

quaternary salt which upon treatment with silver oxide and heating furnishes butadiene-2,3-C¹⁴.

Terminal-labeled butadiene-1,4-C¹⁴ can be made from carboxyl-labeled succinic acid³ utilizing steps (b) through (e) described above.

Experimental

Tetramethylene-2,3-C¹⁴-bis-[trimethylammonium Bromide].—To 1.18 g. (10 millimoles) of succinic acid-2,3-C¹⁴ were added 10 ml. of absolute ethanol, which previously had been saturated with dry hydrogen chloride at 10°, and then 40 ml. of benzene. The reaction mixture was heated to boiling and the water removed with the aid of a "moisture test receiver." After refluxing 15 hours the excess ethanol and a trace of water were removed by distillation, whereas the bulk of the benzene was taken off under vacuum (15 mm.) at room temperature. The ester was transferred to a dropping funnel with 25 ml. of absolute ether. Reduction of the ester was accomplished by adding it dropwise to a well-stirred solution of one gram of lithium aluminum hydride in 150 ml. of absolute ether. After the last addition, the mixture was refluxed one hour before the excess hydride was decomposed by the dropwise addition of water. Sufficient 6 *N* hydrochloric acid now was added to obtain a clear solution and then the 1,4-butanediol-2,3-C¹⁴ was removed by a 74-hour continuous ether extraction. The ether extract containing the diol was transferred to a Cheronis micro porous disperser apparatus and the solvent removed in a stream of nitrogen. Ten milliliters of water was added and the mixture saturated with gaseous hydrogen bromide at 10°. Upon heating the solution to 90–95° while still passing in hydrogen bromide, a cloudiness developed and gradually the heavy 1,4-dibromobutane-2,3-C¹⁴ settled out. After two hours, heating was discontinued, the solution cooled, and the dibromide extracted with ether (five 30-ml. portions). The ethereal solution was washed with brine containing sodium bicarbonate and then dried over calcium sulfate.

Following removal of the drying agent the solution was evaporated at 60° under anhydrous conditions in a 250-ml. ground-glass erlenmeyer flask. To the 1,4-dibromobutane-2,3-C¹⁴ were added 25 ml. of absolute ethanol which had previously been saturated at 10° with anhydrous trimethylamine. The mixture was refluxed for one hour under anhydrous conditions and the excess trimethylamine was allowed to escape through a mercury bubbler. After cooling the mixture, 200 ml. of absolute ether was added and the white precipitate allowed to settle overnight at 4°. The solid was collected by filtration through a sintered glass funnel, followed by extensive washing with absolute ether. The yield of diquaternary salt was 2.16 g. or 65% based on succinic acid.

Butadiene-2,3-C¹⁴.⁴—One and eight-tenths grams of the diquaternary salt was dissolved in 15 ml. of water, and silver oxide from 2.5 g. of silver nitrate and 10 ml. of 8% potassium hydroxide was added. After vigorous stirring the precipitate was filtered off. The decomposition of the substituted ammonium hydroxide was carried out by heating the aqueous solution to boiling (Glas-Col heater temperature—160°) in a stream of helium. Some of the water vapor in the gas stream was removed by a cold-water condenser and the trimethylamine absorbed by bubbling through 3 *N* sulfuric acid. The butadiene-2,3-C¹⁴ was collected in traps cooled by liquid nitrogen. As the decomposition proceeded the temperature was allowed to rise and as the reaction went to completion the temperature of the Glas-Col heater rose to 250°. The butadiene-2,3-C¹⁴ was dried by vacuum distillation (10⁻⁴ mm.) through "indicating" drierite (fifteen passes). A yield of 4.55 millimoles (84%) of butadiene-2,3-C¹⁴ based on the diquaternary salt was obtained. The vapor pressure of the product was 9.65 cm. at -46°, as compared with 9.50 cm. for a sample of ordinary butadiene (99% pure). The over-all yield of butadiene-2,3-C¹⁴ from radioactive carbon dioxide was 49%.

Establishment of Purity of Butadiene-2,3-C¹⁴.—In addition to determining the purity of the tagged butadiene by vapor pressure determination of successive fractions, the specific activity was found of various intermediates in the synthesis, of a derivative, and of a degradation product of butadiene-2,3-C¹⁴.

(4) Willstätter and Heubner, *Ber.*, **40**, 3869 (1907).

By use of the reaction between labeled butadiene and maleic anhydride,⁵ *cis*-Δ⁴-tetrahydrophthalic anhydride-4,5-C¹⁴ was prepared in almost quantitative yield. The material was recrystallized until the assay for C¹⁴ gave a constant specific activity.

TABLE I

| Compound | Microcuries of C ¹⁴ per millimole of compound |
|--|--|
| Ethylene-1,2-C ¹⁴ | 1.63 |
| Succinic acid-2,3-C ¹⁴ | 1.63 |
| Tetramethylene-2,3-C ¹⁴ -bis-[trimethylammonium bromide] | 1.64 |
| Butadiene-2,3-C ¹⁴ | 1.64 |
| <i>cis</i> -Δ ⁴ -Tetrahydrophthalic anhydride-4,5-C ¹⁴ | 1.65 |
| Glyoxal-1,2-C ¹⁴ -2,4-dinitrophenylosazone | 1.64 |

Another check on the purity and also the position of labeling of butadiene-2,3-C¹⁴ was obtained when the diene was degraded by use of ozone. Radioactive glyoxal was isolated as the glyoxal-1,2-C¹⁴-2,4-dinitrophenylosazone, m.p. 320–322° (dec.), which was purified by repeated crystallization.

Radioactive and Chemical Assays.—The compounds listed in Table I were burned to carbon dioxide and the radioactive gas collected in traps cooled by liquid nitrogen. After the oxidation was complete, the amount of carbon dioxide was determined manometrically (the carbon content of all compounds was within 0.3% of the theoretical values) and then transferred to an evacuated ionization chamber using vacuum-line technique. All radioactivity measurements were made by using an ion-chamber in conjunction with a vibrating reed electrometer.⁶

(5) Farmer and Warren, *J. Chem. Soc.*, 897 (1929).

(6) Palevsky, Swank and Grenchik, *Rev. Sci. Instruments*, **18**, 298 (1947).

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Some Observations on Ammonium Tetrafluoroborate

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In a research project involving the use of ammonium tetrafluoroborate, the following physical and chemical properties were observed. These properties are reported inasmuch as most of them have not appeared in the literature and the others are not in accord with previous observations.²

The ammonium tetrafluoroborate was obtained as the technical grade supplied by the General Chemical Company. Only ammonium tetrafluoroborate which had been purified by four crystallizations from water solutions was used in these studies. The purified salt was analyzed by the usual micro-analytical procedures and found to contain 3.91% hydrogen and 13.12% nitrogen compared with the theoretical values of 3.85 and 13.36, respectively.

The presence of the tetrafluoroborate ion in the purified salt was established by its precipitation as the grayish-white compound, nitron tetrafluoroborate. It was impossible to obtain the fine green needles (which upon standing for some time turn yellow) described by Lange.³ In order to check the procedure, aqueous solutions of different concentrations of tetrafluoroboric acid, hexamminechromium(III) tetrafluoroborate, hexamminecobalt(II) tetrafluoroborate and hexam-

(1) Naval Research Laboratory, Washington, D. C.

(2) H. S. Booth and D. R. Martin, "Boron Trifluoride and Its Derivatives," John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 108–111.

(3) W. Lange, *Ber.*, **59**, 2107, 2432 (1926).

minenickel(II) tetrafluoroborate were treated with the stock solution of nitron acetate. Only with an aqueous solution of tetrapyridinecopper(II) tetrafluoroborate did the test fail to give the grayish-white precipitate.

The above precipitate after being washed thoroughly, dried at 120° and analyzed by the usual microanalytical procedures was found to contain 60.02% carbon, 4.04% hydrogen and 14.39% nitrogen compared with the theoretical values for $C_{20}H_{16}N_4HBF_4$ of 59.97, 4.28 and 14.00, respectively.

The melting point of the grayish-white crystals was found to be 228–229° (uncor.) compared with values of 224.5°⁴ and 227°⁵ reported for the green needles.

Lange⁵ observed that the light green needles were obtained only with nitron purchased from Kahlbaum prior to 1935 or from Eastman Kodak Company prior to 1940. After these dates, the nitron from each of these companies produced the grayish-white precipitate with the tetrafluoroborate ion. Lange believes that the earlier samples of nitron must have contained an impurity which reacted with some material apparently always present in solutions containing tetrafluoroborate ion (perhaps a product of hydrolysis) to give the green color. Crystals of nitron tetrafluoroborate up to 2 cm. in length have been grown which are optically clear but possesses a light yellow to brown color.⁵ The melting point observed for grayish-white solid is higher than that observed for the green needles, which supports this hypothesis.

It was of interest to learn if fused ammonium tetrafluoroborate were an electrolyte. Since ammonium tetrafluoroborate is reported to sublime between 230°⁶ and 250°⁷, heating curves were investigated (with and without conductivity measurements) by placing about 90 g. of the purified salt in a polished copper cylindrical liner in a steel bomb. A copper thermocouple well containing a calibrated single-junction, iron-constantan thermocouple was buried in the sample and connected to a Leeds and Northrup Micromax recording potentiometer. A transition point was observed at 205 ± 3°. A transition from the rhombic to an isotropic crystalline state has been observed at 236° using a micro sample on a hot stage microscope.⁸ The latter value is above the lower value reported for the sublimation temperature.⁶ If the rate of heating were too fast, greater error in ascertaining the transition temperature would be encountered using a micro sample than one of 90 g.

The triple point of ammonium tetrafluoroborate was observed at 487 ± 3°. There was an excellent correlation between the break in the heating curve and the sudden increase in conductivity.

A faint odor of ammonia was detected upon opening the bomb after the thermal data were obtained. The salt was a hard, fused, white mass which was tinged very slightly with a small amount of a very pale blue color at the interface of the salt and the copper liner. In the course of this investigation, it was observed also that fused ammonium tetrafluoroborate attacks zirconia and Pyrex glass but not silver or platinum.

Saturated solutions of ammonium tetrafluoroborate in purified acetone, benzene, chloroform, ethanol, pyridine and tetrachloroethane were prepared and allowed to stand in closed vessels at room temperature for two weeks. Fifty-milliliter samples of the supernatant solutions were allowed to evaporate in tared evaporating dishes and the weight of the ammonium tetrafluoroborate residue ascertained. It was found that the solubility of ammonium tetrafluoroborate in each of the above solvents (except ethanol) is less than 2 mg. per 100 ml. of solvent.

(4) E. Wilke-Dörfert and G. Balz, *Z. anorg. Chem.*, **159**, 197 (1927).

(5) W. Lange, Procter and Gamble Co., Ivorydale, Ohio, private communication.

(6) G. H. Curtis, *Iron Age*, **155**, 54 (1945).

(7) W. E. White, (to Aluminum Company of America), U. S. Patent 2,403,148 (July 2, 1946).

(8) D. Vörländer, J. Hollatz and J. Fischer, *Ber.*, **65B**, 535 (1932).

In contradiction to the report of Berzelius⁹ that ammonium tetrafluoroborate is *freely* soluble in ethanol, it was found that the solubility is 0.7 g. per 100 g. of ethanol. Ethanol and aqueous solutions of ammonium tetrafluoroborate are electrolytes.

(9) J. J. Berzelius, *Ann. physik. Chem.*, **78**, 113 (1824); *Stockholm Acad. Handl.*, 284 (1823).

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The Reaction of Anilidophosphoric Chlorides with Aryl Grignard Reagents¹

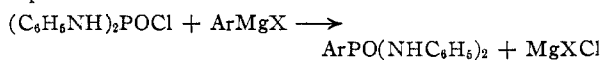
By D. C. MORRISON

These reactions were studied as a possible approach to the synthesis of aromatic phosphonic acids, $ArPO(OH)_2$ from phosphorus oxychloride as starting material. The object of these preparations was to obtain the phosphonic acids in radioactive form from phosphorus oxychloride containing P^{32} .² It was then desired to observe the distribution of these compounds in rats, especially in animals bearing tumors in the hope that some localization in the latter would occur.

These syntheses are analogous to the phosphinic acid preparations of Michaelis and Wegner³ and of Kosolapoff,⁴ where a Grignard reagent is allowed to react with a substituted monoamidophosphoric chloride. The amide groups replace one chlorine atom of phosphorus oxychloride leaving the other two chlorines free to react with the reagent. The product is a substituted amide of a phosphinic acid and can be hydrolyzed to the free acid. These workers employed piperidine and diethylamine, respectively, as the amines used to form the amidochlorides.

In the present work, the amidochlorides were derived from aniline and the type reaction was extended to the use of a substituted diamidophosphoric monochloride. The action of arylmagnesium bromides on monoanilido phosphoric dichlorides gives very poor yields of diaryl phosphinic anilides while the interaction of the Grignards and dianilidophosphoric monochloride gives fair yields of aryl phosphonic dianilides. Hydrolysis of these anilides furnishes the corresponding phosphinic and phosphonic acids. The latter reaction enables phosphonic acids to be prepared from phosphorus oxychloride.

The reaction of dianilidophosphoric chloride with the reagent apparently proceeds according to the equation



An over-all yield of 40% of benzenephosphonic acid dianilide (based on $POCl_3$) in the two-step process was obtained with the phenyl Grignard. A considerable excess of the Grignard reagent is

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(2) Axelrod, *J. Biol. Chem.*, **176**, 295 (1948).

(3) Michaelis and Wegner, *Ber.*, **48**, 316 (1915).

(4) Kosolapoff, *This Journal*, **71**, 369 (1949).