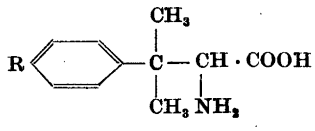

I R = H
II R = OH

gave considerably improved yields of the amino acids. This appeared to be due partly to decreased side reactions leading to nitrogen-free products and partly to easier isolation of the amino acids. Reaction temperature, pH and area of amalgam appeared to be the main factors determining the yields. It was found that at high temperatures (near the boiling point of the mixture) much nitrogen-free material was formed. At room temperature, this side reaction was depressed but the reduction was very slow. At high pH-values (above 7) much nitrogen was lost as ammonia. A large ratio of amalgam area/mole oximinocompound is essential in order to decrease the time required for the reaction, but the high ratio must not be produced by stirring the mixture, since this results in drastically decreased yields (probably by destruction of the molecular orientation at the amalgam surface). By following closely the directions given in the experimental part, it was possible to increase the yield of *neo*phenylalanine to 80—90 % and that of *neo*tyrosine methyl ether to 70—75 %.

In addition to *neo*tyrosine methyl ether, α-hydroxy-β-(*p*-methoxyphenyl)*iso*valeric acid could be isolated from the reaction mixture in about 10 % yield. In the reaction mixture from the reduction of α-oximino-β-phenyl*iso*valeric acid, there was also found some nitrogen-free acid material, probably α-hydroxy-β-phenyl*iso*valeric acid, but this fraction could not be induced to crystallise and was not further investigated.

Experimental: The oximinoacid (0.1 mole) was added to 2 % sodium amalgam (750 g) covered with commercial absolute ethanol (300 ml) in an Erlenmeyer flask of one liter capacity (bottom diameter about 12 cm). Approximately 7 *N* absolute ethanolic hydrogen chloride was added dropwise from a buret to keep the mixture just acid to *p*-bromocresol green (determined by placing a drop of the liquid on a strip of filter paper moistened with a 1 % solution of the indicator). About 75—85 ml acid was required. The temperature of the reaction mixture was kept at 40—50° by appropriate cooling or heating in a water bath. When the reaction ceased, which was indicated by a slowing up and ceasing of the consumption of acid, *N* aqueous hydrochloric acid was added to dissolve the solid precipitate. The solution was separated from the mercury, filtered, evaporated to about 100 ml on the water bath, saturated with hydrogen sulphide, filtered, and the pH adjusted to 6—6.5 by careful addition of ammonia. After storing overnight in the refrigerator the amino acid was filtered off, washed in turn with icecold water (50 ml), acetone (50 ml) and ether (150 ml). The yield of *neo*phenylalanine was 80—90 % and that of *neo*tyrosine methyl ether 70—75 %.

α-Hydroxy-β-(p-methoxyphenyl)isovaleric acid. The combined mother liquors and washings from the reduction of a total of 120 g of α-oximino-β-(*p*-methoxyphenyl)*iso*valeric acid were acidified to pH 1—2 with hydrochloric acid and repeatedly extracted with ether. The extract on evaporation yielded a solid (17.5 g), which was repeatedly crystallised from water. Colourless plates, m.p. 127—128°. (Found: C 64.8; H 7.4; CH_3O 13.6. $C_{12}H_{16}O_4$ requires: C 64.3; H 7.2; CH_3O 13.8).

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Synthetic Plant Hormones

VI. Preparation of some α-Phenoxy and α-1-Naphthoxy fatty Acids * (Addition to Part IV)

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Some further α-aryloxy fatty acids have been prepared in addition to those reported in Part IV [1] of this series, for investigation of their plant growth activity. All the acids were prepared by condensation of the appropriate sodium phenoxide with the ethyl ester of the α-chloro fatty acid. Physical data for the acids not previously

* Part V. *Acta Chem. Scand.* **8** (1954) 119.

described are reported in the experimental part. A detailed report on the plant growth activity of the compounds will be published shortly elsewhere by Dr. B. Hansen, University of Lund.

*Experimental.** *General method.* Sodium (0.1 mole) was dissolved in absolute ethanol (50 ml) and this solution was added to a solution of the phenol (0.1 mole) in a little absolute alcohol. The appropriate ethyl α-chloro fatty ester was added and the mixture refluxed overnight. A solution of sodium hydroxide (0.2 mole) in water (20 ml) was added and the whole refluxed for two hours and then poured into water, filtered and made strongly acid using hydrochloric acid. With the readily oxidisable 2,4-dichloro-1-naphtol, the condensation reaction was carried out in a nitrogen atmosphere.

D,L-α-*4-Chlorophenoxyisovaleric acid*, colourless needles from benzene-petrol. M. p. 97—98°. (Found: Cl 15.4; neutr. equiv. 229. $C_{11}H_{13}ClO_3$ requires: Cl 15.5; neutr. equiv. 228.4).

D,L-α-*2,4-Dichlorophenoxyisovaleric acid* separated as an oil. After distillation (b. p. about 200°/10 mm Hg) it crystallised. Needles from petrol, m. p. 65—66°. (Found: Cl 26.7; neutr. equiv. 262. $C_{11}H_{12}Cl_2O_3$ requires: Cl 26.9; neutr. equiv. 263.1).

D,L-α-*2,6-Dimethylphenoxypropionic acid*, needles from petrol. M. p. 62—63°. (Found: C 68.4; H 7.25; neutr. equiv. 196. $C_{11}H_{14}O_3$ requires: C 68.0; H 7.27; neutr. equiv. 194.2).

D,L-α-(*2,4-Dichloro-1-naphthoxy*)*propionic acid*, needles from chloroform-petrol. M. p. 129°. (Found: Cl 24.5; neutr. equiv. 285. $C_{13}H_{10}Cl_2O_3$ requires: Cl 24.8; neutr. equiv. 285.1).

The authors wish to acknowledge their indebtedness to *Statens Tekniska Forskningsråd* for a Fellowship to one of them (Å. J.) and to *Cancernämnden* for financial support.

* All melting points uncorrected. Petrol refers to the fraction b.p. 40—60°.

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