

0.5 *N* hydrochloric acid by 2,4-dinitrophenylhydrazine. Pyruvic acid was added as a carrier.

Experiments with chlorella are in progress in which the $C^{*}O_2$ uptake will be measured simultaneously by gas as well as radioactive analysis.

The heavy carbon isotope, C^{13} , when made available in sufficient quantity, undoubtedly will be capable of wider application than the short-lived radio-carbon used in these experiments.

We wish to thank Professors James Franck, Robert Emerson, G. K. Rollefson, C. B. Van Neil, D. R. Hoagland, and Dr. M. Burton for many valuable suggestions.

We are indebted to Professor E. O. Lawrence for the use of the cyclotron which made these experiments possible.

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Summary

Using short lived radioactive carbon, C^{11} , as an indicator, the assimilation of $C^{*}O_2$ by barley has been studied. $C^{*}O_2$ fixation has been observed both in the absence and presence of light.

Leaves kept in complete darkness as well as illuminated leaves formed radioactive carbohydrates. When, however, leaves were placed in the dark for two and one-half to three hours prior to the administration of $C^{*}O_2$ the formation in the absence of light of radioactive carbohydrates could not be detected. The chlorophyll contained radioactivity after exposure to $C^{*}O_2$ in the light but not after exposure in the dark.

The bulk of the radioactive material found in the plant is water soluble and is not carbohydrate, carbonate, keto acids, or pigments.⁶

These results seem to indicate that the cell contains substances, either directly involved in photosynthesis or in respiration, which react with $C^{*}O_2$ reversibly in a non-photochemical process.

A more complete report of these and other experiments now in progress will be reported later.

(6) Note added in proof: experiments in progress demonstrate that in the green algae, chlorella, a considerable fraction of the radioactive substances formed is also non-carbohydrate.

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The Condensation of Propene and Isobutene with Benzene in the Presence of Anhydrous Ferric Chloride

BY W. M. POTTS AND L. L. CARPENTER¹

The reaction of alkenes with aromatic hydrocarbons in the presence of anhydrous metallic halides to form alkylated aromatic hydrocarbons was first observed by Balsohn.² Alkylation with ethene and propene in the presence of aluminum chloride³ and propene and butene with boron fluoride⁴ has been investigated. Ferric chloride usually has been found less satisfactory in the Friedel and Crafts reaction than aluminum chloride, but it has been found more satisfactory in the preparation of ketones.⁵ Fractions of cracked gasoline⁶ were condensed with benzene using ferric chloride and monoalkylated benzenes were obtained.

(1) From a thesis by L. L. Carpenter submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering.

(2) Balsohn, *Bull. soc. chim.*, [2] **31**, 539 (1879).

(3) Berry and Reid, *THIS JOURNAL*, **49**, 3142 (1927).

(4) Sianina, Sowa and Nieuwland, *ibid.*, **57**, 1547 (1935).

(5) Nencki, *Ber.*, **30**, 1766 (1897); Meissel, *ibid.*, **32**, 2419 (1899).

(6) Kuryndin, Voevodova and Rosskazova, *J. Applied Chem. (U. S. S. R.)*, **10**, 877 (1937).

In this investigation, propene and isobutene were condensed with benzene using anhydrous ferric chloride as the catalyst. The ferric chloride was sublimed directly into the reaction flask. Propene was obtained by dehydrating isopropyl alcohol with phosphorus pentoxide and isobutene was prepared by heating *t*-butyl alcohol with oxalic acid. There was no evidence of a reaction between the anhydrous ferric chloride and benzene, but heat was evolved upon the passage of the alkene into the well-stirred mixture. The resulting mixture was filtered and the filtrate distilled using a Snyder⁷ eight-bulb column.

Milligan and Reid⁸ reported an optimum temperature of 70–90° for the condensation of ethene with benzene using aluminum chloride, but with propene and benzene at 80° using ferric chloride, there was no condensation. This indicates a lower optimum temperature for ferric chloride. With an excess of benzene, very little diisopropylbenzene is formed. Equimolar quantities of isobutene and benzene with ferric chloride yield *t*-butylbenzene principally; two moles of isobutene to one of benzene yields 1,4-di-*t*-butyl-

(7) Hill and Ferris, *Ind. Eng. Chem.*, **19**, 379 (1927).

(8) Milligan and Reid, *THIS JOURNAL*, **44**, 206 (1922).

benzene as the principal product. There was a marked absence of by-products.

Isobutene was condensed with benzene using aluminum chloride under the same conditions employed with ferric chloride. There was more polymerization of the isobutene and the yield of alkylated benzenes was 11% smaller.

To investigate the relative catalytic activities of ferric and aluminum chlorides on alkenes, two moles of isobutene was passed into separate 100-ml. portions of carbon disulfide containing 0.15 mole of the chlorides. With aluminum chloride, 27 ml. of a product was obtained which distilled between 145–260°, while with ferric chloride, only 10 ml. was obtained and this had a boiling range of 100–228°.

With propene and excess benzene and 0.3 mole of ferric chloride, 91% of the condensation products was isopropylbenzene, b. p. 152–153°, n_D^{20} 1.4930.⁹

With isobutene and benzene in equimolecular ratios and 0.3 mole of ferric chloride, 89% of the condensation products was *t*-butylbenzene, b. p. 167–168°, n_D^{20} 1.4960.⁹ It was converted to the acetamino derivative¹⁰ which melted at 168–170°.

(9) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, N. Y., 1926, Vol. I, p. 277.

(10) Ipatieff and Schmerling, *THIS JOURNAL*, **59**, 1056 (1937); Simons and Archer, *ibid.*, **60**, 986, 2952 (1938).

Two moles of isobutene with one of benzene and 0.15 mole of ferric chloride gave 65% of a solid product which was identified as 1,4-di-*t*-butylbenzene since it melted at 75°; the product obtained by nitrating with fuming nitric and concd. sulfuric acids at 25° melted at 190.5°. The yellow product obtained by oxidation with chromic anhydride in glacial acetic acid sublimed at 100°. This agrees with the properties of 1,4-di-*t*-butylbenzene.¹¹ The solid derivative from the aluminum chloride catalyzed reaction was identical with the product obtained with ferric chloride as shown by a mixed melting point.

Conclusions

1. Ferric chloride will effect condensation of propene and isobutene with benzene at room temperature.

2. Condensation takes place at room temperature in greater yields than at higher temperatures.

3. Ferric chloride produces a larger yield of alkylated benzenes and less polymerization than aluminum chloride.

(11) Beilstein, 4th ed., Vol. V, p. 454.

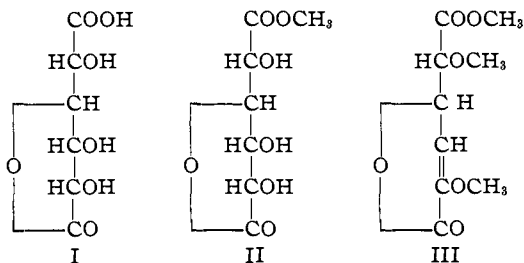
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Saccharolactone Methyl Ester

BY RICHARD E. REEVES

Crystalline saccharolactone (I) recently has been proved by Schmidt and Günthert¹ to be the 3,6-monolactone of saccharic acid. On mild treatment with diazomethane saccharolactone was found to yield a crystalline methyl ester (II), m. p. 113–114°. The structure of the ester was established by applying the procedure of Jackson and Hudson^{1a} as used by Schmidt and Günthert: namely, the isolation of oxalic and *d*-tartaric acids following periodic acid cleavage (between C₄–C₅) and subsequent oxidation with bromine in the presence of calcium carbonate.



(1) O. Th. Schmidt and P. Günthert, *Ber.*, **71**, 493 (1938).

(1a) E. L. Jackson and C. S. Hudson, *THIS JOURNAL*, **59**, 994 (1937).

Saccharolactone methyl ester (II) may be saponified to potassium acid saccharate, or converted to saccharic acid diamide. It gives a crystalline benzylidene compound whose structure has not been determined. The ester also reacts further with ethereal diazomethane to give the unsaturated lactone (III), m. p. 87°, which was previously described by Schmidt, Zeiser and Dippold.²

Experimental

All melting points reported in this paper were observed in a modified Fischer-Johns apparatus mounted on the stage of a polarizing microscope. Specific rotations were determined with the D-line of sodium light and at 26° unless otherwise specified.

Saccharolactone Methyl Ester.—Five grams of saccharolactone,^{3,4} m. p. 132–134°,⁵ was dissolved at room temperature in 350 cc. of dry methanol, and the solution immediately cooled in an ice-bath. To this was added a cold ethereal solution of diazomethane until a faint yellow coloration persisted for a few minutes after thorough mixing.

(2) O. Th. Schmidt, H. Zeiser and H. Dippold, *Ber.*, **70**, 2402 (1937).

(3) H. Kiliiani, *ibid.*, **58**, 2344 (1925).

(4) K. Rehorst and H. Scholz, *ibid.*, **69**, 520 (1936).

(5) A lower melting sample of saccharolactone failed to yield the crystalline ester until purified by recrystallization from ether.