Anal. Calcd. for $C_{28}H_{16}$: C, 95.42; H, 4.59. Found[18b]: C, 95.24; H, 4.72.

The compound dissolved in concentrated sulfuric acid giving a green color which turned blue on prolonged standing.

8-[1-(8-Chloronaphthyl)]-10,11-dihydrobenz[*a*]anthracene (X).—A Grignard reagent was prepared in ether from 9.0 g. (0.037 mole) of 1-bromo-8-chloronaphthalene[15] and 0.95 g. (0.039 g.-atom) of magnesium. The reaction mixture was stirred and heated under reflux for 24 hr. Anhydrous benzene was added as needed to keep the Grignard reagent from crystallizing too much. The ether was distilled and benzene was added to bring the volume to *ca.* 100 ml. In one portion, 9.1 g. (0.037 mole) of 8-keto-8,9,10,11-tetrahydrobenz[*a*]anthracene was added and the solution was heated under reflux for 24 hr. The solution was cooled, decomposed with cold 20% ammonium chloride solution, and extracted with ether. The organic layer was separated, washed with water, dried over anhydrous calcium sulfate, and concentrated to *ca.* 20 ml. The oil was crystallized using acetone, giving 3.5 g. of solid, m.p. 219–220°. The solid was vacuum sublimed at 210° (0.6 mm.) and then recrystallized from 20% benzene–ethanol giving 3.4 g. (23%) of X as colorless needles, m.p. 222–223°. Recrystallization from 1:1 benzene–petroleum ether (30–60°) gave colorless needles, m.p. 225–226°.

Anal. Calcd. for $C_{28}H_{19}Cl$: C, 86.03; H, 4.90; Cl, 9.07. Found: C, 85.63; H, 4.89; Cl, 8.95.

Cyclization of 8-[1-(8-Chloronaphthyl)]-10,11-dihydrobenz[*a*]anthracene (X). A. *Via* Potassium Hydroxide and Quinoline.—A mixture of 0.50 g. (0.0013 mole) of X, 10.0 g. of potassium hydroxide, and 15 ml. of quinoline was heated under reflux for 30 min. The mixture was cooled, decomposed with cold dilute hydrochloric acid, and extracted with ether. The organic layer was filtered. The filtrate was washed with dilute hydrochloric acid, then water, and finally dried over anhydrous calcium sulfate. The solid, crude naphtho[2,1-*a*]perylene was dissolved in benzene and combined with the ether extract. This solution was then concentrated to *ca.* 5 ml. and chromatographed[21] on alumina[22] using petroleum ether[23] as the eluant. A blue fluorescent[24] band appeared, followed by a red band with a green-yellow fluorescence.[24] Concentration and recrystallization of the first band, after elution, gave 0.06 g. of starting material. The red band was eluted, concentrated, and crystallized. The yield was 0.17 g. (36%) of naphtho[2,1-*a*]perylene, m.p. 201.5–203.5°.

B. *Via* Palladium on Charcoal.—A mixture of 0.50 g. (0.0012 mole) of X and 0.10 g. of 10% palladium on charcoal was heated at 310° for 15 min. and then at 350° for 1 hr. The mixture was worked up and chromatographed as described under A. There was obtained 0.26 g. (52%) of compound VIII and 0.11 g. (2%) of III, m.p. 202–203°.

TNF Adduct of Naphtho[2,1-*a*]perylene (III).—A solution of 0.12 g. (0.00034 mole) of naphtho[2,1-*a*]perylene in 40 ml. of hot 10% benzene–ethanol was added to a hot solution of 0.10 g. of 2,4,7-trinitrofluorenone in 40 ml. of 10% benzene–ethanol. On cooling, a black precipitate appeared, 0.10 g. (47%), which on recrystallization from 10% benzene–ethanol gave fine black needles, m.p. 222–223°.

Anal. Calcd. for $C_{41}H_{23}O_6N_3$: C, 73.76; H, 3.17; N, 6.29. Found: C, 73.52; H, 3.44; N, 6.30.

Dibenzo[*ae*]perylene (II).—A mixture of 0.50 g. of 7-(1-naphthyl)benz[*a*]anthracene[25] and 0.5 g. of powdered anhydrous aluminum chloride and 0.5 g. of fuming stannic chloride in 50 ml. of dry benzene was heated in a steam bath for 30 min. The deep red solution was allowed to cool to room temperature and was then decomposed with 100 ml. of 10% hydrochloric acid. The green fluorescent organic layer was separated and the aqueous layer was extracted twice with 50-ml. portions of benzene. The combined benzene extracts were washed with water and dried over anhydrous magnesium sulfate. The solvent was distilled until only *ca.* 10 ml. remained. This solution was chromatographed.[19,21] Two bands appeared on the column, a colorless blue fluorescent band and a red-orange band. The first band was eluted with petroleum ether[23] and discarded. The second band was removed with benzene and the resultant solution concentrated to give red crystals of dibenzo[*ae*]perylene (II), 0.24 g. (48%), m.p. 183–186°.

An analytical sample was prepared by recrystallization of the hydrocarbon from benzene, m.p. 188–189°.

Anal. Calcd. for $C_{28}H_{16}$: C, 95.42; H, 4.28. Found[18b]: C, 95.72; H, 4.37.

The hydrocarbon dissolved in concentrated sulfuric acid giving a Prussian blue color which changed to brown on standing.

TNF Adduct of Dibenzo[*ae*]perylene.[26]—A hot saturated solution of 0.12 g. of dibenzo[*ae*]perylene in benzene was mixed with a hot saturated solution of 0.4 g. of 2,4,7-trinitrofluorenone in ethanol. A brown solid formed immediately, 0.21 g. (quantitative). Four recrystallizations from benzene gave a brown, granular solid, m.p. 253–254°.

Anal. Calcd. for $C_{41}H_{21}N_3O_7$: C, 73.75; H, 3.17; N, 6.30. Found[18b]: C, 73.51; H, 3.61; N, 6.19.

(21) The column used throughout this investigation was 18 × 370 mm.

(22) Fisher's adsorption alumina, 80–200 mesh.

(23) The petroleum ether used as an eluent had a 30–60° boiling point range.

(24) Fluorescent under ultraviolet radiation with a Blak-ray ultraviolet long wave lamp (3660 Å.) as the source.

(25) F. A. Vingiello, A. Borkovec, and W. W. Zajac, Jr., *J. Am. Chem. Soc.*, **80**, 1714 (1958).

(26) This experiment was performed by Mr. Leo Ojakaar.

α-Hydroxy Acid Amides. A Convenient Synthesis

HERBERT E. JOHNSON AND DONALD G. CROSBY

Research and Development Department, Union Carbide Chemicals Company, South Charleston 3, West Virginia

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Using a procedure patterned after the one described for the preparation of α-amino acid amides,[1] a variety of cyanohydrins have been converted in reasonable yield to the corresponding α-hydroxy acid amides. This reaction probably proceeds similarly[1]; an intermediate imido ester salt is formed which, upon heating, eliminates alkyl chloride to produce the desired amide. With the possible exception of a recently reported preparation of α-hydroxyphenylacetamide[2] this report apparently is the first record of an application of the Pinner amide synthesis[3] to the synthesis of α-hydroxy acid amides.

$$\mathrm{RCHCN} + \mathrm{R'OH} + \mathrm{HCl} \longrightarrow \underset{\mathrm{OH}}{\mathrm{RCHCN}}$$

$$\mathrm{RCHCOR'} \longrightarrow \mathrm{RCHCNH_2} + \mathrm{R'Cl}$$
(NH·HCl on the first; O on the second; OH on both)

The best yields of amides were generally obtained by allowing the cyanohydrin to react with isopropyl alcohol saturated with hydrogen chloride. Evaporation of the solvent followed by pyrolysis of the imido ester salt and subsequent distillation produced the hydroxy amide in yields as high as 80%. Alternatively, the synthesis was performed in an inert solvent such as xylene, employing a slight excess over equivalent quantities of an alcohol. After a suitable reaction time with hydrogen chloride, the reaction mixture was heated under reflux to decompose the imido ester salt and the product recovered by a filtration of the cooled mixture. The combined versatility of these two procedures was sufficient to allow the preparation of the various α-hydroxy amides tabulated in Table I.

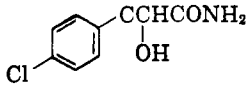
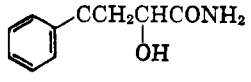
(1) H. E. Johnson and D. G. Crosby, *J. Org. Chem.*, **27**, 798 (1962).

(2) R. Roger and D. G. Neilson, *Chem. Rev.*, **61**, 179 (1961), ref. 329.

(3) Refer to S. M. McElvain and B. E. Tate, *J. Am. Chem. Soc.*, **73**, 2233 (1951), for pertinent references.

TABLE I

α-HYDROXY ACID AMIDES

Amide	M.p., °C.	Lit. m.p., °C.	Method[a]	% yield
$CH_3CHCONH_2$ (OH)	74–75	74[b]	B	59
$CH_3CH_2CHCONH_2$ (OH)	104–105	105[c]	A	55
$(CH_3)_2CCONH_2$ (OH)	97–99	96–98[d]	B	80
$(CH_3)_2CHCHCONH_2$ (OH)	102–104	104[e]	B	78
$CH_3CH_2CCONH_2$ (CH_3, OH)	68–69	160[f]	B	56
$(CH_3)_2CHCH_2CHCONH_2$ (OH)	81–82	51–52[g]	A	79
$CH_3CH_2CHCHCONH_2$ (CH_3, OH)	49–56[h]		B	70
$CH_3(CH_2)_5CHCONH_2$ (OH)	151–152	150[i]	B	44[l]
	124–125	122–123[j]	A	45
	110–112	111–112[k]	A	71

[a] Method A: inert solvent with equivalent quantities of alcohol. Method B: alcohol used as a solvent. [b] J. Wislicenus, *Ann.*, **133**, 257 (1865). [c] H. Bredereck, R. Gompper, and G. Theilig, *Ber.*, **87**, 537 (1954). [d] G. Ciamician and P. Silber, *ibid.*, **38**, 1671 (1905). [e] A. Lipp, *Ann.*, **205**, 1 (1880). [f] G. Ciamician and P. Silber, *Ber.*, **47**, 1806 (1914). *Anal.* Calcd. for $C_5H_{11}NO_2$: C, 51.26; H, 9.46; N, 11.96. Found: C, 51.27; H, 9.73; N, 11.94. [g] P. Nicolle, *Bull. soc. chim. France*, [4] **39**, 55 (1926). *Anal.* Calcd. for $C_6H_{13}NO_2$: C, 54.94; H, 9.99; N, 10.68. Found: C, 55.13; H, 9.68; N, 10.75. [h] An obvious mixture of isomers. *Anal.* Calcd. for $C_6H_{13}NO_2$: C, 54.94; H, 9.99; N, 10.68. Found: C, 55.16; H, 10.03; N, 10.63. [i] E. Erlenmeyer and O. Sigel, *Ann.*, **177**, 102 (1875). [j] H. G. Rule, *J. Chem. Soc.*, **113**, 3 (1918). [k] A. McKenzie, G. Martin, and H. G. Rule, *ibid.*, **105**, 1583 (1914). [l] Recrystallized yield.

Some ammonium chloride (up to 15%) was always formed during the reaction sequence and limited attempts were made to overcome its formation. Since this salt formation is most likely the result of alcoholysis of the imido ester, a brief study of the effect of various alcohols on the formation of ammonium chloride was conducted. Contrary to the striking effects of "subtle" changes in alcohol structure observed in the related synthesis of α-amino acid amides[2], little difference in the course of the reaction was noted when 2-propanol, 2-butanol, and 3-pentanol were employed as solvents.

Those α-hydroxy acid amides analogous to the essential α-amino acids valine, leucine, and phenylalanine were evaluated for their ability to replace them nutritionally in a mouse diet. As expected, complete replacement was observed.

Experimental[4]

2-Hydroxy-3-phenylpropionamide. Procedure A.—A mixture of 649 g. (4.41 moles) of phenylacetaldehyde cyanohydrin, 210 g. (4.57 moles) of ethanol, and 2.6 l. of dry benzene (dry xylene was used in all other cases) was saturated with anhydrous hydrogen chloride (358 g.) at 25°. The mixture was stirred for 20 hr. at 25° and then heated under reflux for 6 hr. During this time the product precipitated and was collected after cooling the mixture to 10°. A total of 586 g. of light yellow crystalline product was obtained, m.p. 107–112° and was found to contain 6% ammonium chloride as calculated from a chloride analysis. The product was crystallized from 3 l. of benzene containing 450 ml. of ethanol to give 450 g. (62%) of colorless crystals, m.p. 110–112°.

2-Hydroxy-3-methylbutyramide. Procedure B.—A solution of 500 g. (5.06 moles) of isobutyraldehyde cyanohydrin in 3 l. of isopropyl alcohol was saturated with anhydrous hydrogen chloride at 25–30°. The mixture was stirred at 25° for 20 hr. and then excess alcohol and hydrogen chloride were removed by evaporation under reduced pressure. The remaining residue was heated slowly to 170° under 20–50-mm. pressure and then cooled to room temperature. Two liters of ethanol was added and the ammonium chloride present was removed by a filtration (11 g.). Evaporation of the ethanol followed by distillation of the residue gave 461 g. (78%) of colorless distillate, b.p. 145–150° (2 mm.) m.p. 93–98°. Crystallization from an isopropyl ether–ethanol mixture raised the melting point to 102–104°.

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(4) Melting points are corrected.

The Brominating Properties of Tetramethylammonium Tribromide[1a]

MOSHE AVRAMOFF,[1b] JUDITH WEISS, AND OZJASZ SCHÄCHTER

Daniel Sieff Research Institute, Weizmann Institute of Science, Rehovoth, and Chemistry Department, Bar Ilan University, Ramat Gan, Israel

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Organic ammonium perbromides are considered mild brominating agents. Pyridinium bromide perbromide was introduced by Djerassi and Scholz for the bromination of keto steroids and has since been used widely in place of bromine, which occasionally causes undesired substitution or oxidation reactions.[2] Unlike N-bromosuccinimide (NBS), it lacks the ability to perform allylic bromination. Marquet and coworkers preferred phenyltrimethylammonium perbromide (PTAP) to pyridinium bromide perbromide because of the greater stability of the former.[3] With this reagent they were able to brominate ketones and 1,3-dioxolanes, without affecting isolated ethylenic double bonds, present in the same molecule. Its mild brominating characteristic and specificity were shown in the reaction with 2-acetyl-6-methoxynaphthalene. In tetrahydrofuran 2-bromoacetyl-6-methoxynaphthalene was obtained, while in acetic acid a 1:1 mixture of this bromoacetyl compound and the nuclear substituted derivative, 2-acetyl-5-bromo-6-methoxynaphthalene was formed. Although NBS is considered a specific reagent for allylic bromination,[4] it can bro-

(1) (a) Taken in part from the M.S. thesis of J. Weiss, Bar Ilan University, 1963; (b) Weizmann Institute of Science, Rehovoth, Israel.

(2) C. Djerassi and C. R. Scholz, *J. Am. Chem. Soc.*, **70**, 417 (1948); P. C. Merker and J. A. Vona, *J. Chem. Educ.*, **26**, 613 (1949); J. A. Vona and P. C. Merker, *J. Org. Chem.*, **14**, 1048 (1949); N. B. Lorette, T. B. Gage, and S. H. Wender, *ibid.*, **16**, 930 (1951).

(3) A. Marquet, M. Dvolaitzky, H. B. Kagan, L. Mamlock, C. Onannes, and J. Jacques, *Bull. soc. chim. France*, 1822 (1961); A. Marquet and J. Jacques, *ibid.*, 90 (1962).

(4) C. Djerassi, *Chem. Rev.*, **43**, 271 (1948).