPAN
RECEIVED AUGUST 6, 1938

Identification of Methylisopropylcarbinol in Sharples Diethylcarbinol

BY FRANK A. KARNATZ AND FRANK C. WHITMORE

In connection with another research,[1] an attempt was made to obtain pure 3-pentanol by a series of careful fractional distillations of a sample of commercial diethylcarbinol supplied by the Sharples Solvents Corporation. It was noted that even after many fractionations the material of almost constant refractive index boiled over a range of 4°. Since the refractive index of methylisopropylcarbinol is very near that of 3-pentanol ($n^{20}\mathrm{D}$ 1.4095 and 1.4100, respectively), the lower boiling portion of the sample was carefully refractionated by parts in an efficient column. In this way a fraction was obtained, b. p. 111.5° (732 mm.), $n^{20}\mathrm{D}$ 1.4096, which gave the α-naphthylurethan of methylisopropylcarbinol,[2] m. p. and mixed m. p. 108–110°.

The identification of this alcohol, which had not been found in the hydrolysis products of the chloropentanes by previous investigators,[3] is of considerable theoretical interest. It demonstrates that the hydrolysis of 3-chloro-2-methylbutane to the alcohol does not involve complete rearrangement. The conversion of the alcohol to the chloride even under the mildest conditions gives the rearranged product, 2-chloro-2-methylbutane.[4] Both these conversions are being studied further to determine the relative amounts of rearranged and non-rearranged products from each.

STATE COLLEGE, PENNA.
RECEIVED SEPTEMBER 28, 1938

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(1) Whitmore and Karnatz, THIS JOURNAL, **60**, 2536 (1938).

(2) Whitmore and Johnston, *ibid.*, **55**, 5022 (1933).

(3) Ayres, *Ind. Eng. Chem.*, **21**, 899 (1929); Clark, *ibid.*, **22**, 439 (1930).

(4) Whitmore and Johnston, THIS JOURNAL, **60**, 2265 (1938).

The Stability of Dry Potassium Ferrocyanide

By Robert B. Loftfield[1] and Elijah Swift, Jr.

In the course of a previous investigation,[2] it was noticed that sometimes dry potassium ferrocyanide undergoes a slight decomposition. Since this salt is one of the few quadrivalent salts that is sufficiently stable to be useful in precise electrochemical investigations[3] where the effect of ionic charge on the properties of solutions is being studied, it seemed of some importance to determine the conditions under which decomposition takes place.

Mallinckrodt reagent grade potassium ferrocyanide was precipitated from saturated solution at 0° by adding an equal volume of cold 95% alcohol. The crystals were allowed to grow for several hours and then were centrifuged and washed with cold 95% alcohol. This process was repeated and the salt was dried by sucking off the excess alcohol with a water pump. After standing in a clear glass bottle exposed to the ordinary laboratory light for over a year, no change in color could be observed by comparison with freshly prepared salt, and no odor of hydrogen cyanide was perceptible in the bottle.

The salt was dehydrated as in previous investigations[3] in order to get a sample whose exact composition would be known. About 0.5 g. of the salt was placed in a platinum boat in a Richards bottling apparatus and a slow stream of nitrogen was allowed to flow over the sample while heating to 90°. The nitrogen was removed with a water pump and the tube flushed out several times with nitrogen and finally left evacuated for one to two hours while the temperature was maintained at 90–100°. The tube was then filled with nitrogen and the salt cooled in a slow stream of the gas. This method of preparing the salt was found by Jones and Jelen[3a] to give material of constant weight.

Fabris[4] has stated that there is a considerable loss of cyanide[5] when this salt is heated above 50° in air. To check this statement, samples of salt were heated to 100° for three hours in a slow stream of air, the effluent gas being passed through a solution of sodium hydroxide. The Prussian blue test applied to this solution was negative, showing that less than 0.01% of the salt was lost as cyanide in this process. Negative tests for cyanide were also obtained when samples of salt were heated in a slow current of nitrogen, using the Prussian blue test and the specific ferric thiocyanate test.[6] It seems evident that this salt may be dehydrated safely at 100°, although decomposition will take place at higher temperatures.[7]

After the dehydrated salt had come to room temperature, half of the boat was covered with platinum foil and the salts exposed to illumination. After two hours of illumination with a "Pointalite" bulb and forty hours' illumination with a 200-watt tungsten bulb 15–20 cm. above the surface, no change in the color of the salt was observed. The tube was then flushed out several times with dry oxygen and the process repeated. After about forty hours of exposure a slight change in the color of the salt was observed, and after seventy-two hours there was a decided greenish-blue color on the surface of the salt. This color was much less pronounced underneath the foil where the light could reach the salt only indirectly; while another sample kept in dry oxygen in the dark for seventy-two hours failed to show any color change whatever. Presumably the reaction involves the formation of Prussian blue, but the amount of material formed was too minute to be analyzed readily, and it was not thought worth while to investigate this reaction further. The test was repeated by placing a fresh sample in dry oxygen in direct sunlight, and the same result was observed after one or two hours' exposure. A control sample of the hydrated salt showed no reaction whatsoever under any of the above conditions.

Another sample of the anhydrous salt was placed in an atmosphere of moist oxygen and exposed to illumination. No reaction was observed, probably because the salt picked up moisture and went into the more stable hydrated form before any appreciable photochemical reaction could take place.

To determine whether the anhydrous salt is deliquescent, a sample was placed in a container saturated with water vapor at room temperature (30°). The salt quickly picked up even more than the three moles of water normally present and deliquesced to a sticky mass. Microscopic examination of the dehydrated salt showed that the crystals are practically intact after dehydration, since there is no change in the gross form and the smallest crystals appear quite as clear as before dehydration. Larger, clear crystals become translucent after dehydration, due to their breaking up into smaller units, but they also retain the same shape, and do not break up into an amorphous white powder.[8] It is probable that the dehydrated material will go back to the same photochemically stable trihydrate on exposure to moisture.

On the basis of this investigation, we believe that potassium ferrocyanide is sufficiently stable to be used in precise investigations if the following conditions are observed:

1. The salt must not be dehydrated at temperatures greater than 100°.
2. The dehydrated salt must be kept out of contact with moisture before and during weighing, but not necessarily after.
3. The dehydrated salt must be kept in the dark to prevent decomposition.

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(1) Harvard National Scholar, '41.

(2) E. Swift, Jr., This Journal, **60**, 728 (1938).

(3) (a) Grinnell Jones and F. C. Jelen, *ibid.*, **58**, 2561 (1936); (b) Grinnell Jones and R. E. Stauffer, *ibid.*, **58**, 2558 (1936).

(4) Fabris,, *Gazz. chim. ital.*, **61**, 527 (1931).

(5) Autenrieth, "The Detection of Poisons," P. Blakiston's Son and Co., Philadelphia, Penna., 1921, p. 21, states that many other substances will react in the same way as hydrogen cyanide, and that the test used by Fabris is not conclusive evidence of the presence of this gas.

(6) According to McAlpine and Soule, "Qualitative Chemical Analysis," D. Van Nostrand Co., New York, N. Y., 1933, p. 460, the thiocyanate test is good to 1 p. p. m. or better.

(7) One sample of salt heated to 140° lost about 0.1% of cyanide.

(8) Roscoe and Schorlemmer, "Treatise on Chemistry," The Macmillan Co., New York, 1907, Vol. II, p. 1230.

We wish to thank Mr. E. B. Damon and Dr. W. A. Ray for the kind loan of apparatus used in this investigation.

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GALESBURG, ILLINOIS
RECEIVED JULY 18, 1938

Changes in the Physical Properties of Regenerated Cellulose by Liquid Ammonia

BY RICHARD G. ROBERTS

During the dialysis of proteins and hormones contained in bags made from regenerated cellulose film and placed in liquid ammonia, it was observed that the bags changed in size and in flexibility. Therefore, a series of comparative tests on some of the physical properties of the film and ammonia-treated film was made. The film used in these tests was du Pont Cellophane number 600.

The film was cut into strips of convenient size and placed in a Dewar flask. Liquid ammonia, previously dried over metallic sodium, was added to immerse the film sample completely. The film was not previously dried by us. The Dewar flask was tightly stoppered, and attached to a mercury seal. The liquid ammonia boiled off in about twenty-four hours, and any excess ammonia gas was removed by a vacuum pump.

Physical properties showing an increase:	
Tear strength (Elmendorf test)	200.0%
Tensile strength	70.6%
Thickness (flat micrometer)	152.4%
Weight (per unit area)	27.3%
Physical properties showing a decrease:	
Length (with grain)	8.3%
Width (cross grain)	17.8%
Area	24.7%

Ratios: Increase of tear strength to decrease in area, approximately 8 to 1. Increase of tensile strength to decrease in area, approximately 3 to 1.

It has been shown that bags made from regenerated cellulose film may be used conveniently for dialyzing experiments in liquid ammonia, although some space must be allowed for shrinkage.

The author wishes to thank Montgomery Ward and Company, Chicago, Illinois, for the use of apparatus in their testing laboratory.

THE DEPARTMENT OF CHEMISTRY
CHICAGO MEDICAL SCHOOL
CHICAGO, ILLINOIS
RECEIVED AUGUST 29, 1938

The Specificity of the Fermentation Test for Vitamin B_1

BY ALFRED S. SCHULTZ, LAWRENCE ATKIN AND CHARLES N. FREY

The fermentation method for the determination of vitamin B_1[1-3] has been in successful operation for some time. The effect of 2-methyl-5-ethoxymethyl-6-aminopyrimidine has been described.[2] We have assayed a wide variety of substances such as non-autoclaved yeast, rice polish, vitamin pills and concentrates, solutions of crystalline vitamin, and milk, and no evidence of the interfering substance has been found. In an investigation on the metabolism of vitamin B_1,[4,5] we found reason to believe that a portion of the fermentation stimulating effect of urine is not due to vitamin B_1. While this did not appear to alter the significance of the results, it was thought very desirable to find a method for differentiating between the intact vitamin molecule and any possible breakdown product. A way of doing this has been found in the differential oxidation of the vitamin B_1 in the presence of the aminopyrimidine.

Alkaline ferricyanide in the cold will readily oxidize the vitamin to thiochrome. Preliminary experiments with a sample of thiochrome obtained from Merck and Company showed it to be inactive in the fermentation reaction. The aminopyrimidine is more resistant to oxidation and it is a simple matter to oxidize B_1 preferentially when present in addition to aminopyrimidine. A solution containing 8 gamma of the aminopyrimidine and 8 gamma of thiamin hydrochloride in a volume of 35 ml. was treated with 2.5 ml. of 1% $K_3Fe(CN)_6$ and 2.5 ml. of 50% NaOH. After standing at room temperature for five minutes the solution was neutralized with dilute sulfuric acid and made to 100 ml. A 25-ml. aliquot of this was tested in the usual manner by gas test. It gave a stimulation which corresponded exactly to 2 gamma of the aminopyrimidine (*i. e.*, the B_1 was destroyed) Parallel experiments showed that the neutralized oxidizing solution was without influence on controls with either thiamin hydrochloride or aminopyrimidine.

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(1) A. S. Schultz, L. Atkin and C. N. Frey, THIS JOURNAL, **59**, 948 (1937).

(2) A. S. Schultz, L. Atkin and C. N. Frey, *ibid.*, **59**, 2457 (1937).

(3) A. S. Schultz, L. Atkin and C. N. Frey, *ibid.*, **60**, 1514 (1938).

(4) A. S. Schultz, R. F. Light and C. N. Frey, *Proc. Soc. Exptl. Biol. Med.*, **38**, 404-406 (1938).

(5) R. F. Light, A. S. Schultz, L. Atkin and L. J. Cracas, *J. Nutr.*, **16**, 333 (1938).

This technique greatly increases the specificity of the fermentation method and an investigation of the conditions necessary for its application to substances like animal tissue and excreta is under way.

THE FLEISCHMANN LABORATORIES
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RECEIVED SEPTEMBER 16, 1938

COMMUNICATIONS TO THE EDITOR

CRYSTALLINE COPPER-PROTEIN POSSESSING TYROSINASE ACTIVITY

Sir:

A crystalline material has been obtained from the aqueous extract from the wild mushroom, *Lactarius piperatus*, which may be phenol oxidase, or closely related to it. The crystals were six-sided plates and undoubtedly belonged to the hexagonal system. They were insoluble in water, dilute acids and salt solutions, but soluble in an aqueous solution of secondary sodium phosphate. Analysis showed a copper content of 0.25 and 13.6% nitrogen. Their phosphate solution was active in promoting the aerobic oxidation of *p*-cresol and catechol.

The procedure followed in obtaining the crystals can be described briefly as follows. The aqueous extract of the ground mushrooms was precipitated with 0.6 saturated ammonium sulfate, redissolved in water, the latter made 0.2 saturated with ammonium sulfate and the precipitate discarded. The filtrate obtained in the last operation was reprecipitated with 0.6 saturated ammonium sulfate, the precipitate formed redissolved in water and the solution treated with three volumes of cold acetone. The precipitate thus obtained was dissolved in water and treated with alumina. The liquid separated from the alumina contained about 50% of the active oxidase. This liquid was treated with boneblack and after filtering the filtrate was again precipitated with 0.6 saturated ammonium sulfate. The precipitate from the last operation was taken up in water and had an activity of 7000 units per cc. when determined according to the Graubard and Nelson method as modified by Adams and Nelson [THIS JOURNAL, **60**, 2472 (1938)]. When this liquid was gradually acidified by acetic acid, changing the *p*H from 6.5 to 5, and allowed to stand in the ice box, crystals separated.

DEPARTMENT OF CHEMISTRY HAROLD R. DALTON
COLUMBIA UNIVERSITY J. M. NELSON
NEW YORK CITY

RECEIVED NOVEMBER 25, 1938

TETRAMETHYLPLATINUM AND HEXAMETHYLDIPLATINUM

Sir:

Tetramethylplatinum has been prepared in 46% yield from trimethylplatinum iodide and methylsodium. It is the most soluble organoplatinum compound so far prepared, being readily soluble in the cold in benzene, acetone, ether and petroleum ether (b. p. 60–68°). The compound crystallizes from petroleum ether as large hexagonal crystals which decompose but do not melt at elevated temperatures. *Anal.* Pt, 76.84; C, 18.32; H, 4.31. We have found that the compound is one of several by-products of the Pope and Peachey [*J. Chem. Soc.*, **95**, 571 (1909)] reaction for the preparation of trimethylplatinum iodide from platinic chloride and methylmagnesium iodide. Hydrogen chloride converts tetramethylplatinum to trimethylplatinum chloride. *Anal.* Pt, 70.20; Cl, 13.10.

Hexamethyldiplatinum has been synthesized in 60% yield by heating trimethylplatinum iodide with powdered potassium in dry benzene. *Anal.* Pt, 81.13; C, 14.55; H, 3.92. The compound is very soluble in benzene, acetone and ether, but only slightly soluble in cold petroleum ether. It is best crystallized from a benzene–petroleum ether solution. Molecular weight determinations show that hexamethyldiplatinum is not dissociated at the freezing point of benzene [mol. wt.: calcd., 480.4; found, 482]. Iodine in ether con-