TABLE II

Sample	O^{18}, %
1. Original H_2O	4.0
2. Water in equilibrium with algae: light run	3.01
3. Water in equilibrium with algae: dark run	3.06
4. CO sample from xanthophyll fraction of photosynthesized (5 hr.) algae (50% carotenoid)	0.245
5. CO sample from xanthophyll fraction of algae kept in the dark (40% carotenoid)	0.233
6. Normal H_2O	0.204[a]

[a] Thode and Smith, National Research Council of Canada, Atomic Energy Project Report MC-57 (revised), May, 1944.

or from the steroid material. It apparently could not result from exchange with hydroxyl groups already present, however, since such exchanges for ordinary alcohols have been shown to be extremely slow.[8] The mass spectrographic analysis was of sufficient accuracy that the additional enhancement of the light run is real for this one experiment, but the result would have to be obtained several times before the enhancement could be regarded as general. The experiment is thus inconclusive; it suggests only that it would be worthwhile to repeat the work with water of high oxygen 18 content (30–50%) so that the various carotenoid pigments could be isolated in pure form in sufficient quantities for mass analysis, and so that more than one experiment could be run. Such experiments might provide a real clue as to the path of oxygen in photosynthesis.

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RECEIVED OCTOBER 23, 1950

The Preparation of 2-Methyl-2,3-dihydrobenzofuran

BY JACOB ENTEL, CLARENCE H. RUOF AND H. C. HOWARD

Alkylated dihydrobenzofurans can be readily produced by refluxing allylic bromides with phenols in the presence of potassium carbonate, rearranging the resulting allyl phenyl ethers to the 2-allylphenols and then closing the ring in the latter with hydrobromic acid.[1] In large scale reactions substitution of the allylic chlorides for the corresponding bromides is economically desirable; such attempts, however, usually result in substantially decreased yields. The use of large quantities of sodium iodide along with the allylic chloride[1] to increase the yields is objectionable due to the cost of the iodide. Reagents cheaper than hydrobromic acid for the ring closure are also desirable.

In the present work a Williamson reaction using allylic chlorides gave yields of allylphenols comparable to those previously obtained with the expensive bromides and a mixture of zinc chloride with hydrochloric acid was successfully substituted for the hydrobromic acid in the ring closure.

Experimental

To 2.5 liters of absolute methanol in a 5-liter 3-necked flask fitted with a reflux condenser and mercury-sealed stirrer was slowly added 235 g. (10.2 moles) of sodium in small pieces. Then 940 g. of phenol (10 moles) in 1 liter of absolute methanol was added slowly and followed by 890 ml. of allyl chloride. After refluxing for 30 hours with stirring, the methanol was distilled off and the organic material was filtered free of precipitated sodium chloride. After washing with 10% potassium hydroxide and drying over anhydrous potassium carbonate, the allyl phenyl ether was fractionated *in vacuo;* yield of the ether 1080 g. (80.6% yield) with b.p. 85 (19 mm.) and $n^{25}D$ 1.5185.[1]

After rearranging the ether by heating as described by Tarbell,[1] 300 g. of the 2-allylphenol was dissolved in 1200 ml. of glacial acetic acid and mixed with 180 g. of anhydrous zinc chloride in 600 ml. of concentrated hydrochloric acid. After refluxing for 30 minutes the mixture was cooled and poured into 2.5 liters of cold water. The organic layer was separated, washed with 10% aqueous potassium hydroxide, extracted with ether and fractionated through a 60-plate column to give 155 g. (51.5% yield) of 2-methyl-2,3-dihydrobenzofuran, b.p. 197° (740 mm.), $n^{25}D$ 1.5284.[1] Triplicate runs gave the same yields.

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RECEIVED OCTOBER 20, 1950

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[1] D. S. Tarbell. "Organic Reaction," edited by R. Adams, Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 22-26.

A New Short-Lived Isotope of Cesium[1]

BY RICHARD W. FINK AND EDWIN O. WIIG

A search has been made for neutron-deficient Cs^{128}, previously expected to be quite short-lived.[2] Spectroscopically pure cesium chloride was bombarded for 2 hours with 96 Mev. protons in the Rochester 130-inch cyclotron in order to prepare 2.4 day Ba^{128}, originally reported[3,4] to decay by emission of 3.0 Mev. positrons through hitherto unknown Cs^{128} to stable Xe^{128}.

Radioactive barium was isolated from the CsCl target by a chemical procedure involving three precipitations of barium chromate from a buffered ammonium acetate–acetic acid solution with extensive washings with 1% ammonium acetate to free it from target CsCl. The $BaCrO_4$ was next dissolved in 2 *M* hydrochloric acid, and the chromate reduced by boiling with excess hydroxylamine hydrochloride. This was followed by precipitation of chromic hydroxide with ammonium hydroxide. Finally, the barium chloride solution was evaporated and ignited lightly to expel ammonium salts and the barium activities taken up in a drop of HCl. About 200 milligrams of $BaCl_2$ crystals was then added and periodically the cesium daughters growing in were extracted with concentrated HCl from the solid $BaCl_2$. Over a period of 9 days after bombardment, a total of 16 such parent–daughter separations were performed.

A typical decay curve of the cesium daughters so isolated is shown in Fig. 1, where the half-lives observed were 10 day Cs^{131}, daughter[5] of 12 day Ba^{131}; 31 hour Cs^{129}, daughter of 2.0 hour Ba^{129}; and new Cs^{128}, daughter of 2.4 day Ba^{128}. The best value for the half-life of Cs^{128} is an average of 11 different determinations and is 3.13 ± 0.2 minutes. The time lapse between cessation of bombardment and completion of chemical separa-

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[1] This work was performed under contract with the U. S. Atomic Energy Commission.

[2] R. W. Fink, F. L. Reynolds and D. H. Templeton, *Phys. Rev.*, **77**, 614 (1950).

[3] C. C. Thomas, Jr., and E. O. Wiig, THIS JOURNAL, **72**, 2818 (1950).

[4] R. W. Fink and D. H. Templeton, *ibid.*, **72**, 2818 (1950).

[5] K. Way, *et al.*, *Nuclear Data*, National Bureau of Standards Circular 499 (1950).

tion was 3.5 hours, and since appearance of 5.5 hour Cs^{127} was not observed, formation of Ba^{127}, which is expected to be shortlived, did not occur in bombardment of CsCl with 96 Mev. protons.

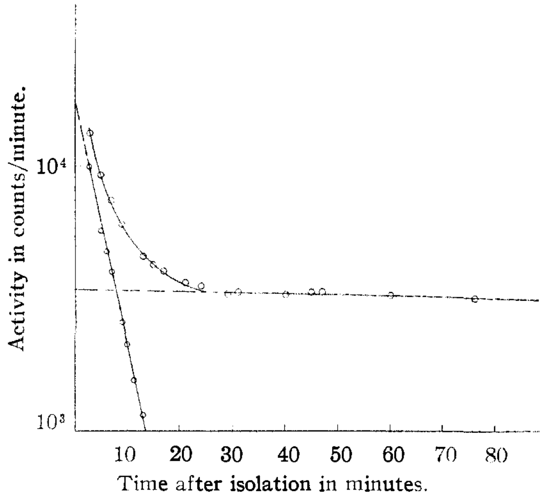

Fig. 1.

The combined yield of Cs^{128} plus Cs^{129} daughters, after subtraction of 10 day Cs^{131}, is shown in Fig. 2, where in each case the yield is that from extrapolation to instant of isolation from barium parents. On this curve, portions marked A represent the presence of 31 hour Cs^{129}, arising from 2.0 hour decay of Ba^{129}, while portion B shows only 3.13 minute Cs^{128} daughter, arising from decay of 2.4 day Ba^{128}. The genetic relationships for these activities are therefore proved.

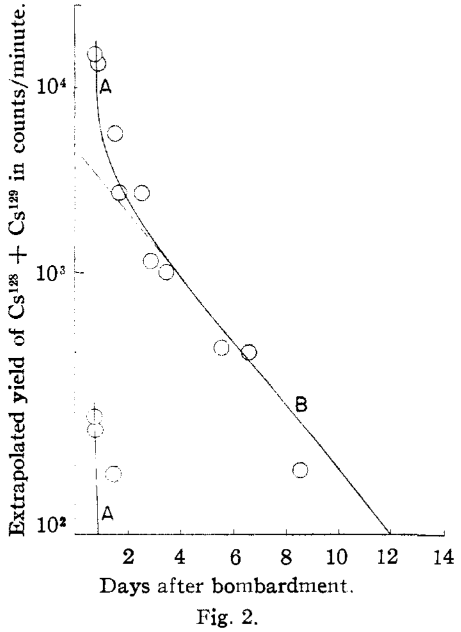

Fig. 2.

No radiations of Cs^{128} have yet been characterized, but one expects that since Ba^{128} is a long-lived even–even nuclide, Cs^{128} may be the 3 Mev. positron emitter in equilibrium with its parent, as noted in a previous communication.[3]

We are appreciative of the coöperation of Dr. Sidney W. Barnes and the crew of the 130-inch cyclotron in these experiments.

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The Partial Reduction of the Double Bond in 2-Hexenoic Acid by Lithium Aluminum Hydride[1]

BY ROBERT W. FREEDMAN AND ERNEST I. BECKER

The reduction of aliphatic unsaturated acids by means of lithium aluminum hydride has been reported to take place without saturation of the double bond.[2] However, with α,β-unsaturated acids a temperature effect has been reported in that acrylic acid is converted to allyl alcohol at room temperature and in part to *n*-propanol at 100°.[3] The reduction of cinnamic acid led to hydrocinnamyl alcohol even at room temperature[2] unless the lithium aluminum hydride was added to the acid with cooling, in which case cinnamyl alcohol was obtained.[3] The purpose of this work is to report the partial reduction of the α,β-double bond in an aliphatic acid at ordinary temperatures.

Two different samples of 2-hexenoic acid were separately reduced with lithium aluminum hydride. Quantitative bromination[4] of the product showed that 25.0–28.5% saturation of the double bond had occurred.

The mixture of alcohols was separated by adding bromine and fractionally distilling the mixture at reduced pressure. The distillate consisting of *n*-hexanol was converted to the allophanate, m.p. 160–161°, which did not depress the melting point of the authentic allophanate, m.p. 160–161°.[5]

The 2-hexen-1-ol was obtained from the dibromide by treatment with alcoholic potassium iodide[6] and zinc in dilute acetic acid. The allophanate melted at 154.4–155.5° and the 3,5-dinitrobenzoate melted at 64.5–65.5°.

Experimental

All melting points are corrected.

Reduction of 2-Hexenoic Acid.—A solution of 91.2 g. (0.80 mole) of 2-hexenoic acid (purified commercial sample m.p. 32°) in 100 ml. of ether was added dropwise to 45 g. (1.18 moles) of lithium aluminum hydride in 1500 ml. of ether with stirring. Water was added cautiously, cooling with ice, until no further reaction occurred. The mixture was poured into 1200 g. of water and ice containing 133 g. of sulfuric acid and the aqueous layer extracted with three 250-ml. portions of ether. The combined extracts were washed with saturated potassium carbonate and dried with ignited potassium carbonate. The mixture was distilled using a 20-plate, glass helix-packed column of the total reflux variable take-off type, collecting 46.2 g. (0.46 mole, 58%) of product, b.p. 94.6–100° (95 mm.), $n^{25}D$ 1.4273–1.4300. The major portion distilled at 100° (95 mm.) and its refractive index varied gradually from $n^{25}D$ 1.4293 to $n^{25}D$ 1.4300. Two fractions were found to be 71.5 unsaturated upon titration with bromine.[4]

Isolation of *n*-Hexanol.—A solution of 24.6 g. of the partially saturated 2-hexen-1-ol in 100 ml. of carbon tetra-

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[1] This work was supported by a Frederick Gardner Cottrell grant from the Research Corporation.

[2] R. F. Nystrom and W. G. Brown, THIS JOURNAL, **69**, 2548 (1947).

[3] F. A. Hochstein and W. G. Brown, *ibid.*, **70**, 3484 (1948).

[4] Ben Brae, *Anal. Chem.*, **21**, 1461 (1949).

[5] A. Béhal [*Bull. soc. chim.*, [7] **25**, 473 (1919)] reported a melting point of 165°.

[6] R. Schoenheimer, *J. Biol. Chem.*, **110**, 461 (1935).