culate the relative amounts of photosynthesis in any two portions of the spectrum. These values calculated from the rough physical measurements agree within a few per cent. with the experimentally determined values in all cases. Thus these primary absorption curves may be considered as representing the relative amounts of photosynthesis at equal incident quantum intensity.

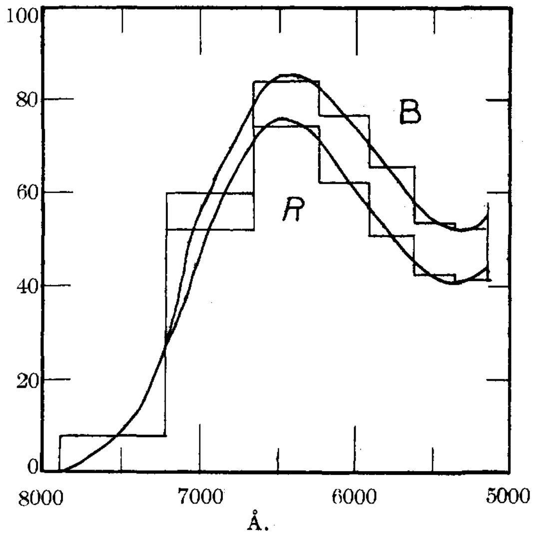

Fig. 1.

The fact that the amount of photosynthesis depends on the primary absorption spectrum seems fairly well established since the relationship holds for a large number of experiments with different ranges of wave lengths and different colors of trees as well as with experiments with semi-monochromatic radiation from filtered sodium and mercury sources. It offers a quantitative explanation of all our experimental results, published in botanical journals from 1933 on. Just why the amount of photosynthesis should agree with this arbitrary value rather than with the true absorption is still a matter of speculation.

VERMONT AGRICULTURAL EXPERIMENT STATION
BURLINGTON, VERMONT
HUNTER COLLEGE
NEW YORK CITY
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Diazo Coupling of 5-Hydroxy-6-methylhydrindene

BY LOUIS F. FIESER AND WARREN C. LOTHROP

In a previous report [THIS JOURNAL, **58**, 2050 (1936)] we stated that the above compound (I) failed to couple with diazotized *p*-nitroaniline in alkaline solution, whereas in parallel tests 5-hydroxy-4,7-dimethylhydrindene and 6-hydroxy-5,8-dimethyltetralin coupled readily under the same conditions. On preparing a further quantity of I in order to investigate its behavior with other coupling agents, we first tried to effect a coupling with diazotized *p*-nitroaniline under other conditions and found that this indeed can be accomplished. Each of seven solutions containing 0.1 g. of I in 10.5- to 20-cc. portions of sodium hydroxide solutions of concentrations varying from 0.119 to 2.49 *N* was treated at 0° with 2.5 cc. of an aqueous solution containing approximately one equivalent of the diazo compound and 0.000021 mole of hydrochloric acid, and after ten minutes the mixtures were boiled and the precipitate collected. The crude *p*-nitrobenzeneazo derivative of I (m. p. 210–215°) was obtained in yields decreasing steadily from 36% in the most weakly alkaline medium to a negligible amount (*ca.* 1%) in the most alkaline solution. The purified azo compound formed brown-red needles, m. p. 230–232° (calcd.: C, 64.63; H, 5.08. Found: C, 64.32; H, 5.34). Similar results were obtained even with aniline, the benzeneazo compound forming red needles, m. p. 141–143° (calcd.: C, 76.16; H, 6.39. Found: C, 75.97; H, 6.60).

We are investigating the conditions of the couplings more fully and making a further comparison with related compounds; but it seems desirable to correct at once the impression given in the earlier report that the hydrindene derivative I departs entirely from the behavior characteristic of a phenol having a free ortho position.

CONVERSE MEMORIAL LABORATORY
HARVARD UNIVERSITY
CAMBRIDGE, MASSACHUSETTS
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Allomucic Acid

BY FRED L. HUMOLLER AND WM. F. MCMANUS

Recently we published a paper on the preparation of new derivatives of *l*-allonic and *l*-altronic acids. While we were mainly concerned in this paper with the interesting behavior of allonic acid and its lactones, we also described briefly several new compounds related to the above two acids, among them allomucic acid. Dr. Th. Posternak has been kind enough to point out to us that in 1935 he had published an account of the preparation of allomucic acid from *d*-allonolactone. Unfortunately we had overlooked this publication[1] and the statement in our publication, "Posternak did not report, however, the preparation of allomucic acid," does a grave injustice to Dr. Posternak. After having read his paper no one can doubt Dr. Posternak's claim of priority of the preparation of allomucic acid.

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(1) Posternak, *Helv. Chim. Acta*, **18**, 1283 (1935).

LOYOLA UNIVERSITY
SCHOOL OF MEDICINE
CHICAGO, ILL.

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Hydrogen-Deuterium Exchange in Acetate Solution

BY SYLVESTER LIOTTA AND VICTOR K. LA MER

In the course of a study of acetate-ion catalyzed reactions in heavy water, it became necessary to determine the extent of the exchange between the hydrogens of the methyl group and the deuterium of the solvent. From the results of early investigations[1,2,3] little or no exchange was to be expected, while from later work[4,5] varying degrees of exchange could be expected, depending upon temperature and time of contact.

Heavy water (d^{25}_{25} 1.1000, approximately 93% D) was purified by distillation *in vacuo* to remove possible catalysts. Anhydrous sodium acetate was added to produce a 10% solution. After standing for two weeks in a Pyrex vessel at 25–30°, the solvent was recovered by distillation *in vacuo*. The density was redetermined by filling the same pycnometer. Sodium acetate and acetic anhydride were then added to make a final concentration of 10% and 1%, respectively. After two weeks at 25–30°, the solution was neutralized with caustic soda and the same procedure repeated.

Solvent before addn. of sodium acetate, g.	10.5417
Solvent after first distn., g.	10.5413
Solvent after second distn., g.	10.5420

If any exchange occurs either in slightly acid or slightly alkaline solution at room temperature it is exceedingly slow.

DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY
NEW YORK, N. Y.

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(1) Bonhoeffer, *et al.*, *Z. physik. Chem.*, **B23**, 171 (1933).

(2) Lewis and Schutz, THIS JOURNAL, **56**, 493 (1934).

(3) Klar, *Z. physik. Chem.*, **B26**, 335 (1934).

(4) Hall, Bowden and Jones, THIS JOURNAL, **56**, 750 (1934).

(5) Wynne-Jones, *Chem. Rev.*, **17**, 115 (1935). Results of Turkevich. Table 3, 200 hrs. at 80° yields 85% exchange.

An Improved Method for Synthesizing Isobutyl Ethyl Ether

BY E. M. MARKS, DAVID LIPKIN AND BERNARD BETTMAN

According to Cerchez[1] aliphatic ethers can be synthesized from alkyl sulfates and magnesium alcoholates. In several instances he obtained yields of 60–70%. In preparing isobutyl ethyl ether by this method from diethyl sulfate and magnesium isobutylate, we obtained the product in only about 30% yield.

By substituting sodium for magnesium in the Cerchez method we have succeeded in raising the yield of isobutyl ethyl ether to 70%. Experimental conditions for optimum results are as follows: 93 g. (1.25 mole) of anhydrous isobutyl alcohol is placed in a 500-ml. round-bottomed flask fitted with a reflux condenser and 12.5 g. (0.54 mole) of sodium added. The mixture is allowed to react until refluxing has ceased, after which it is heated in an oil-bath at 120–130° for two and three-quarters hours. At the end of this time a portion of the sodium remains undissolved. The mixture is then cooled to 105–115° and 77.1 g. (0.5 mole) of pure diethyl sulfate added gradually during a two-hour period. Reaction is vigorous and steady refluxing takes place during addition of the sulfate. After all has been added, refluxing is continued for two hours. The reaction mixture is then permitted to cool to room temperature (overnight) after which an equal weight of crushed ice is added, followed by a slight excess of dilute sulfuric acid. The ether is then steam-distilled out of the flask, separated from the aqueous portion of the distillate, given three equal-volume washes of 30% sulfuric acid, to remove most of the unreacted isobutyl alcohol, washed twice with water and dried over anhydrous potassium carbonate. The dried product is then refluxed over sodium ribbon for three hours to remove all traces of alcohol and finally is distilled through a precision fractionating column of the type recommended by Podbielniak.[2] The yield of isobutyl ethyl ether was 70%, based on diethyl sulfate. The boiling point, density and refractive index of our ether agreed with the recorded values[3] within the experimental error.

Several variables in this synthesis have been studied. (1) If the isobutyl alcohol is not dried rigorously, the yield of ether is reduced to

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(1) Cerchez, *Bull. soc. chim.*, **43**, 762 (1928).

(2) Podbielniak, *Ind. Eng. Chem., Anal. Ed.*, **5**, 135 (1933).

(3) Norris and Rigby, THIS JOURNAL, **54**, 2088 (1932).