dried over anhydrous sodium sulfate, filtered and the filtrate evaporated to dryness *in vacuo*, the residual crystals were collected and recrystallized from boiling ethylene dichloride. The colorless crystals so obtained melted at 109–110°. A mixed melting point with an authentic sample of the nitrobase of the *erythro* series gave no depression.

Calcd. for $C_9H_{12}N_2O_4$: N, 13.20. Found: N, 13.28.

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Preparation of Macrocrystalline Fluorapatite Containing Radioactive Phosphorus

BY GLENN V. ELMORE AND E. O. HUFFMAN

RECEIVED APRIL 5, 1952

The properties of fluorapatite, $Ca_{10}(PO_4)_6F_2$, are important in the technology of phosphate fertilizers, a field with which the Tennessee Valley Authority is concerned. The thermodynamic properties of fluorapatite were evaluated recently,[1] and other properties of the compound are being studied.

Fluorapatite containing radioactive phosphorus was needed in a study of the kinetics of solution of the apatite. A product of high specific activity was wanted, and existing methods of preparation[2,3] were considered unsuitable because of the difficulty of conducting such operations as mixing, grinding and screening without undue hazard to the operator. A method devised for the preparation of macrocrystals of radioactive apatite in a high degree of purity is the subject of the present report.

Method of Crystallization.—Fluorapatite can be prepared from a melt of its components in a flux. Thus, when a melt of an orthophosphate of calcium or potassium in an excess of calcium fluoride was heated at 1400° in a vacuum, part of the solvent calcium fluoride was vaporized, and crystals of fluorapatite were formed. Removal of the excess calcium fluoride was incomplete, however, even after 24 hours of heating.

Substitution of alkali metal fluorides for the calcium fluoride resulted in melts from which the non-apatite fluoride could be evaporated completely at 1200° in a vacuum. Although good fluorapatite was obtained with either sodium fluoride or potassium fluoride, the sodium salt was preferred because it was less hygroscopic.

When the fluoride was evaporated from the melt in an externally heated porcelain tube, the vapor attacked the porcelain and caused contamination of the fluorapatite with silica. To avoid this contamination, the platinum crucible containing the charge was suspended in a vertical glass tube and heated by induction. The glass wall remained cool and did not contaminate the apatite. The fluoride vapor condensed on the glass.

The melt had a pronounced tendency to creep over the edge of the crucible during evaporation of the solvent. Crystals formed on the outside of the container, and the inside was essentially empty at the end of an experiment. This creeping of the melt removed part of the solvent from the hot interior of the crucible to the cooler exterior where its evaporation was incomplete. Complete evaporation of the solvent in 5 hours was effected by suspending the crucible and its contents inside a second platinum crucible of slightly larger diameter and heating the outer crucible at 1200° by induction. This arrangement provided an external source of heat for the crucible containing the charge. Good crystals of fluorapatite were deposited on the outside of the inner crucible.

The method finally developed for the crystallization of fluorapatite was shown to be equally suitable for the preparation of macrocrystalline chlorapatite from a solution of its components in sodium chloride or potassium chloride.

In subsequent application of the method to the growth of crystals of fluorapatite, a high-quality laboratory preparation of microcrystalline fluorapatite was the source of the apatite components. The microcrystalline material conveniently supplied the components in correct ratio and essentially free of impurities. The method of its preparation has been described.[1]

A spectrographic analysis of a typical macrocrystalline fluorapatite prepared from the smaller crystals showed the following percentages of impurities: Na_2O, 0.14; MgO, 0.1; SrO, 0.01; SiO_2, 0.05; Fe_2O_3, < 0.01; Al_2O_3, < 0.01; CuO, < 0.002. The preparation gave a strong apatite pattern[4] by X-ray diffraction. No other crystalline phase was detected in the X-ray analysis.

A microscopic examination showed that the colorless rod crystals of fluorapatite were optically clear and free of growth imperfections other than elongated air cavities. The crystals ranged from 1 to 5 mm. in length. The (0001) cleavage was prominent. The crystals were hexagonal and uniaxial (−) with $n_\epsilon = 1.627$ and $n_\omega = 1.631$. Traces of platinum, calcium oxide and α-tricalcium phosphate were detected as crystalline impurities. A 3-hour digestion of the apatite with a neutral solution of ammonium citrate at 60° removed all the calcium oxide and α-tricalcium phosphate except isolated fine-grained deep-seated inclusions.

Incorporation of P^{32}.—To prepare radioactive fluorapatite, 0.1 g. of the microcrystalline apatite was dissolved in several milliliters of concentrated nitric acid and mixed with 2 ml. of a solution containing 50 mc. of carrier-free P^{32} as phosphate in nitric acid.[5] The amount of P^{32} was minute in proportion to the phosphorus from the apatite but was enough to impart a high specific activity to the final product.

The solution was evaporated in a platinum crucible without boiling. The nitrate in the residue was decomposed at red heat. Sodium fluoride then was added, and fluorapatite was crystallized from the mixture in the manner described.

The radioactive crystals, upon microscopic examination, appeared to be of the same high quality as that reported for the non-radioactive preparations. The refractive indexes of the two types of preparations were identical.

Acknowledgment.—K. L. Elmore suggested the crystallization of fluorapatite from an alkali fluoride as a solvent. J. R. Lehr made the microscopic examinations, J. P. Smith the X-ray examinations and Frances M. Youngblood the spectrographic analyses.

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(1) E. P. Egan, Jr., Z. T. Wakefield and K. L. Elmore, THIS JOURNAL, **73**, 5581 (1951).

(2) G. Chaudron and R. Wallaeys, *Bull. soc. chim. France*, D132 (1949).

(3) R. Wallaeys and G. Chaudron, *Compt. rend.*, **230**, 1867 (1950).

(4) St. Náray-Szabó, *Z. Krist.*, **75**, 387 (1930).

(5) Supplied by Isotopes Division, United States Atomic Energy Commission, Oak Ridge, Tenn.

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Bromination, Iodination and Phenylation of Thianaphthenes

BY RUSSELL GAERTNER

RECEIVED APRIL 28, 1952

In continuation of studies of the effect of a "blocking" group in the ortho position on abnormal reactions of arylmethyl Grignard reagents,[1] 2-bromo-3-(bromomethyl)-thianaphthene (I) was obtained by the action of N-bromosuccinimide on 2-bromo-3-methylthianaphthene. I appeared to react normally in the cyclic Grignard reactor, but only polymers and traces of impure products could be isolated from the reactions with ethyl chlorocarbonate and formaldehyde. The presence of a trace of a coupling product, presumably 1,2-bis-(2-

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(1) R. Gaertner, THIS JOURNAL, **74**, 2991 (1952).

bromo-3-thianaphthenyl)-ethane, also indicated the presence of a Grignard reagent.

2-Iodothianaphthene was prepared by the action of iodine on 2-thianaphthenyllithium[2]; thianaphthene was converted directly to 3-iodothianaphthene by iodine and mercuric oxide. The structures of both isomers were confirmed by carbonation of the Grignard reagents. Attempts to chloromethylate the iodo compounds failed.

Decomposition of N-nitrosoacetanilide in excess thianaphthene gave as the only isolable product 2-phenylthianaphthene, which was desulfurized by Raney nickel to bibenzyl. Although this appears to be the first report of free-radical substitution in the thianaphthene series, the low yield and the fact that other isomers may have been present in the intractable mixture preclude any complete conclusion concerning orientation at this time.

Acknowledgment.—This work was supported by a grant-in-aid from the Graduate School and made possible by gifts of thianaphthene by Jefferson Chemical Company, New York, N. Y.

Experimental[3]

2-Bromo-3-(bromomethyl)-thianaphthene.—A solution of 12.4 g. of 2-bromo-3-methylthianaphthene,[4] 9.7 g. of N-bromosuccinimide and 0.4 g. of benzoyl peroxide in 130 ml. of carbon tetrachloride was heated under reflux for 90 minutes, cooled, filtered, and the solvent replaced by ligroin (b.p. 70–90°) by distillation. A total of 14.4 g. (86%) of needles separated; m.p. 97–99.5°, b.p. 148–151° (0.5 mm.) (dec.). After recrystallization and sublimation at 100° (0.1 mm.), 2-bromo-3-(bromomethyl)-thianaphthene melted at 97.6–98.6°.

Anal. Calcd. for $C_9H_6Br_2S$: C, 35.32; H, 1.98. Found: C, 35.55; H, 2.23.

When 19.3 g. of the halide was converted in the cyclic reactor,[5] titration of an aliquot after hydrolysis indicated a 67% yield of reagent, which gave a green Gilman test. The reagent was allowed to react with ethyl chlorocarbonate and formaldehyde. In the first case, the acidic fraction obtained by alkaline hydrolysis was polymeric and had a wide melting range (about 200–240° with decomposition). From the neutral material, by recrystallization from benzene–hexane, was isolated 1.2 g. of crude 1,2-bis-(2-bromo-3-thianaphthenyl)-ethane. By recrystallization from ethanol–benzene, colorless crystals were obtained, m.p. 195–196°.

Anal. Calcd. for $C_{18}H_{12}Br_2S$: C, 47.80; H, 2.68. Found: C, 48.04; H, 2.64.

By conversion of 21.3 g. of the bromide, and reaction with formaldehyde, only a taffy-like polymer was obtained.

3-Iodothianaphthene.—To a solution of 44.4 g. of thianaphthene in 70 ml. of benzene, heated at 55–65°, were added during an hour in small alternate portions with stirring 54 g. of yellow mercuric oxide and 76 g. of iodine. Filtration and aspiration of the benzene, followed by distillation of the residue, gave, in addition to 15.7 g. of recovered starting material, 39.6 g. (71%, based on recovery) of a dark brown liquid which was decolorized by passing a solution in benzene through a column of charcoal and alumina. When redistilled, 3-iodothianaphthene (d^{20}_4 1.898, $n^{20}_D > 1.7$) was a very light yellow mobile liquid boiling mainly at 120–121° (1.6 mm.), which darkened rapidly in the light.

Anal. Calcd. for C_8H_5IS: C, 36.94; H, 1.94. Found: C, 37.11; H, 2.18.

It was recovered unchanged from an attempted chloromethylation at 90° in the presence of zinc chloride, only a trace of higher-boiling material being formed. The iodo compound (19.5 g.) reacted normally with magnesium, forming a nearly immiscible layer under ether. Carbonation yielded 7.4 g. (55%) of 3-thianaphthoic acid, m.p. 176–177.5°. Additional crude material (1.4 g., m.p. 150–165°) from the mother liquors may have contained isomeric acids.

2-Iodothianaphthene.—Thianaphthene (67 g.) was converted to the lithium derivative[2] and this solution was added dropwise with stirring to a mixture of 252 g. of iodine and 100 ml. of ether with cooling in a salt–ice-bath. The mixture was stirred and allowed to warm to room temperature and water was added. The excess iodine was removed from the solvent layer by shaking with sodium thiosulfate solution. The recovered crude thianaphthene weighed 48.2 g. and probably contained butyl iodide. The dark product (37.4 g., 29% based on total starting material), distilled in a sausage flask, boiled principally at 119–120° (1.6 mm.), m.p. 59–62°. Recrystallization from hexane (charcoal) and sublimation at 70° (0.3 mm.) gave nearly colorless crystals, m.p. 63.4–65°.

Anal. Calcd. for C_8H_5IS: C, 36.94; H, 1.94. Found: C, 36.89; H, 2.13.

An attempted chloromethylation failed. Conversion of 13 g. to the Grignard reagent, also ether-immiscible, and carbonation gave an unexpectedly low yield (1.02 g., 12%) of pure 2-thianaphthoic acid, m.p. 242–243°.

N-Nitrosoacetanilide and Thianaphthene.—A solution of 25 g. of the nitrosoamide[6] was dissolved in 200 g. of molten thianaphthene at 32°. The dark red solution (in a 500-ml. flask) began slowly to evolve a gas; when left unattended for 30 minutes, it apparently reacted violently, foaming and spattering almost exactly half of the total reaction mixture onto the desk and floor. Unchanged thianaphthene in the residue was removed by distillation *in vacuo*, followed by 10.5 g. of an amber liquid, b.p. 150–155° (0.3 mm.); it solidified to a slushy mixture. No other distillate could be obtained up to a temperature in the bath of 220°. Recrystallization of the mixture from benzene–methanol and benzene–hexane gave 1.63 g. of white plates, m.p. 171–173°. Further recrystallization and sublimation at 100° (0.1 mm.) gave 2-phenylthianaphthene,[7] m.p. 174.2–175.2°.

Anal. Calcd. for $C_{14}H_{10}S$: C, 79.96; H, 4.79. Found: C, 80.00; H, 5.05.

Further confirmation of the structure was obtained by heating 1.00 g. with about 12 g. of Raney nickel catalyst in 70 ml. of ethanol for 3 hours to give 0.81 g. of colorless crystals, m.p. 49–51° (alone and mixed with authentic bibenzyl).

Only thianaphthene (as 2.5 g. of the picrate) could be isolated from the mother liquors in the original recrystallization. Benzene, hexane, ether, ethanol and methanol were tried unsuccessfully as solvents to obtain another picrate. An attempt to prepare a 1,1-dioxide[8] produced a gummy polymer.

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[2] D. A. Shirley and M. D. Cameron, This Journal, **74**, 664 (1952), prepared this reagent and described a number of its reactions, including that with bromine.

[3] Melting points, but not boiling points, are corrected. Microanalyses were by Micro-Tech Laboratories, Skokie, Illinois.

[4] R. Gaertner, This Journal, **74**, 2185 (1952).

[5] See, for typical procedures, R. Gaertner, *ibid.*, **73**, 3934 (1951).

[6] W. S. M. Grieve and D. H. Hey, *J. Chem. Soc.*, 1797 (1934).

[7] A. W. Horton, *J. Org. Chem.*, **14**, 761 (1949), prepared this compound from 2-phenylthiophene.

[8] F. G. Bordwell, B. B. Lampert and W. H. McKellin, This Journal, **71**, 1702 (1949).

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3-Nitrodurene

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Received February 22, 1952

3-Nitrodurene was first reported by Willstätter and Kubli[1] in 1909 to result from the reaction of 3-iododurene with silver nitrite. The compound was not isolated, but its formation was demonstrated by identifying as 3-aminodurene the

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[1] R. Willstätter and H. Kubli, *Ber.*, **42**, 4159 (1909).