COMMUNICATIONS TO THE EDITOR

SIR JAMES IRVINE'S VIEW ON THE CONSTITUTION OF DI- AND POLYSACCHARIDES

Sir:

In a recent communication Irvine and McGlynn [THIS JOURNAL, **54**, 358 (1932)] comment on the use of 2,3,6-trimethylglucose as a reference substance in structural investigations and urge that "much further work and the application of new methods are alike necessary before definite constitutions can be assigned to the disaccharides and polysaccharides which are convertible into 2,3,6-trimethylglucose." These conclusions are valid in so far as work initiated by Irvine is concerned, but they do not represent the present state of carbohydrate chemistry. No less than six years ago, and before the publication of Irvine and Black's paper on maltose [*J. Chem. Soc.*, 862 (1926)] an explicit statement of the ambiguity caused by the use of 2,3,6-trimethylglucose as a reference substance was given by Charlton, Haworth and Peat [*ibid.*, 98 (1926)] and in the same year (1926) Haworth and Peat [*ibid.*, 3094 (1926)] developed a new experimental method which solved completely the problem left undecided by the isolation of a trimethylhexose as a scission product of a fully methylated disaccharide. This method has been employed to determine the constitution of maltose, lactose, cellobiose, melibiose, 4-glucosido-mannose and 4-glactosido-mannose [*ibid.*, 544, 1527, 2809, 3146 (1927); 1349, 1354 (1931)]. Recently its use has been extended to problems connected with the polysaccharides, starch, glycogen and xylan [Haworth and Percival, *ibid.*, 1342, 2850 (1931)]. In addition to the full treatment given in the original papers, an ample discussion of the various problems has appeared in a monograph [Haworth, "Constitution of Sugars," Edward Arnold and Co., London, 1929] and on various occasions in summary form [see, for example, *Helv. Chim. Acta*, 534 (1928)]. No reference whatever to any of this work is made by Irvine and McGlynn.

In describing the conversion of 2,3,6-trimethylglucose, *via* its γ-methylglucoside into tetramethyl-γ-glucose, the latter authors have not observed that this series of transformations was carried out by Schlubach and Bomhard in 1926 [*Ber.*, **59**, 845 (1926)]. Comment is necessary also on the conclusions drawn by Irvine and McGlynn from their experiments on the oxidation of 2,3,6-trimethylglucose. It is well known that in aqueous solution both γ- and δ-lactones enter into equilibrium with their parent acids. In those cases where both γ- and δ-lactones are obtainable from one acid (as with 2,3,6-trimethylgluconic acid) it is clear that no evidence of preferential oxidation to one particular lactone can be obtained by treatment of the sugar with bromine water, extraction of the aqueous solution with chloroform several hours after the commencement of the

reaction, and the mere isolation of that lactone on evaporation of the chloroform. Similar considerations apply when the oxidation is conducted in the presence of an excess of calcium carbonate, with the additional complication that under these conditions most of the product may pass through the stage of the calcium salt from which the organic acid, not the lactone, is liberated on acidification. The experimental procedure of these authors is ill-adapted to the problem they have in view and definite conclusions concerning the preferential formation of either lactone during the oxidation cannot be drawn from their present results.

CHEMISTRY DEPARTMENT　　　　　　　　　　　　　　　　E. L. HIRST
THE UNIVERSITY OF BIRMINGHAM
ENGLAND
RECEIVED APRIL 13, 1932
PUBLISHED JUNE 6, 1932

THE EFFECT OF FOREIGN GASES ON UNIMOLECULAR REACTIONS

Sir:

The recent communication by Steacie [THIS JOURNAL, **54**, 1695 (1932)] suggests a generalization that has apparently not been made hitherto, *viz.*, that foreign gases do not activate unimolecular reactions. The earliest experimental evidence on this subject is the work of Daniels [THIS JOURNAL, **47**, 1602 (1925)], who showed that the rate of decomposition of nitrogen pentoxide in the presence of nitrogen falls off at about 0.01 mm. partial pressure. Later experiments show that the behavior is the same in the absence of nitrogen.

The conspicuous exception to this generalization is the action of hydrogen on certain organic compounds at elevated temperatures. The explanation of this exceptional behavior is to be sought in the fact that a reaction between the hydrogen and organic molecule would be predicted by an organic chemist.

While we do not know much about the conditions under which translational energy is converted into vibrational energy [see Kassel, Rice, *Chem. Rev.*, **10**, 11 (1932)], the evidence is that this process does not take place readily. The early attempts to calculate the limiting pressure for the unimolecular decomposition of nitrogen pentoxide were without significance because only translational energy was considered.

On the other hand, vibrational energy is only transferred readily when there is a sharp resonance between the colliding molecules.

DEPARTMENT OF CHEMISTRY　　　　　　　　　　　　　W. H. RODEBUSH
UNIVERSITY OF ILLINOIS　　　　　　　　　　　　　　　M. J. COPLEY
URBANA, ILLINOIS
RECEIVED APRIL 25, 1932
PUBLISHED JUNE 6, 1932

POLYHALIDES CONTAINING FLUORINE

Sir:

The literature contains no evidence of the existence of polyhalides containing fluorine, save a mention by Cremer and Duncan [*J. Chem. Soc.*, **133**, 2243 (1931)], in a study of the dissociation pressures and other properties of the polyhalides, of the absorption of iodine bromide by cesium fluoride. On the basis of absorption taking place, they concluded that a compound, probably having the formula CsFIBr, was formed.

Several years ago work was started in this Laboratory on the preparation of polyhalides containing fluorine. We have found the following four methods for the preparation of alkali polyhalides containing fluorine.

(1) To a saturated solution of the alkali fluoride one equivalent of iodine is added and the solution chlorinated to the disappearance of the iodine color. On cooling crystals which were very nearly homogeneous were obtained.

(2) The same process as (1) with the modification of using a solution acidified with hydrochloric acid gave a better yield. Recrystallization of the products from either of these methods gave homogeneous anisotropic needle-like orange crystals.

(3) A mixture in the proportion of one molecule of alkali fluoride to one atomic weight of iodine was intimately mixed by grinding and chlorinated to constant weight. The final product was an orange-yellow solid which on recrystallization from water gave a good yield of the same orange-yellow crystals as before.

(4) To the acidulated saturated solution of the alkali fluoride was added a slight excess of an aqueous solution of iodine trichloride. The same orange-colored polyhalide immediately separated as gleaming needles.

Adsorbed water was carefully removed before analysis. Since the crystals tend to lose halogen, it is best to keep them in tightly stoppered bottles. The potassium salt is very unstable and so far we have been unable to get consistent analyses of it. However, the rubidium and cesium salts are quite stable, decomposing in the open air to white salts of the corresponding fluorides, respectively, at approximately 300°, and well above 300°.

Anal. Calcd. for $CsFICl_3$: Cs, 34.49; Cl, 27.62; I, 32.96. Found: Cs (perchlorate method), 34.27, 34.33; Cl, 27.61, 28.06; I, 33.38, 32.81.

The melting point of the $CsFICl_3$ in a sealed tube is 194°. The crystals exhibit parallel extinction and have a specific gravity of 3.565.

Anal. Calcd. for $RbFICl_3$: Rb, 25.30; Cl, 31.50; I, 37.58. Found: Rb, 25.27, 25.47; Cl, 31.46, 31.52; I, 37.52, 38.05.

The melting point of the $RbFICl_3$ in a sealed tube is 172°. It has a specific gravity of 3.159 and exhibits parallel extinction under crossed nicols.

The potassium salt has the same crystal form as the others and qualitative analysis shows the presence of potassium, chlorine, fluorine and iodine. The investigation of this and other polyhalides containing fluorine is being continued and will be reported in detail later.

MORLEY CHEMICAL LABORATORY
WESTERN RESERVE UNIVERSITY
CLEVELAND, OHIO
RECEIVED APRIL 30, 1932
PUBLISHED JUNE 6, 1932

HAROLD SIMMONS BOOTH
CARL F. SWINEHART
WILLIAM C. MORRIS

THE ATOMIC WEIGHTS OF H(2) AND Be(9)

Sir:

Among the lighter elements there are two whose atomic weights are of especial interest at this period, H(2) and Be(9). Since H(2) is a probable nuclear building unit and is also the simplest complex nucleus reported to date (excluding neutrons) an accurate knowledge of its atomic weight gives a measure of the interaction energy of two protons and one electron, which energy may be a fundamental unit of the nucleus.

Another such unit may be the proton–electron interaction energy obtainable from the difference in mass of the neutron(1) and an atom of H(1). The accurate mass of Be(9) is necessary in calculating the mass of the neutron(1) [Chadwick, *Nature*, Feb. 27, 1932].

Until these atomic weights have been accurately determined we may predict values, that for H(2) being obtained by a simple calculation, based on the assumption that the lighter $4N + 2$ elements contain N α particles and one H(2) nucleus. Aston [*Proc. Roy. Soc.* (London), **A115**, 487 (1927)] gives for the packing fractions of Li(6) and B(10), 2.00 $\pm$ 0.10 and 1.35 $\pm$ 0.05 $\times 10^{-3}$ mass units (probable errors are assumed to be $^1/_3$ maximum allowable error). Using the packing fraction for helium, 0.54 $\pm$ 0.03, we obtain from the data for Li(6)

$$4(0.54 \pm 0.03) + 2A_1 = 6(2.00 \pm 0.10) + D_1$$
$$\text{or} \quad A_1 = (4.92 \pm 0.36) + D_1/2 \tag{1}$$

and for B(10)

$$A_2 = (4.59 \pm 0.37) + D_2/2 \tag{2}$$

where A_1 and A_2 represent the packing fraction of H(2) and the D's the mass defects of Li(6) and B(10) with respect to He(4) and H(2). Although these equations do not uniquely determine the packing fraction of H(2), they set a lower limit to its atomic weight at $(2.0098 + D_1 \pm 0.0007)$ from (1) and $(2.0092 + D_2 \pm 0.0007)$ from (2). From a consideration of the binding energies in some of the lighter nuclei, we may estimate values for the mass defects of Li(6) and B(10) to be $D_1 = 1.2 \pm 0.4$ and $D_2 = 2.4 \pm 0.6 \times 10^{-3}$ m. u. These values give H(2) an atomic weight of 2.0110

$\pm$ 0.0011 from (1) and 2.0116 $\pm$ 0.0013 from (2); mean *2.0113* $\pm$ *0.0012* (mass spectrograph scale). The agreement is satisfactory. This gives 4.3 $\pm$ 1.2 $\times$ 10^{-3} m. u. for the binding energy of the H(2) nucleus.

The chemical atomic weight of beryllium determined by Hönigschmid [*Ber.*, **55B**, 4 (1922)] is 9.018 $\pm$ 0.002. This is almost certainly too high, for while beryllium exists to 99.95% as Be(9) and to about 0.05% as Be(8) [Watson and Parker, *Phys. Rev.*, **37**, 167 (1931)], no isotope of mass number greater than 9 has been reported. Assuming the nucleus of Be(9) to contain 2 α particles, 1 proton and 1 electron, an upper limit for its atomic weight is 9.011 (chemical scale). This value has neglected the binding occurring between the constituents of the nucleus, which from disintegration experiments [Chadwick, *Proc. Roy. Soc.* (London), **A130**, 463 (1931)] has a value 5 $\pm$ 2 $\times$ 10^{-3} m. u., which is about that expected from the differences in mass defects of corresponding members of the $4N + 1$ and $4N$ series. Assuming this as a mass defect for Be(9), its atomic weight becomes 9.006 $\pm$ 0.002, and correcting for 1 part in 2000 of Be(8) gives *9.005* $\pm$ *0.002* for the atomic weight of beryllium. Since this is 0.013 m. u. less than the present chemical value a redetermination is necessary.

From the probable value of the mass of Be(9) and Chadwick's disintegration experiments we can make a rough estimate of the mass of the neutron(1), which indicates that it is little different from that of its isobar, H(1). If neutrons are formed exothermically from protons and electrons, it would seem highly probable that their formation could be effected in the laboratory and the energy change detected as radiation. The existence of H(2) nuclei [Urey, Brickwedde and Murphy, *Phys. Rev.*, **39**, 164 (1932)] and neutrons(1) suggests that all known atomic nuclei could originate from protons and electrons through a succession of *two body collisions, e. g.,* 2H(2) nuclei $\longrightarrow$ 1 α particle, etc.

CHEMISTRY DEPARTMENT   NORMAN S. GRACE
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA
RECEIVED MAY 5, 1932
PUBLISHED JUNE 6, 1932

KINETICS OF THE THERMAL DISSOCIATION OF GASEOUS ETHYL BROMIDE

Sir:

More exact experimental data on simple reactions are urgently needed for testing theories of unimolecular reactions, particularly with reference to the falling-off of the rate-constant at low pressures. The reaction

$$C_2H_5Br = C_2H_4 + HBr$$

has been studied for several years in this Laboratory, and a preliminary

report by E. T. Lessig is now in press. With improved technique and proper allowance for the reverse reaction, this reaction now appears to be as satisfactory a unimolecular reaction as any yet reported.

The data at pressures above 100 mm. in the range 390 to 420° are well expressed by the formula

$$k = 3.85 \times 10^{14} e^{-54,800/RT}$$

Below 120 mm. k falls off, and at 20 mm. it has only about one-third of its high pressure value. In this low pressure region the reaction appears to be purely second order. Calculations indicate 22 squared terms on the basis of present theories. Theory I of Rice and Ramsperger [THIS JOURNAL, **49**, 1617 (1927)] is not adequate to explain the facts. Temperature coefficients at the low pressures suggest that Kassel's Theory III [*J. Phys. Chem.*, **32**, 225 (1928)] may fit better than Theories II or I.

The addition of nitrogen, and of hydrogen, causes the value of k at low pressures to *decrease*. According to present accepted theories the addition of foreign gases should increase the value of k. Unless some unexpected specific chemical effect exists, the results suggest that certain aspects of present theories of unimolecular reactions should be critically reassessed.

The influence of other foreign gases of increasing complexity is now being investigated.

LABORATORY OF PHYSICAL CHEMISTRY   E. L. VERNON
UNIVERSITY OF WISCONSIN   FARRINGTON DANIELS
MADISON, WISCONSIN
RECEIVED MAY 9, 1932
PUBLISHED JUNE 6, 1932

THE EINSTEIN RELATION AND TEMPERATURE COEFFICIENT IN THE PHOTOBROMINATION OF CINNAMIC ACID

Sir:

Exact measurements on the photobromination of cinnamic acid, now in progress, show clearly that it is possible to obtain a quantum efficiency of 1 and a temperature effect of zero in agreement with simple photochemical theory, when accompanying thermal reactions are suppressed. They show, too, how the temperature coefficient of the total reaction can vary with the concentration.

The experiments were carried out in a quartz cell of 15-cc. capacity. Light of 4358 Å. was isolated from the spectrum of a capillary quartz mercury arc by means of a monochromator. The change in bromine concentration after fifteen minutes' illumination was measured and compared with the change in the control kept in the dark. The concentration of cinnamic acid was the same in all cases.

The results are summarized in the accompanying figure where Φ, the number of molecules of bromine consumed per quantum of light absorbed, is plotted against the concentration of bromine. This concentration is expressed in moles of bromine per liter of 0.00567 molar cinnamic acid in carbon tetrachloride. The reaction is a chain reaction, the products of the bromination apparently contributing some of their energy to activate new molecules of bromine.

The striking regularity with which Φ decreases as the dilution increases suggests that the energized products of the reaction gradually lose their activation by collision with the molecules of carbon tetrachloride. At infinite dilution the deactivation of products by the solvent should be so complete that no chain reaction is possible. Under these conditions, where secondary thermal reactions are eliminated, the quantum yield should be exactly 1. Extrapolation of the experimental curves to infinite dilution shows that this prediction is correct.
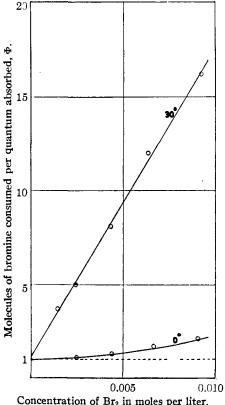
Furthermore, at infinite dilution where the reaction is purely photochemical, the temperature effect should be zero. Again the graphs support this prediction in a striking manner. The curves at 30 and 0° both extrapolate, within the limit of experimental error, to the same value of Φ, namely 1.
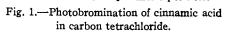
In the more concentrated solutions the reaction is about eight times as fast at 30 as at 0°. The ratio of rates for a 10° difference in temperature is 1 at infinite dilution and increases to a limiting value of 2 in the more concentrated solutions. This value is in agreement with that of ordinary thermal reactions.

Experimental measurements and calculations are being continued.

Fig. 1.—Photobromination of cinnamic acid in carbon tetrachloride.

LABORATORY OF PHYSICAL CHEMISTRY   WALTER H. BAUER
UNIVERSITY OF WISCONSIN   FARRINGTON DANIELS
MADISON, WISCONSIN

ISOLATION OF GLUTATHIONE FROM POTATO TUBERS TREATED WITH ETHYLENE CHLOROHYDRIN[1]

Sir:

Treatment of freshly-harvested potato tubers with ethylene chlorohydrin, a chemical that breaks their dormancy,[2] increases the sulfhydryl content of the expressed juice as shown by the nitroprusside test and by the sulfur reduction method.[3] In order to find whether this increase in sulfhydryl was due to an increase in glutathione, the procedure of Hopkins[4] for the isolation of glutathione was applied to the juice of potatoes treated with ethylene chlorohydrin.

Cut pieces of freshly-harvested potato tubers were dipped in a 1.6% solution of ethylene chlorohydrin, the excess solution drained off and the pieces placed in a closed container for twenty-four hours. They were then planted in moist soil for five days. After washing free of soil, the pieces were peeled, ground through a food chopper, the juice was expressed through cheesecloth, and the starch centrifuged out. The juice was boiled to coagulate the proteins, cooled, and filtered through glass wool. Following the procedure of Hopkins the cuprous salt of glutathione was isolated. In one experiment 1.5 liters of the boiled, filtered juice yielded 870 mg. The copper content was 17.48%; calcd., 17.26%.

The cuprous salt prepared by the above method was suspended in water and decomposed with hydrogen sulfide. After filtering out the cupric sulfide, the hydrogen sulfide was removed in a stream of hydrogen and the filtrate evaporated in a vacuum desiccator over sulfuric acid. When reduced to small volume, absolute alcohol was added and the glutathione allowed to crystallize. The yield from 395 mg. of the cuprous salt was 190 mg. of crystalline glutathione. An additional 70 mg. was obtained by bringing the mother liquor to dryness. The crystalline fraction was analyzed for nitrogen (micro Kjeldahl) and sulfur (Parr bomb).

Anal. Subs., 23.04 mg.: 10.8 cc. of $N/50$ H_2SO_4. Subs., 0.1141 g.: 0.0862 g. $BaSO_4$. Calcd. for $C_{10}H_{17}N_3SO_6$: N. 13.7; S, 10.42. Found: N, 13.1; S, 10.38.

By the same procedure, 970 mg. of the cuprous salt yielded 650 mg. of glutathione. This was recrystallized and the first fraction, which weighed 275 mg., was analyzed.

Anal. Subs., 30.99 mg.: 14.7 cc. of $N/50$ H_2SO_4. Subs., 0.1024 g.: 0.0771 g. $BaSO_4$. Found: N, 13.3: S, 10.34.

Using the same procedure, no glutathione could be isolated from the juice of untreated tubers, although qualitative tests indicated that a small

[1] Herman Frasch Foundation for Research in Agricultural Chemistry, Paper No. 36.

[2] Denny, *Am. J. Botany.* **13**, 118 (1926).

[3] Guthrie and Wilcoxon, *Contrib. Boyce Thompson Inst.*, **4**, 99 (1932).

[4] Hopkins, *J. Biol. Chem.*, **84**, 269 (1929).

amount was present.   When potatoes that had been stored for several months were treated with ethylene chlorohydrin, the cuprous salt could be isolated, but in smaller yield than with freshly-harvested tubers.   In one experiment, 1 liter of juice yielded 280 mg. of the cuprous salt; in another 600 cc. yielded 60 mg.   The copper content of the latter preparation was 17.15%.

This is believed to be the first isolation of glutathione from a seed plant.

BOYCE THOMPSON INSTITUTE   JOHN D. GUTHRIE
FOR PLANT RESEARCH, INC.
YONKERS, NEW YORK
RECEIVED MAY 12, 1932
PUBLISHED JUNE 6, 1932

E. L. HIRST'S COMMENTS ON IRVINE AND McGLYNN'S PAPER ON "A POSSIBLE SOURCE OF ERROR IN DETERMINING THE CONSTITUTION OF DI- AND POLYSACCHARIDES"[1]

Sir:

The criticisms made by Dr. E. L. Hirst reveal that in his reading of the paper to which he refers he has overlooked the essential features of the work described.   Constitutions are not assigned to di- and polysaccharides but attention is directed, systematically and on the evidence of experimental work described for the first time, to possible sources of error in determining the constitution of these compounds by the methylation method.   It is the case that the possibility of 2,3,6-trimethylglucose functioning in both a normal and a γ-form has already been suggested but our omission of any reference to Schlubach and Bomhard [*Ber.*, **59,** 845 (1926)] does not involve that we overlooked previous work on the subject.   It is at least unlikely that, as the originator of the method of solving the constitution of di- and polysaccharides by methylation, the efforts of other workers in this field should have been overlooked by me. But it may be pointed out that Schlubach and Bomhard merely converted the sugar into tetramethyl-γ-glucose through the intermediate formation of an unpurified glucoside, while in our case this glucoside was isolated after vacuum distillation as a pure compound, was analyzed and, among other reactions, was subjected to the graded hydrolysis which is obviously an essential part of the experimental scheme.   The tautomerism of 2,3,6-trimethylglucose is in consequence no longer conjectural but is based on experimental evidence.

With regard to his criticisms of our studies on the oxidation of trimethylglucose, Dr. Hirst assumes that, when this reaction is carried out in the presence of calcium carbonate under the conditions we describe, the whole of the acid produced is transformed into the calcium salt.   Such is

---

[1] Irvine and McGlynn, THIS JOURNAL, **54,** 358 (1932).

not the case and his criticism is pointless. The remaining papers he quotes were known to us.

THE UNIVERSITY, ST. ANDREWS, SCOTLAND   JAMES C. IRVINE

AMMONIUM ACETATE AS A NEUTRAL BUFFERED STANDARD
Sir:

On theoretical grounds, Williams and Lyman [THIS JOURNAL, **54,** 1911 (1932)] point out that ammonium acetate should be a good buffer at the neutral point, with P_H value practically independent of concentration. They suggest it, therefore, as a practically useful standard for hydrogen ion work and accurate titrations to P_H 7, which can be prepared in one minute. They do not describe the method for preparing the solution, but the emphasis upon the brief time required and statement that concentration is of minor importance suggest that it is only necessary to dissolve a few grams of the dry salt in a little water to secure a standard solution accurately buffered at P_H 7.

In this Laboratory, ammonium acetate solutions buffered near P_H 7 have been much used in the extraction of exchangeable bases from soil. In a description of the procedures employed [Schollenberger and Dreibelbis, *Soil Science*, **30,** 161 (1930)] attention has been directed to the fact that solutions of "C. P. Analyzed Reagent" ammonium acetate in pure water are likely to be far from neutral; with several lots of the salt, normal solutions so prepared were near P_H 5, indicating the presence of about one mole of free acetic acid to two of ammonium acetate. Preparation of the solution by mixing equal volumes of accurately prepared 2 N solutions of acetic acid and ammonia was recommended. Experience has been that a solution so prepared is invariably very nearly neutral.

According to a well-known authority [Morley and Muir, "Watt's Dictionary of Chemistry," 1899, Vol. I, p. 9], pure ammonium acetate may be prepared by saturating glacial acetic acid with dry ammonia, and is then dry, white and odorless. It is difficult to crystallize, the aqueous solution tending to lose ammonia on evaporation, leaving an acid salt.

The crystalline salt sold as a reagent is often quite moist, with a strong odor of acetic acid, indicating either improper preparation or subsequent deterioration. Hence, a solution of commercial reagent quality ammonium acetate may be of doubtful value as a neutral buffer standard. Implicit reliance upon the purity and neutrality of a solution of the crystallized salt is certainly unjustifiable.

SOIL CHEMISTRY LABORATORY   C. J. SCHOLLENBERGER
OHIO AGRICULTURAL EXPERIMENT STATION
WOOSTER, OHIO

AN ADDITION COMPOUND OF DIETHYLAMINE AND PHENYLBORIC ACID

Sir:

An addition compound has been prepared with diethylamine and phenylboric acid. It was expected that these should combine in a one to one ratio since boron trifluoride forms stable one to one addition compounds with ammonia or amines[1] and triphenylboron behaves in a similar manner.[2] Analyses, however, have shown that this substance contains three molecules of phenylboric acid to one of diethylamine.

This compound is readily prepared by allowing equal molal quantities[3] of the two substituents to react in anhydrous ether solution. There is a slight initial rise in temperature and after a few minutes a white solid (m. p. 85°) is precipitated. It is readily soluble in alcohol, acetone, benzene, chloroform, glacial acetic acid and dioxane, and sparingly soluble in diethyl ether, petroleum ether, water and carbon tetrachloride. When heated with water it decomposes, giving off diethylamine quantitatively.

The nitrogen content was obtained by heating the substance in dilute alkali and titrating the diethylamine which was volatilized with the vapors. It was observed that phenylboric acid could be titrated in the presence of glycerine just like boric acid itself, so the phenylboric acid (or possibly boric acid) residue in the Kjeldahl flasks was titrated in this manner. Independent boron analyses were obtained by heating the substance in bomb tubes with nitric acid, neutralizing the nitric acid to the methyl red end-point, and titrating the boric acid to the phenolphthalein end-point in the presence of glycerine.

Determination	Found, %		Calculated for $(C_6H_5B(OH)_2)_3 \cdot (C_2H_5)NH$, %
Nitrogen	3.20	3.18	3.19
Boron from residue of N_2 analysis	7.63	7.37	7.40
Boron, Carius determination	7.21	7.28	7.40

It should be pointed out that these analyses do not preclude the possibility that this compound may have lost one molecule of water. This work is being continued.

DEPARTMENT OF CHEMISTRY   G. E. K. BRANCH
UNIVERSITY OF CALIFORNIA   DAVID L. YABROFF
BERKELEY, CALIFORNIA
RECEIVED MAY 25, 1932
PUBLISHED JUNE 6, 1932

---

[1] Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, 1924, Vol. V, p. 122; Kraus and Brown, THIS JOURNAL, 51, 2690 (1929).

[2] Stock and Zeidler, *Ber.*, **54**, 531 (1921); Krause, *ibid.*, **57**, 813 (1924).

[3] It was first prepared in this manner since the one to one addition compound was expected.

ALLYL ETHERS OF HETEROCYCLIC ENOLS

Sir:

During research carried out in connection with the preparation of substances allied in structure to the alkaloid coniine, it became necessary to study the preparation and pyrolysis of the allyl ethers of heterocyclic enols. It is well known that α- and γ-N-heterocyclic enols show a marked tautomeric mobility of the enolic hydrogen between oxygen and nitrogen with preferential attachment to the nitrogen. The O-ethers are more difficult to prepare than the N-ethers, the best yields of the former being obtained via the silver salts or chlorine substituted derivatives.

The alkoxy ethers on heating usually undergo a rearrangement of the alkyl group, which wanders invariably to the nitrogen atom in preference to a nuclear carbon atom. One might expect that the allyl group would undergo an analogous migration [cf. Hurd, "The Pyrolysis of Carbon Compounds," The Chemical Catalog Company, 1929, pp. 205 and 223]. Tschitschibabin and Jeletsky [*Ber.*, **57**, 1158–61 (1924)] report having pyrolyzed O-allyl-carbostyril into the N-isomeride.

It has been found in the course of the present work that the migration of the allyl group can occur from oxygen to the adjacent β-unsaturated carbon atom. Thus 4-allyloxyquinaldine pyrolyzes almost quantitatively on heating for a short time, at 200°, to 3-allyl-4-hydroxyquinaldine, the constitution of which has been proved by its synthesis from α-allyl-β-phenyl-aminocrotonic ester. This is interesting since, in the case of 4-methoxy-quinaldine, migration of the methyl group takes place to the nitrogen atom [Conrad and Limpach, *Ber.*, **20**, 956 (1887)].

The significance of these results, and of those obtained with other oxy-N-heterocyclic substances, will be reported shortly in greater detail.

DEPARTMENT OF ORGANIC CHEMISTRY   BURNETT MANDER-JONES
UNIVERSITY OF SYDNEY   VICTOR MARTIN TRIKOJUS
SYDNEY, AUSTRALIA
RECEIVED MAY 25, 1932
PUBLISHED JUNE 6, 1932

NEW BOOKS

Chemistry at the Centenary (1931) Meeting of the British Association for the Advancement of Science. W. Heffer and Sons, Ltd., Cambridge, England, 1932. Price, 7/6, net.

The experience of a century has taught scientists in general and chemists in particular to expect papers of interest and pronouncements of lasting importance at the meetings of the British Association. It is hard for us to say whether the attractively published volume before us, a complete record of the Proceedings of the Chemistry Section, contains any pronouncement of an epoch-making character, but it is easy to discover that every paper is an interesting account of some of the very latest work. A scholarly dis-