that any significant racemization accompanies the hydrogenation of the olefin with platinum oxide.[5,6]

Dr. E. L. Eliel has pointed out to us that one may compute an upper limit to the rotation of the chloride from the rotation of the ether of α-phenethyl alcohol[7] and from the formation[8] of this ether from optically active chloride. This value is 129° which is probably within the experimental uncertainty of both procedures.

Although Gerrard's preparation of α-phenethyl chloride gives material of high rotation, yields are but about 40%. The rest of the carbinol apparently remains as a phosphoric ester. Extending the reaction time to three weeks does not improve yields. At the completion of the phosphorus oxychloride addition, the reaction mixture is a white viscous mass. Addition of pentane did not affect this or improve yields. A mixture prepared from carbinol (0.125 mole), phosphorus oxychloride (0.125 mole), pyridine (0.375 mole) and chloroform (150 cc.) remained liquid and gave a yield of crude chloride of 70%. On the view that the reaction, as ordinarily run, was limited by unavailability of chloride ion to react with phosphoric esters, a mixture similar to the one above was prepared with the addition of pyridine hydrochloride (0.75 mole per mole of pyridine). Yields of crude chloride of 82% and of purified chloride of 70% were obtained. The rotations are but 86% of those obtained by the unmodified procedure of Gerrard, but for many applications the increased yield will make the procedure advantageous.

Experimental

All rotations are homogeneous and given for 1 dm. For optically pure phenylmethylcarbinol, $\alpha^{25}\mathrm{D}$ 43.7°.[9]

Preparation of α-Phenethyl Chloride.—0.466 mole of phosphorus oxychloride was added to a solution of 1.40 moles of pyridine and 0.466 mole of phenylmethylcarbinol, $\alpha^{25}\mathrm{D}$ $-38.93°$, in 300 cc. of pentane with the temperature maintained at $-10°$ to 0° during the addition. After 16 hours at 5° followed by 24 at 25°, the reaction mixture was decomposed with ice and extracted with ether. After washing, the ether extract was evaporated and pentane added. This solution was washed with three portions of 85% phosphoric acid and then with water. It was dried with potassium carbonate and distilled at 17 mm., b.p. 78–82° (uncor.), yield 43%, $\alpha^{25}\mathrm{D}$ $+97.4$; correcting to optically pure starting material, $\alpha^{25}\mathrm{D}$ $+109°$.

The procedure of improved yields follows: 0.463 mole of hydrogen chloride gas was passed into a solution of 1.07 moles of pyridine and 0.204 mole of phenylmethylcarbinol, $\alpha^{25}\mathrm{D}$ $+10.95°$, in 200 cc. of chloroform, with the reaction mixture kept at $-15°$. 0.204 mole of phosphorus oxychloride was added with the solution at about the same temperature. After a day at room temperatures, it was decomposed with ice. The chloroform layer was extracted with 85% phosphoric acid, washed, dried and distilled at 8 mm., b.p. 68°, yield 70%, $\alpha^{25}\mathrm{D}$ $-23.65°$ or corrected to optically pure carbinol $-94°$.

4-Phenyl-1-pentene was prepared by action of sodium allyl on α-phenethyl chloride following the preparation of 4-methyl-1-decene by Letsinger and Traynham[10] save that the octane was not replaced by hexane and the chloride was added at -45 to $-20°$. From chloride of $\alpha^{25}\mathrm{D}$ 77.89°, 4-phenyl-1-pentene was obtained by fractionation at reduced pressures, $\alpha^{25}\mathrm{D}$ $-5.92°$, $n^{20}\mathrm{D}$ 1.5032. This material undoubtedly contained unreacted chloride. It was hydrogenated over Raney nickel at room temperatures and three atmospheres of hydrogen and then fractionated to give 2-phenylpentane, $\alpha^{25}\mathrm{D}$ $-9.26°$, $n^{20}\mathrm{D}$ 1.4872. The infrared absorption spectrum of this material was indistinguishable from that of an authentic sample of 2-phenylpentane, so that unreacted chloride had been destroyed by hydrogenolysis.

From Cram's value[4] for 2-phenylpentane, $\alpha^{23}\mathrm{D}$ 15.00°, and our measurement of the temperature coefficient, $\alpha^{25}\mathrm{D}$ 14.91°. Whence, the maximum rotation of the chloride is $77.89 \times 14.91/9.26 = 125.4°$.

In other experiments with chloride of lower rotation, the 4-phenyl-1-pentene was fractionated in a small Stedman column: b.p. 187–188° (uncor.), $n^{25}\mathrm{D}$ 1.5020, yield from chloride, about 80%. The sign of rotation and presumably the configuration were inverted from that of α-phenethyl chloride. This product was much freer of unreacted chloride perhaps, in part, owing to decomposition of any unreacted chloride on the metallic packing. From hydrogenation of such material, $\alpha^{25}\mathrm{D}$ 16.1° for optically pure 4-phenyl-1-pentene. This is a lower limit since possibly present was a small amount of unreacted chloride which owing to its much larger rotation of opposite sign would have a rather large effect on the rotation of the 4-phenyl-1-pentene.

Similar preparation of the pentene, but with allylmagnesium bromide replacing sodium allyl, gave pentene whose rotation was but 43% of that prepared *via* sodium allyl.

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The System Thorium Nitrate–Water–Nitric Acid at 25° and the Hydrates of Thorium Nitrate[1]

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The literature on the hydrates of thorium nitrate has long been confused. A dodecahydrate,[4–6] hexahydrate,[7–10] hemihydrate $(Th(NO_3)_4\cdot 5.5H_2O)$,[11] pentahydrate,[12,13] tetrahydrate[5] and dihydrate[14] have all been reported. Since there seemed to be considerable uncertainty as to the composition of the hydrate crystallizing from aqueous solutions, it was deemed advisable to make a more careful study of this system.

The present paper is an investigation of the hydrates of thorium nitrate and the ternary system thorium nitrate–water–nitric acid at 25°. The

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results of these studies show that the stable hydrates of thorium nitrate at 25° are the pentahydrate and the tetrahydrate.

Experimental

Method.—Mixtures of water and nitric acid were saturated with Baker and Adamson Reagent Grade thorium nitrate at a temperature around 70°, and the solutions were then equilibrated in a bath at 25 ± 0.03° for a minimum period of 48 hours. In the low water region "anhydrous nitric acid," and an anhydrous thorium nitrate[15] were used to prepare the solutions. The method of wet residues[16] was used. Thorium nitrate was determined by ignition of the sample to thoria. Water was determined by titration with the Karl Fischer[17] reagent. Nitric acid was estimated by difference. Nitrogen analyses were made using the du Pont nitrometer method.

Solids used for identification purposes and for powder X-ray diffraction pictures were dried between sheets of filter paper.

Materials.—Thorium nitrate, Baker and Adamson Reagent Grade (labeled $Th(NO_3)_4 \cdot 4H_2O$), whose maximum limits of impurities were 0.003% for chloride and 0.01% for sulfate was used. The solid had no well-defined crystalline shape. The hydration was well in excess of the tetrahydrate, and the material evidently contained hydrolyzed salt. *Anal.* ThO_2, 47.15 ± 0.1%; water, 15.90 ± 0.2%. Nitric acid, General Chemical Div., 70%, s p. gr. 1.42, and anhydrous nitric acid, General Chemical Div., "total acidity 100% minimum" were the other materials used.

Discussion

The ternary system $Th(NO_3)_4$–H_2O–HNO_3 at 25° is depicted in Fig. 1. The invariant liquid of the pentahydrate–tetrahydrate pair is at 17.70% water and 28.67% thorium nitrate and that of the tetrahydrate–anhydrous pair at 5.10% water and 21.13% thorium nitrate.

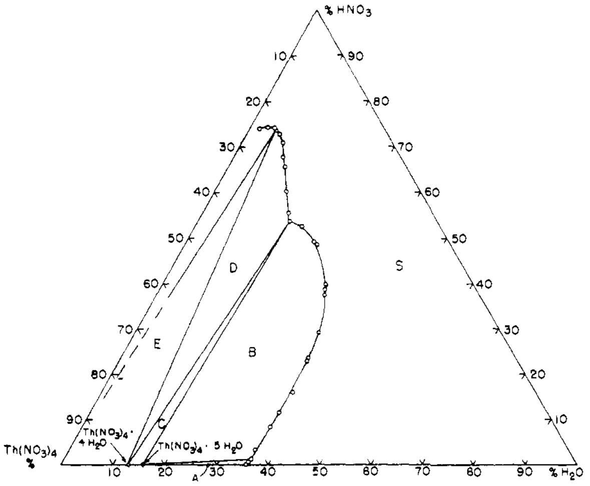

Fig. 1.—The system $Th(NO_3)_4$–HNO_3–H_2O at 25°: A, region of hydrolysis; B, pentahydrate and variable liquid; C, pentahydrate, tetrahydrate and liquid; D, tetrahydrate and variable liquid; E, tetrahydrate, anhydrous phase and liquid; S, homogeneous solution.

Thorium Nitrate Pentahydrate.—Thorium nitrate pentahydrate crystals isolated from the phase studies, and from crystallization experiments at 25° are clear and transparent. They are describable as pyramidal crystals, truncated by basal pinacoids, biaxially positive, and highly birefringent. *Anal.* Calcd.: ThO_2, 46.33%; water, 15.79%. Found: ThO_2, 46.33 ± 0.1; water, 15.79 ± 0.1%. X-Ray diffraction patterns of powdered crystals are different from those of the tetrahydrate.

Thorium Nitrate Tetrahydrate.—Thorium nitrate tetrahydrate isolated from the equilibrium studies, and from crystallizations at 25° (from concentrated nitric acid in a desiccator over concentrated sulfuric acid) is finely crystalline. The solid can be prepared free of nitric acid by pumping at 50° (10 mm.), or by several days desiccation over potash. *Anal.* Calcd.: ThO_2, 47.84%; water, 13.04%. Found: ThO_2, 47.86%; water, 13.09%. The X-ray diffraction pattern of the powdered crystals is different from that of the pentahydrate.

Anhydrous Solid.—The powdered anhydrous solid isolated from the low-water region of the ternary system, and of composition suggested by the "wet residues" tie-line extrapolation to be $Th(NO_3)_4 \cdot 2HNO_3$, showed an X-ray diffraction pattern identical with that of a nitrogen dioxide addition product of thorium nitrate, which had been prepared earlier by a different procedure.[15] Experimental difficulties make it improbable that a solid free of nitrogen dioxide may be prepared by equilibration at 25°. Jander and Wendt[18] have observed that anhydrous nitric acid will decompose at room temperature, even when protected from light and air, and forms a yellow color. We have confirmed this observation. One of the decomposition products must be nitrogen dioxide since a freshly opened container of anhydrous nitric acid was found to contain 5% of the nitrogen as nitrogen dioxide as determined by ceric sulfate titration.[19] Since the nitrogen dioxide addition product seems to be more stable than other possible anhydrous thorium nitrates under these conditions, equilibrium study of the anhydrous end of the ternary system seems impractical at room temperature.

Possible Higher Hydrates.—There has been much variation in the literature on the description of the solid isolated from aqueous solutions. As previously mentioned, it has been variously identified as the dodecahydrate,[4–6] hexahydrate,[7,8] 5.5 hydrate[11] and pentahydrate.[12] It has long been known that when thorium salts dissolve in water, the solutions become acidic. For example, a 0.1 *N* thorium nitrate solution shows a *p*H of 2.46, ample evidence of hydrolysis. The analyses of solids we have isolated from aqueous solutions, and which we believe may be partially hydrolyzed, fit well with the analytical data of the solid Templeton[11] chose to call a hemi-hydrate ($Th(NO_3)_4 \cdot 5.5H_2O$), and with that of Fuhse's hexahydrate.[8]

Solid	ThO_2, %	H_2O, %
$Th(NO_3)_4 \cdot 6H_2O$	44.91	18.36
Templeton's 5.5-hydrate	45.7 ± 0.1	17.5 ± 0.1
Fuhse's hexahydrate	45.5	17.6
Our solids from aq. soln.	45.6 ± 0.2	17.3 ± 0.2
$Th(NO_3)_4 \cdot 5H_2O$	46.33	15.79

These solids are probably one and the same. It is observed that Fuhse[8] and Templeton[11] describe

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their crystals as being truncated octahedra with the main interfacial angle of 142°. This description corresponds with the shape and face angle of the pure pentahydrate crystals, prepared by Hebert and Lister[12] and ourselves.

The data on which our belief is based that the material of this analysis is primarily pentahydrate, with an admixture of some hydrolyzed material and possibly some mother liquor, is essentially the following. All of the material crystallized at room temperature and subjected to X-ray diffraction analysis has shown the pattern of the pure pentahydrate, which indicates a low content of other material. In at least one case, large clear crystals have been obtained, for which the thoria analysis gives 46.24%, and nitrogen analysis gives a nitrate/Th ratio of 3.98, obviously pentahydrate. In cases where cloudy crystals are obtained, small crystals, etc., the analysis approaches the typical values for the usual product from water. If the crystallization is performed at 100° or at 80°, the thoria runs very high (47.2%, 47.5%) without the water content showing appreciable reduction (17.8%, 16.0%) so that material balances calculated on the assumption that the thorium is all present as nitrate run appreciably over 100%. Crystallizations at 25° fail to show this effect definitely, other than that the water values run higher than for the pentahydrate. In view of the fact that second crops of crystals from the same mother liquor tend to give higher thoria values and higher material balances than first crops (presumably by loss of nitric acid through evaporative concentration of the solution), and with the other facts mentioned in this paragraph, some hydrolysis must be assumed. The nitrogen–thorium ratios, however, in the cases where they have been measured, do not deviate significantly from 4. The tendency for large crystals to be cloudy suggests that part of the effect may be due to greater inclusion of mother liquor in the absence of added acid. Typical material crystallized from water and then desiccated at reduced pressure over sulfuric acid gave analyses of 46.64% thoria and 16.28% water, and at a still later time, 46.89% thoria. The thoria values are much too high even for pentahydrate, and the hypothesis of partial hydrolysis seems justifiable. When pentahydrate is allowed to stand over aqueous sulfuric acid, or even water, to raise its water content, and then desiccated over concentrated acid, with a short time over phosphorus pentoxide, the terminal analysis is only 46.23% thoria, 16.28% water, corresponding to a slightly damp pentahydrate. In any case, the addition of only 1% nitric acid to the system gives clean pentahydrate as the solid phase separating.

In the attempt to prepare higher hydrates comparable to those in the older European literature,[4–6] crystallization at 4° was used as being more comparable to the winter temperatures of those laboratories than the 25° temperature customary here. From water, solids with approximately 6 molecules of water per thorium were obtained, which had no well-defined crystalline shape and appeared wet. Gentle drying of the solids by pressing between filter paper sheets lowered the water content, and the analyses approached the compositions of the solids isolated from aqueous solutions at 25°. From 1% nitric acid solutions at 4° poorly characterized solids with as much as 10 molecules of water per thorium were obtained, but these also lost water, as visible droplets, when brought to room temperature.

Possible Lower Hydrates.—Although Marshall, Gill and Secoy[10] reported a transition from tetrahydrate to a lower hydrate at 151°, Templeton[11] on studying the system to 160° failed to identify a lower hydrate. Kolb[14] reported isolating a dihydrate from fuming nitric acid solutions at 105–110°. The solids we isolated under these conditions were always highly decomposed and contained water approximating four molecules per thorium. No indications of a dihydrate were found in our ternary phase studies, though it is conceivable that such a hydrate might have a stability region too short to be resolved in this system.

Grateful acknowledgment is made to the following members of the Argonne National Laboratory staff for occasional assistance: to Stanley Siegel for the taking and interpretation of the X-ray powder diagrams of the solids studied in this paper; to L. H. Fuchs for assistance in the crystallographic characterization of the pentahydrate; and to Miss Mary Lou Sjoholm for assistance with the nitrogen analyses.

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Alkylation of Duryl Phenyl Ketone with the Grignard Reagent

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Conjugate addition of a Grignard reagent to an aromatic ketone in such a way as to involve an aromatic ring has been realized by a number of workers among whom Kohler and Nygaard[2] were the first to appreciate the nature of the reaction. From the recent work of Mosher and Huber[3] it is apparent that Schmidlin and Wohl accomplished a change of this type in 1910.[4]

Although the products of such reactions normally are dihydroaromatic compounds, fully aromatic derivatives have been obtained by the action of certain alkylmagnesium halides on duryl phenyl ketone, *i.e.*, this ketone appears to undergo direct alkylation.[5] This alkylation is unusual also in that it proceeds without resort to "forcing" conditions. Moreover, it leads to the formation of *p*-alkylated derivatives whereas in other reactions an ortho-position usually is involved. In other words, this type of alkylation corresponds to 1,6-addition, which rarely occurs with Grignard reagents. It is with the observation that the products are not of

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