rivalent platinum which is not converted into an aquo compound even by concentrated hydrochloric acid.

Summary

1. A new complex compound of quadrivalent manganese has been prepared which has the composition $K_2[Mn(C_2O_4)_2(OH)_2]\cdot 2H_2O$. The barium and chloropentamminecobalti salts were also isolated.

2. The absorption spectrum was measured in the visible region.

BUFFALO, NEW YORK RECEIVED JUNE 19, 1936

NOTES

Sodium Fluorenone as a Dehydrating Agent[1]

By H. E. BENT AND H. M. IRWIN, JR.

The most rapid method of drying an organic liquid is to dissolve in it some compound which reacts rapidly with water. For this purpose sodium benzophenone has been widely used although this involves using an alkali metal, sodium–potassium alloy or some other material which introduces considerable hazard into such work. Fluorenone has the advantage over benzophenone that it will react readily with dilute sodium amalgam to form an addition compound which has a deep green color and therefore like benzophenone gives a definite indication by its color of the absence of water. Dry solvent is then obtained by distilling from this solution.

The object of this investigation is to compare the efficiency of sodium fluorenone with the customary drying agents, magnesium perchlorate and activated alumina. Since the compound formed by the addition of sodium to fluorenone is more stable than that formed with benzophenone, it is important to be sure that the ketyl is still sufficiently reactive to be an effective drying agent.

A dilute solution of sodium fluorenone was prepared for this work by introducing 0.025 g. of fluorenone and evacuating with a mercury pump for one hour. Three to five cubic centimeters of a saturated amalgam (about 1%) was then added *in vacuo* and 50 cc. of dry ether. Shaking produced a solution which was sufficiently concentrated to react with at least one hundred times as much water as is retained by the glass on its surface.[2] A tube, connected to the reaction flask by a capillary capable of being broken and thereby opened by a magnetic hammer, carried four side-tubes. The first two were empty and used as a check on the method. The third and fourth contained activated alumina and magnesium perchlorate, respectively. The samples of alumina and magnesium perchlorate were prepared by exposing them in a thermostat to one liter of air saturated with water vapor at 25°. The quantity of water absorbed by the sample was at least one hundred times as much as was necessary to destroy the sodium fluorenone with which it came in contact, while still being small enough to give the very low vapor pressure characteristic of the dehydrating agent. The tubes containing the solid dehydrating agents were evacuated for a short time before sealing the apparatus, and immediately the capillary was broken in order to prevent diffusion from one solid to the other. The fluorenone was decolorized in the first empty tube on account of moisture on the glass and in the vapor state. In the second tube the solution retained its color. In the third and fourth tubes the solution was immediately decolorized by the alumina and by the magnesium perchlorate, indicating that the vapor pressure of water was sufficiently high to be removed by the ether solution of sodium fluorenone. A duplicate run verified the conclusion from this experiment.

The vapor pressure of water is given as 0.003 mm. for alumina and the water is given as unweighable in 210 liters for magnesium perchlorate.[3] If unweighable means less than 1 mg. this would give a vapor pressure of less than 0.005 mm. If we assume that in the presence of a small amount of water the ketyl is converted to fluorenone and fluorenole,[4] then we can estimate a mini-

---

[1] This problem was studied as a reading period assignment in the first course in physical chemistry at Harvard University.

[2] Bent and Lesnick, THIS JOURNAL, **57**, 1246 (1935).

[3] Yoe, *Chem. News*, **130**, 340 (1935).

[4] Bachman, THIS JOURNAL, **55**, 1179 (1933).

mum value for the equilibrium constant for the reaction

$$NaR + H_2O = NaOH + {}^1/_2R + {}^1/_2RH_2$$

Since the sodium hydroxide is present as a solid we may express the equilibrium constant by the equation

$$K = (R)^{1/2}(RH_2)^{1/2}/(NaR)(H_2O)$$

If we assume, as a consequence of the complete destruction of the green color of the solution, that the reaction goes at least 99.9% to completion, then we obtain

$$K = 0.5 \times 999 \times 23/0.003 = 3.8 \times 10^6$$

referring the vapor pressure of water to that of pure liquid water as the standard state. This gives a value for ΔF of -9.0 kcal. These figures represent the minimum efficiency of sodium fluorenone as a drying agent. In any normal procedure a large excess of the drying agent would be used which would result in the removal of water until the pressure is at least as low as 10^{-7} mm.

CONTRIBUTION FROM THE
CHEMICAL LABORATORY
HARVARD UNIVERSITY
CAMBRIDGE, MASS.

RECEIVED JULY 30, 1936

The Vapor Density of Hexaphenylethane

BY H. E. BENT AND E. S. EBERS

In a recent publication the statement is made that hexaphenylethane probably does not dissociate in the vapor state.[1] In order to verify this statement an attempt was made to measure directly the vapor density of hexaphenylethane. This measurement combined with the previous data on the vapor pressure would give the molecular weight in the vapor state.

Since the vapor pressure of hexaphenylethane at 120° is only 0.004 mm. a very large volume would be necessary in order to produce a weighable amount of compound. For this purpose a ten-liter flask was attached to the fiber gage used in the previous research and to a capsule of hexaphenylethane. Ground joints controlled by electromagnets were so arranged as first to saturate the ten-liter flask with the ethane and then, closing the ethane capsule, condense the vapor in a small ampoule. The flask could then be saturated again and the vapor a second time condensed and in this way any desired amount of material obtained.

The method was checked by determining the vapor density and the molecular weight of triphenylmethane. The result was high by about 20% which we assume to be due to adsorption. As it was expected that difficulty would be encountered with hexaphenylethane on account of decomposition a procedure was adopted with triphenylmethane which would avoid this difficulty as far as possible. The ground joint to the pump was opened just enough to reduce the pressure to about three-fourths of the saturation pressure. After the pressure had become constant the valves to the pump and to the capsule of sample were closed simultaneously and the valve to the receiver opened for a time sufficiently long to condense about half of the total amount of material in the ten-liter flask. The valve to the receiver was then closed and the pressure again measured, the difference between the initial and the final pressure giving a measure of the amount of material condensed. This process was repeated about ten times and the flask then cooled and the receiver cracked off. The amount of material was determined by weight, both by difference and by evaporation of the solution of the compound to dryness in a crucible. This method of operating between three-fourths and three-eighths saturation would also be effective in avoiding condensation in the ten-liter flask or in removing adsorbed material from the surface of the glass during condensation.

When the method was applied to hexaphenylethane it was found that decomposition was too rapid to permit even an approximate determination of the vapor density. In a flask of such a large size decomposition was so great that even with the pump operating the pressure remained several times that of hexaphenylethane for a space of three hours at 120° (the valve to the solid remaining open). By this time apparently all of the ethane had decomposed for the pressure gradually decreased. However, the material in the flask was no longer hexaphenylethane but a decomposition product for on closing off the flask the pressure remained perfectly constant. Under these conditions hexaphenylethane decomposes rapidly enough to be measured easily. We concluded, therefore, that it is not possible to meas-

---

[1] G. R. Cuthbertson and H. E. Bent, THIS JOURNAL, 58, 2000 (1936).

ure the vapor density of hexaphenylethane by this method on account of rapid decomposition.

MALLINCKRODT CHEMICAL LABORATORY
HARVARD UNIVERSITY
CAMBRIDGE, MASS.

RECEIVED AUGUST 3, 1936

Relative Reactivities of Organometallic Compounds. XIV. Orientation in Metalation

BY HENRY GILMAN AND ROBERT H. KIRBY

Schlenk and Meyer[1] have shown that Abeljanz[2] did not obtain phenylpotassium from benzene and potassium. However, Schorigin[3a] very probably had phenylpotassium in hand, despite the confusion due to the paucity of experimental data.[4] We have found that carbonation of the products resulting from interaction of benzene, diethylmercury and potassium gives benzoic acid (45% yield) as well as phthalic and terephthalic acids. The same products, in different quantities, are obtained when sodium is used in place of potassium.

The organo-alkali compounds appear to arise largely as a consequence of metalation by ethylalkali compounds

$$C_6H_6 + C_2H_5K \longrightarrow C_6H_5K + C_2H_6$$

and not by the action of the alkali metals or their amalgams on benzene, for the evolved gas consists predominantly of ethane and contains only small quantities of ethylene and hydrogen.[5] The isolation of phthalic and terephthalic acids establishes the intermediate formation of *o*- and *p*-dialkalibenzenes, and indicates that phenylsodium (or potassium) orients subsequent metalation to the *ortho* and *para* positions. Mercuration may not follow such orientation.[6] It is noteworthy that isophthalic as well as terephthalic acid has been obtained from successive interaction of benzene, diamylmercury, sodium and carbon dioxide in the interesting studies by Morton and Hechenbleikner.[7]

The results are consistent with some of the earlier generalizations on relative reactivities of organometallic compounds,[8] particularly the increase in reactivity of RM compounds with increase in atomic weight of the alkali metal. For example, Mr. R. V. Young, in a study of organoalkali compounds, has shown that ethyl-lithium does not metalate benzene during a two-month period at room temperature;[3b] the over-all metalation of benzene by ethylsodium is less than that by ethylpotassium; and ethylpotassium gives much more of the dimetalated compounds than does ethylsodium.[9]

The metalations reported are merely special cases of general metalation which may be a direct metathesis, and, when RM compounds are used, a metathesis resulting in the formation of the salt of the stronger acid. Metalation of aromatic nuclei by RM compounds may involve preliminary addition, with subsequent elimination of RH.[10] Metalation by RM compounds is, of course, possible with all compounds, saturated as well as unsaturated, for all hydrogens are acidic to varying degrees from the viewpoint of metalation. A pertinent illustration is the metalation of saturated aliphatic hydrocarbons of the R_3CH type by ethylpotassium. In such cases, it is unlikely that unsaturated compounds are intermediates, even though it has been shown that RM compounds can act as dehydrogenating agents.[11]

Experimental Part

Metalation with Ethylpotassium.—To a suspension of 3.13 g. (0.08 g. atom) of potassium shavings in 35 cc. of benzene was added 5.17 g. (0.02 mole) of diethylmercury. Reaction set in at once as was evident by amalgamation of the potassium, evolution of gas and warming of the benzene. The mixture was stirred without heating for forty-eight hours, cooled to 7° and carbonated with carbon dioxide gas. The yields of products, based on diethylmercury, were 33% benzoic acid and 14% terephthalic acid (mixed melting point of dimethyl ester). The odor of propionic acid was noticeable. and a strong fluorescein test established the presence of phthalic acid. Isophthalic acid was not isolated, but may have been present in small quantities. The gas evolved contained 8 cc. of ethylene,

---

[1] Schlenk and Meyer. *Ber.*. **46**, 4060 (1913).

[2] Abeljanz, *ibid.*, **9**, 10 (1876).

[3] (a) Schorigin. *ibid.*. **43**, 1938 (1910): (b) *ibid.*. **41**, 2723 (1908).

[4] Wooster. *Chem. Rev.*, **11**, 8 (1932). See, also. Schlenk and Holtz. *Ber.*. **50**, 262 (1917).

[5] There is a possibility of some di-alkali compound being formed by self-metalation of phenylalkali compound. Incidentally, it is likely that the spontaneous transformations of some of the more reactive alkylalkali compounds involve self-metalation to give polymetalated types culminating in carbides [see ref. 12].

[6] Gilman and Kirby. *J. Org. Chem.*, **1**, 146 (1936).

[7] Morton and Hechenbleikner. THIS JOURNAL. **58**, 1024 (1936). Dr. Morton and co-workers have shown, in some unpublished studies, that phthalic acids are obtained in this reaction when diamylmercury is replaced by amyl chloride.

Possibly the amylidene disodium of Morton may orient differently from ethylsodium. A pertinent illustration is the different orientation effects of the very closely related phenyl-calcium and phenyl-lithium compounds in metalations.

[8] Gilman and Nelson, *Rec. trav. chim.*, **55**, 518 (1936).

[9] The extent of metalation varies with the R group. A 77% yield of benzoic acid was obtained from benzene and *n*-butylsodium followed by carbonation.[6]

[10] Gilman and Breuer. THIS JOURNAL, **56**, 1123 (1934).

[11] An illustration is the study by C. W. Bradley on the conversion of 1,4-dihydrodibenzofuran by phenyl-lithium to 4-dibenzofuryl-lithium and dibenzofuran.

2.5 cc. of hydrogen and 535 cc. of ethane, all volumes being corrected.

In a second experiment, using 75 cc. of benzene, reaction started slowly and four hours elapsed before an appreciable quantity of mercury separated. The yields were: 45% of benzoic acid and 17% of terephthalic acid.

From a third experiment, which differed from the second only in limiting the time of reaction to twenty hours, the yield of benzoic acid was 33% and the yield of terephthalic acid was 11%. Positive fluorescein tests were also obtained in the second and third experiments.

Metalation with Ethylsodium.—The procedure was identical with the first experiment with ethylpotassium, 1.84 g. (0.08 g. atom) of sodium being used. Reaction set in immediately. The products identified were: 41% of benzoic acid; a small quantity of terephthalic acid (mixed melting point with dimethyl ester); and phthalic acid (as indicated by a positive fluorescein test). The gas evolved contained 12 cc. of ethylene, 10 cc. of hydrogen and 420 cc. of ethane. Incidentally, the limited evolution of ethylene and hydrogen belies any considerable metalation by alkali hydride which arises from the thermal decomposition of ethylalkali compound.[12]

---

(12) Carothers and Coffman, THIS JOURNAL, **51**, 588 (1929).

CONTRIBUTION FROM THE
CHEMICAL LABORATORY OF
IOWA STATE COLLEGE
AMES, IOWA

RECEIVED JUNE 18, 1936

Comparison of the Total Nitrogen in Wheat Seeds by the Gunning (Modified Kjeldahl) and the Dumas Combustion Methods

BY W. Z. HASSID

Smyth and Wilson[1] analyzed peas for total nitrogen before and after germination in distilled water, in salt solution media and in alkaloids. The peas showed an increase of 0.2 to 0.3% nitrogen in the dry residue after germination.

In the opinion of these authors, the increase in nitrogen was not the result of atmospheric nitrogen assimilation, but was due to the inadequacy of the Kjeldahl method to measure the total nitrogen in the ungerminated peas. By the official Kjeldahl procedure only 90% of the total nitrogen as compared with the Dumas combustion method could be obtained, and this varied with different modifications of the official procedure. On the basis of these results, Smyth and Wilson concluded that in the process of germination the nitrogen of the seeds was converted into compounds which were more easily determinable by the Kjeldahl method than those in the dry seeds.

Since Smyth and Wilson's results cast doubt on the validity of the conclusions drawn by Lipman and Taylor[2] and others who obtained similar results relative to the power of green plants to fix atmospheric nitrogen, it seemed desirable to make a study of the modified Gunning method and the Dumas combustion method as a means of determining the nitrogen in seeds and seedlings. To this end, wheat seeds of the "little club" variety were subjected to analysis for total nitrogen by both the modified Gunning and Dumas combustion methods.

TABLE I

N ANALYSIS OF 12 SAMPLES OF WHEAT SEEDS BY THE MODIFIED GUNNING METHOD

Sample no.	Sample wt.	% N	
1	1.0000	2.27	Average 2.25%
2	1.0000	2.20	
3	1.0920	2.18	
4	1.4060	2.25	
5	1.4060	2.25	
6	1.4040	2.27	
7	1.4000	2.25	
8	1.4000	2.25	
9	1.4026	2.25	
10	1.4000	2.20	
11	1.4010	2.30	
12	1.4020	2.31	

N ANALYSIS OF 6 SAMPLES OF WHEAT SEEDS BY THE DUMAS METHOD (COMBUSTION)

Sample no.	Sample wt.	% N	
1	1.0205	2.25	Average 2.28%
2	1.1100	2.27	
3	1.0000	2.28	
4	1.0344	2.31	
5	1.0000	2.30	
6	1.0000	2.29	

A study of the table makes it clear that the modified Gunning method as used in this experiment yields as much nitrogen as the Dumas method for the wheat seeds analyzed. It appears, therefore, that such results as were obtained by Lipman and Taylor and by others who claimed to have shown nitrogen fixation by wheat plants cannot be invalidated on the basis of the results and conclusions of Smyth and Wilson, cited above.

DIVISION OF PLANT NUTRITION
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIF.

RECEIVED AUGUST 17, 1936

---

(1) E. M. Smyth and P. W. Wilson, *Biochem. Z.*, **282**, 1 (1935).

(2) C. B. Lipman and J. K. Taylor, *J. Franklin Inst.*, 475–506 (1924).