data, from which reliable values of the rate constants are obtained.[10–12]

Since 1951 Delahay and his co-workers have published in THIS JOURNAL a series of papers dealing with the same or similar questions. In the course of their work the authors have gradually approached the results[13,14] which in a more general form were already obtained in 1947. The apparently simplified treatment of the recombination process suggested by Delahay[13] is similar to that also discussed in our paper (*cf.* ref. 5, p. 350). Though this paper is mentioned by Delahay, the meaning of the heterogeneous rate constant used in his treatment is obviously misunderstood. Whilst it is true that the heterogeneous constant can be defined as the product of the thickness of this layer and of the rate constant of recombination, the thickness of this layer is by no means related to the distance between two molecules of the reacting substance in the solution. This erroneous assumption regarding the thickness of the reaction layer led Delahay even in his later publications[14–16] to a false computation of the rate and the equilibrium constants for the ring-aldehydo transformations of various aldoses.[14] With proper treatment the rate constants cannot be evaluated unless the respective equilibrium constants are known from other measurements (*cf. e.g.*, the rate of dehydration of formaldehyde[17]).

The treatment by Delahay and Stiehl[18] of catalytic currents observed at the electro-reduction of ferric ions in the presence of hydrogen peroxide and strictly valid only for a plane electrode, is included, as mentioned above, in the solution of the general schemes worked out by Koutecký.[7] Its application to this special case was discussed in detail by Pospíšil.[19] Its solution by Miller[20] represents an improvement since it distinguishes the effect of the growth of the electrode on the kinetic and diffusion component of the limiting current by introducing an empirical factor for the kinetic component. This effect was exactly allowed for first by Koutecký[8] and verified by Pospíšil,[19] Blažek and Koryta[11] and Koutecký, Brdička and Hanuš.[12]

As far as the processes due to the "slow electron transfer" are concerned, the first solution of this problem considering the mass transfer to the plane electrode was given by Smutek,[21] Delahay and Strassner,[22] Evans and Hush[23] and Kambara and Tachi.[24] Later on Delahay[25] presented the results in a more comprehensive form giving useful criteria for the shapes of irreversible waves. However, the former computations of Delahay and Strassner[22] applied to the iodate ions are dubious, since the authors do not consider the fact that owing to the recombination of the iodate ion with hydronium ions a complex wave is obtained.[26] The polarographic problem of the "slow electron transfer" respecting the growth of the dropping electrode against the electrolyte was rigorously treated by Mejman[27] for the case of the one-way electron process. The extension to an electron transfer both ways has been worked out recently by Koutecký.[9] Discussion of the methods concerning the evaluation of the rate constants involved in the polarographic electrode process is the subject of a recent communication.[28]

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(+)α-Phenethyl Chloride and (−)2-Phenylpentane[1]

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RECEIVED OCTOBER 16, 1953

This note describes experiments which place upper and lower limits upon the rotation of optically active α-phenethyl chloride *via* conversion of α-phenethyl alcohol to the chloride and *via* conversion of the chloride to 2-phenylpentane. It also describes a preparation of α-phenethyl chloride of high rotation in much improved yield.

Gerrard[2] has described a preparation of the chloride employing pyridine and phosphorus oxychloride which gives much larger rotations than methods previously employed. We have confirmed these results and obtained a chloride the rotation of which very slightly exceeded the highest reported by Gerrard. This establishes a lower limit to $\alpha^{25}\text{D}$ of 109°.

Employing the Letsinger[3] modification of the Wurtz reaction, optically active α-phenethyl chloride was converted to 4-phenyl-1-pentene by reaction with allylsodium. This was hydrogenated to 2-phenylpentane. From the ratio of the observed rotation of this material to that reported for the optically pure material by Cram,[4] the upper limit to the rotation of α-phenethyl chloride is 126°. No assignment can be made of the difference between 109° and 126° as to loss of optical purity in forming the chloride from the alcohol and in forming the olefin from the chloride. It is unlikely

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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, $\alpha^{25}D$ 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, $\alpha^{25}D$ −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%, $\alpha^{25}D$ +97.4; correcting to optically pure starting material, $\alpha^{25}D$ +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, $\alpha^{25}D$ +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%, $\alpha^{25}D$ −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 $\alpha^{25}D$ 77.89°, 4-phenyl-1-pentene was obtained by fractionation at reduced pressures, $\alpha^{25}D$ −5.92°, $n^{20}D$ 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, $\alpha^{25}D$ −9.26°, $n^{20}D$ 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, $\alpha^{23}D$ 15.00°, and our measurement of the temperature coefficient, $\alpha^{25}D$ 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.), $n^{25}D$ 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, $\alpha^{25}D$ 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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RECEIVED AUGUST 10, 1953

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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[1] This work will be used as part of a thesis to be submitted by J. R. Ferraro to the Graduate School of the Illinois Institute of Technology in partial fulfillment of the requirements for a Ph.D. degree.

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