Anal. Calcd. for $C_{16}H_{13}O_4N$: C, 67.82; H, 4.63. Found: C, 67.54; H, 4.88.

o-**Hydroxyphenyl** α-**Oximinoethyl Ketone.**—*o*-Benzoyloxyphenyl α-oximinoethyl ketone (8.4 g.) in alcoholic solution was treated with 15 cc. of 5 *N* sodium hydroxide solution. After fifteen minutes the solution was diluted with water and made just acid to litmus with acetic acid. The yellow oil which separated was dissolved in ether. The ether solution was washed with a solution of sodium carbonate and dried over sodium sulfate. After removal of the ether the partially crystalline residue was dissolved in hot petroleum ether. The large yellow plates which separated on cooling melted at 85–88°. Another recrystallization did not change the melting point. Ferric chloride produced a deep red color in alcoholic solution.

Anal. Calcd. for $C_9H_9O_3N$: C, 60.31; H, 5.07. Found: C, 60.19; H, 5.23.

o-**Benzoyloxyphenyl** α-**Aminoethyl Ketone.**—The oximino ketone was reduced catalytically in absolute alcohol solution following the conditions of Hartung and Munch.[2] The uptake of hydrogen did not stop completely when two moles had been absorbed but the rate fell off quite sharply at that point. However, much of the hydrogen was used up in side reactions since the yield of amine was only 30%. A large proportion of the oximino ketone was recovered unchanged. This was accompanied by a small amount of oil which was not investigated.

After removal of the catalyst the solution was evaporated under reduced pressure to about 25 cc. and an equal volume of dry ether added. The hydrochloride of the amine separated as long interlacing needles which decomposed at about 180° without melting. For recrystallization it was dissolved in hot alcohol containing 1 cc. of concd. hydrochloric acid. After filtration acetone was added slowly. The crystals which separated apparently contained one-half molecule of water. However, loss of weight at 120° was negligible. After two hours at 125–130° there was some loss of weight but there was also evidence of some decomposition.

Anal. Calcd. for $C_{16}H_{16}O_3NCl$: C, 62.83; H, 5.82. Calcd. for $C_{16}H_{16}O_3NCl\cdot 0.5H_2O$: C, 61.03; H, 5.45. Found: C, 61.00, 61.35; H, 5.50, 5.48.

The free base was prepared by neutralization of an aqueous solution of the hydrochloride with sodium carbonate. It precipitated as fine needles. After recrystallization from petroleum ether they melted at 112–114°. They reduced Fehling's solution.

Anal. Calcd. for $C_{16}H_{15}O_3N$: C, 71.34; H, 5.62. Found: C, 71.32; H, 5.75.

Summary

o-Benzoyloxy α-oximinoethyl ketone has been prepared. It has been converted into *o*-hydroxyphenyl α-oximinoethyl ketone by hydrolysis and into *o*-benzoyloxyphenyl α-aminoethyl ketone by catalytic hydrogenation.

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ROCHESTER, MINN.

RECEIVED OCTOBER 1, 1934

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[2] Hartung and Munch, THIS JOURNAL, **51**, 2262 (1929).

COMMUNICATIONS TO THE EDITOR

A BENZALDEHYDE ELECTRODE

Sir:

In "the difficult alkaline range" of *p*H we have substituted benzaldehyde for quinhydrone in a regular quinhydrone *p*H determination apparatus, and, using a saturated calomel electrode as reference, have made reproducible determinations between *p*H 7 and 13.64. Checked against a hydrogen electrode, the deviations in *p*H units in a large number of measurements were: 0.00–0.09 unit, 44.36%; 0.10–0.19 unit, 33.12%; 0.20–0.29 unit, 14.57%; 0.30–0.39 unit, 5.30%; 0.40–0.49 unit, 2.65%; above 0.50 unit, 0.00%. Comparable to colorimetric readings, therefore, the benzaldehyde electrode gave accuracy within 0.2 *p*H in 77.48% of the determinations.

The determinations were carried out in 50-cc. Pyrex beakers, with 40 cc. of the solution and 0.4 cc. of benzaldehyde mixed by a stirrer at 1200 r. p. m. The electrode was a 10-cm. coil of platinum wire. The connection was through a salt bridge into saturated potassium chloride, into which the calomel electrode tip dips.

From the data a master curve has been plotted, smoothed mathematically, which presents potentials as ordinates against *p*H values as abscissas. The coefficient of correlation between the *p*H values obtained with the benzaldehyde electrode and with the hydrogen electrode between *p*H 7 and 14 is 0.996 ± 0.0006. The most reproducible region is between *p*H 9 and 14.

A linear relationship was found to exist between the common logarithm of the absolute potential of the benzaldehyde electrode (found by adding 0.5266, the so-called absolute potential of the saturated calomel electrode, to the observed potential) and the corresponding pH value. The equation for this relationship is

$$\text{Log}_{10} E = -0.0633\, p\text{H} + 0.4080$$

where E is the absolute potential of the benzaldehyde electrode.

In contrast to the quinhydrone system, the benzaldehyde system is irreversible. The chemical change involved seems to be the reduction of benzaldehyde to benzyl alcohol; hydrions and electrons both being present, a potential with reference to the other half-cell (calomel) is influenced by the pH of the solution into which the benzaldehyde is stirred.

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RECEIVED AUGUST 2, 1934

THE ATOMIC WEIGHT OF PROTACTINIUM

Sir:

Part of the one tenth gram of protactinium oxide, recently isolated by M. S. Agruss and the writer [THIS JOURNAL, **56,** 2200 (1934)] has been used for the first direct determination of the atomic weight of protactinium. An x-ray photograph of this material kindly taken by Dr. W. C. Pierce had shown no impurities.

The classical method of M. C. de Marignac [*Ann. chim. phys.* [IV] **9,** 250 (1866)] for tantalum was utilized for this determination. Potassium protactinium fluoride (K_2PaF_7) was prepared from the oxide. It crystallizes in beautiful colorless sharp long needles, very insoluble in water containing 0.5% of hydrogen fluoride. It is stable in air and can easily be dried to constant weight at 20 or 100°. This was reconverted into the oxide by fuming with sulfuric acid, diluting with water, precipitating with ammonia, filtering the hydroxide, and igniting and weighing as oxide. All operations were carried out in and with platinum equipment. All the chemicals were highly purified. A very sensitive ultra microbalance [K. W. H. Kühlmann, Hamburg, Germany] was used; all weights were corrected to vacuum. Further details will be given in a subsequent paper.

The first preliminary analysis gave 61.18 parts of the oxide and 39.67 parts of potassium sulfate per 100 parts of potassium protactinium fluoride. Assuming the formula to be K_2PaF_7 and protactinium to have an atomic weight of 231, 61.29 and 39.40 parts, respectively, should have been obtained. This agreement definitely establishes the pentavalency of protactinium and the formula Pa_2O_5 for the oxide.

The two final determinations gave the following results:

K_2PaF_7, g.	Pa_2O_5, g.	$2K_2PaF_7:Pa_2O_5$	At. wt., Pa
0.091907	0.056274	1.6332	230.4
.070047	.042913	1.6323	230.8

For the atomic weights of the other elements the 1934 values of the International Committee were used [G. P. Baxter, Mme. P. Curie, O. Hönigschmid, P. Lebeau and R. J. Meyer, THIS JOURNAL, **56,** 753 (1934)].

The mean value of the atomic weight of protactinium is 230.6, or in whole numbers 231, with an accuracy of about ±0.5 unit. This value is in complete agreement with F. W. Aston's results on actinium lead (AcD = 207), obtained by means of his mass spectrograph.

For a precision atomic weight determination the analysis of the recently discovered $PaCl_5$ [A. V. Grosse, THIS JOURNAL, **56,** 2200 (1934)] will probably be more suitable; however, the latter can be used to its full advantage only when larger quantities of protactinium will be available. Such a determination is planned in the future.

We are much indebted to the management of the Universal Oil Products Co., Chicago, for placing at our disposal the facilities of their Research Laboratories.

KENT CHEMICAL LABORATORY A. V. GROSSE
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RECEIVED OCTOBER 3, 1934

HALOGENATION INHIBITION BY OXYGEN

Sir:

Bauer and Daniels [THIS JOURNAL, **56,** 2014 (1934)] present evidence for the inhibition of the halogenation of cinnamic acid by oxygen and in their last paragraph suggest that the influence of oxygen on reactions of this type may be quite general.

In these Laboratories the inhibiting effect of oxygen on certain halogenation reactions has been observed in many instances, and is the subject of patents granted to this Company.