(loss of CHO). The clear liquid began to darken when left at room temperature for a number of days.

1-Pentyne-3-hydroxy-4-one Ethylene Ketal (5).—Compound **2** (5 g, 43 mmol) was dissolved in tetrahydrofuran distilled from calcium hydride (20 ml) and added to a solution of ethynylmagnesium bromide, prepared from magnesium (2 g, 83 g-atoms), ethyl bromide (6 ml, 84 mmol), and acetylene gas, over a 30-min period. The reaction was stirred at room temprature under a positive pressure of nitrogen for an additional 12 hr. The brown reaction mixture was then carefully poured onto a cooled solution of saturated ammonium chloride. The aqueous phase was extracted with three 150-ml portions of ether. The combined ether extracts were dried, filtered, and evaporated under vacuum. Glc of the yellow oil obtained indicated that one product had formed in essentially quantitative yield. The oil could be distilled under high vacuum to yield a clear liquid boiling at 112–118° (5 Torr). In actual practice the product obtained was pure enough to carry through to the next reaction. The product was stored in the cold, since it readily darkened at room temperature. Spectra data were obtained on a sample that was pure by glc analysis: nmr (CCl_4) δ 1.32 (s, 3 H), 2.29 (d, J = 2 Hz, 1 H), 2.87 (s, 1 H), 3.92 (s, 2 H), 3.94 (s, 2 H), 4.09 (d, J = 2 Hz, 1 H); ir (neat) λ_{max} 2.8 (broad), 3.05, 4.72, 9.4 (broad), 9.6 μ; mass spectrum m/e 142 (parent ion).

1-Pentyne-3,4-dione 4-Ethylene Ketal (1).—Compound **5** (20 g, 0.14 mol) was dissolved in acetone (100 ml) in a three-neck flask fitted with an overhead stirrer and a 125-ml addition funnel. The reaction was cooled to 0° and stirred vigorously. The Jones reagent was added dropwise over a period of 1 hr until a red color persisted (65 ml). The reaction was filtered and the green chromium salts were washed with ether. The aqueous phase was extracted with three 150-ml portions of ether. The ether extracts were combined and back-washed once with saturated sodium chloride solution. The ether extracts were then dried, filtered, and evaporated under vacuum. Glc of the yellow liquid obtained indicated that only one product had formed, with the yield being greater than 90%. The yellow liquid could be distilled under high vacuum to yield a colorless liquid boiling at 65–71° (5 Torr), which darkened if kept out of the freezer for a prolonged period of time. Spectral data was obtained on a sample pure by glc analysis: nmr (CCl_4) δ 1.40 (s, 3 H), 3.31 (s, 1 H), 3.97 (s, 4 H); ir (neat) λ_{max} 3.08, 4.79, 5.92 8.3 (broad), 9.8 μ (broad); mass spectrum parent ion − 15 (loss of CH_3), parent ion − 53 (loss of C_3HO).

Registry No.—**1**, 39050-38-9; **2**, 39050-39-0; **3**, 26924-35-6; **5**, 39050-41-4; MVK, 78-94-4; ethylene glycol, 107-21-1.

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Synthesis of 2-Substituted 2,4a-Ethanophenanthrenes

JOEL G. WHITNEY* AND KYU TAI LEE

Pharmaceuticals Division, Biochemicals Department, E. I. du Pont de Nemours and Company, Inc., Wilmington, Delaware

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The 2,4a-ethanophenanthrene ring system has been little explored in the chemical literature.[1]

This paper describes a novel two-step synthetic route to the 2,4a-ethanophenanthrene ring system (Scheme I).

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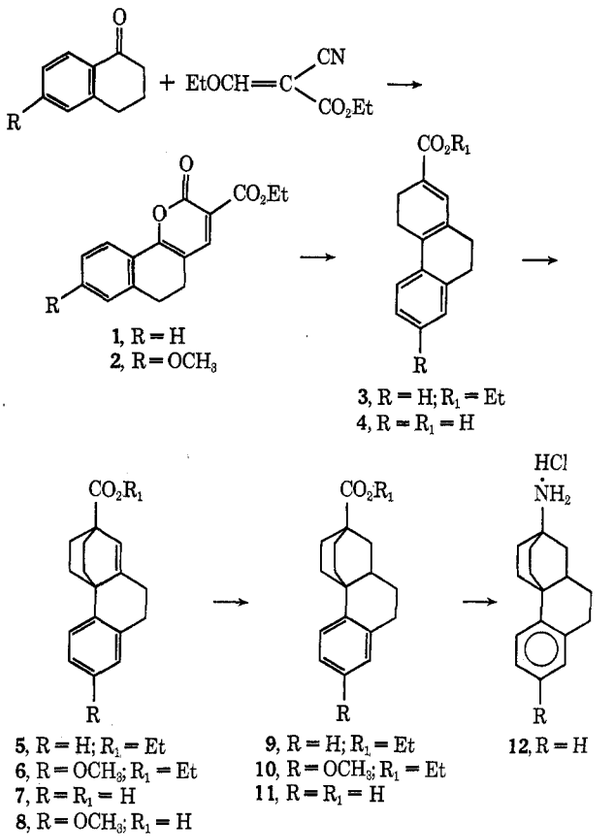
SCHEME I



Base-condensation of α-tetralone with ethyl ethoxymethylenecyanoacetate followed by hydrolysis afforded ethyl 5,6-dihydro-2-oxo-2*H*-naphtho[1,2-*b*]pyran-3-carboxylate (**1**). The pyran **1** was allowed to react with ethylene at 3000 atm to give ethyl 2,3,4,4a,9,10-hexahydro-2,4a-ethanophenanthrene-2-carboxylate (**5**). The use of ethylene at 1000 atm gave the intermediate ethyl 3,4,9,10-tetrahydrophenanthrene-2-carboxylate (**3**).

Hydrogenation of **5** yielded ethyl 1,2,3,4,4a,-9,10,10a-octahydro-2,4a-ethanophenanthrene-2-carboxylate (**9**). The structure of esters **3**, **5**, and **9** were characterized by conversion to the corresponding carboxylic acids **4**, **7**, and **11**.

Similarly, ethyl 7-methoxy-1,2,3,4,4a,9,10,10a-octahydro-2,4a-ethanophenanthrene-2-carboxylate (**10**) was prepared from 6-methoxy-α-tetralone.

1,2,3,4,4a,9,10,10a-Octahydro-2,4a-ethanophenanthrene-2-amine hydrochloride (**12**) was synthesized from the corresponding acid **11**.

Experimental Section

Melting points were determined on a Thomas-Hoover "Unimelting" apparatus and are uncorrected. Infrared spectra were determined on a Perkin-Elmer Model 21 spectrometer in Nujol. Nmr spectra were obtained on a Varian A-60 spectrometer with $(CH_3)_4Si$ as the internal standard. Uv spectra were obtained on a Cary Model 14PM spectrometer.

Ethyl 5,6-Dihydro-2-oxo-2*H*-naphtho[1,2-*b*]pyran-3-carboxylate (1).—To a solution of 0.55 mol of NaOEt in 500 ml of dimethoxyethane, 84.5 g (0.5 mol) of ethyl ethoxymethylenecyanoacetate and then 73 g (0.5 mol) of α-tetralone were added dropwise. The reaction mixture was stirred overnight at room temperature and poured onto 500 ml of 3 *N* HCl. Yellow crystals were collected by filtration and washed with Me_2CO. A mixture of the crystals and 500 ml of H_2O was warmed on the

steam bath for 3 hr, cooled, and filtered to give 112.4 g (83%) of **1**, mp 145–147°. Two recrystallizations (EtOH) gave an analytical sample: mp 148–149°; ir 1750 cm^{-1} (C=O); nmr (DMSO) δ 1.4 (t, 3, CH_3), 2.9 (m, 4 H), 4.35 (q, 2, OCH_2), 7.0–8.0 (m, 5 H).

Anal. Calcd for $C_{16}H_{14}O_4$: C, 71.10; H, 5.23. Found: C, 71.16; H, 5.34.

Ethyl 8-Methoxy-5,6-dihydro-2-oxo-2*H*-naphtho[1,2-*b*]pyran-3-carboxylate (2).—6-Methoxy-α-tetralone (470 g, 2.67 mol) was converted by the procedure described above to **2**, mp 141–143°. Recrystallization (DMF–H_2O) gave 550 g (68.5%) of analytically pure **2**: mp 150.5–152°; ir 1750 cm^{-1} (C=O); nmr (CF_3CO_2H) δ 0.9 (t, 3, CH_3), 2.2 (s, 4 H), 3.2 (s, 3, OCH_3), 4.0 (q, 2, OCH_2), 6.4–7.4 (m, 3 H), 8.0 (s, 1 H).

Anal. Calcd for $C_{17}H_{16}O_5$: C, 67.99; H, 5.37. Found: C, 67.76; H, 5.43.

2,3,4,4a,9,10-Hexahydro-2,4a-ethanophenanthrene-2-carboxylic Acid (7).—The pyran **1** (50 g, 0.185 mol) was allowed to react with ethylene at 3000 atm at 200° for 14 hr to give 47.3 g (91%) of **5**, mp 50–51°, ir 1730 cm^{-1} (C=O). A mixture of 7 g (24.8 mmol) of **5** an 125 ml of 2 *N* NaOH was heated at reflux for 12 hr, cooled, washed twice with Et_2O, and acidified with concentrated hydrochloric acid to give 5.77 g (92%) of **7**, mp 217–225°. One recrystallization (EtOH) gave an analytical sample: mp 227–228°; ir 1700 cm^{-1} (C=O); nmr (DMSO) δ 1.3 (m, 4 H), 2.0 (m, 4 H), 2.5 (m, 4 H), 6.2 (s, 1 H), 7.3 (m, 4 H).

Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.12. Found: C, 80.06; H, 6.86.

Ethyl 8-Methoxy-2,3,4,4a,9,10-hexahydro-2,4a-ethanophenanthrene-2-carboxylate (6).—Similarly, 82.5 g (0.275 mol) of the pyran **2** gave with ethylene 73 g (85%) of colorless crystals (EtOH) of **6**, mp 92–92.5°, ir 1725 cm^{-1} (C=O).

Anal. Calcd for $C_{20}H_{24}O_3$: C, 76.89; H, 7.74. Found: C, 77.17; H, 7.81.

3,4,9,10-Tetrahydrophenanthrene-2-carboxylic Acid (4).—The pyran **1** (10 g, 37 mmol) was allowed to react with ethylene at 1000 atm at 200° for 14 hr to give 9 g (96%) of a reddish oil **3**, ir 1700 cm^{-1} (C=O). The oil was hydrolyzed with 2 *N* NaOH to give 6.55 g (74%) of **4**, mp 184–186°. One recrystallization (EtOH) gave an analytical sample: mp 188–189°; ir 1775 cm^{-1} (C=O); uv (EtOH) 353 nm (ε 19,600); nmr (DMSO) δ 2.5 (m, 8 H), 7.0 (s, 1 H), 7.2 (m, 4 H).

Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.99; H, 6.25.

7-Methoxy-2,3,4,4a,9,10-hexahydro-2,4a-ethanophenanthrene-2-carboxylic Acid (8).—A mixture of 460 g (1.47 mol) of **6**, 80 g (2 mol) of NaOH, and 1000 ml of diethylene glycol was heated at 160° for 2 hr. The mixture was cooled, diluted with H_2O, and acidified with concentrated hydrochloric acid to give 410 g (99%) of **8**. One recrystallization (CH_3CN) gave an analytical sample, mp 213–216°, ir 1700 cm^{-1} (C=O).

Anal. Calcd for $C_{18}H_{20}O_2$: C, 76.03; H, 7.09. Found: C, 76.24; H, 7.07.

1,2,3,4,4a,9,10,10a-Octahydro-2,4a-ethanophenanthrene-2-carboxylic Acid (11).—The ester **5** (25 g, 88.7 mmol) was hydrogenated in EtOH with 5% Pt–C at 3 atm at room temperature. Filtration and concentration of the filtrate gave 24.15 g (96%) of **9**, mp 74–79°, ir 1730 cm^{-1} (C=O). Hydrolysis of **9** with 2 *N* NaOH gave 19.8 g (91%) of **11**, mp 205–207°. One recrystallization (EtOH) gave an analytical sample: mp 209–210.5°; λ 1700 cm^{-1}; nmr (DMSO) δ 1.8 (m, 13 H), 2.75 (t, 2 H), 7.15 (m, 4 H).

Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.62; H, 7.90.

Ethyl 7-Methoxy-1,2,3,4,4a,9,10,10a-octahydro-2,4a-ethanophenanthrene-2-carboxylate (10).—A mixture of 69.6 g (0.2 mol) of **6**, 200 ml of EtOAc, and 0.2 g of 10% Pd/C was hydrogenated at 50 psi and room temperature to give 70 g (100%) of **10**. One recrystallization (*i*-PrOH–H_2O) gave an analytical sample, mp 65.5–67.5°, ir 1730 cm^{-1} (C=O).

Anal. Calcd for $C_{20}H_{26}O_3$: C, 76.40; H, 8.34. Found: C, 76.69; H, 8.40.

1,2,3,4,4a,9,10,10a-Octahydro-2,4a-ethanophenanthrene-2-amine Hydrochloride (12).—A solution of 6.0 g (23.4 mmol) of the acid **11** and 2.6 g (25.7 mmol) of Et_3N in 80 ml of Me_2CO was cooled to 0°. Maintaining this temperature, 2.8 g (25.8 mmol) of $ClCO_2Et$ was added, the reaction was stirred for 30 min, and then a solution of 3.1 g (47.7 mmol) of NaN_3 in 8 ml of H_2O was added. After the reaction mixture was stirred for an additional 30 min, it was poured onto ice and extracted with 4 × 50 ml of toluene. The combined extracts, after drying over $MgSO_4$, were gently heated until N_2 evolution ceased. Concentration under vacuum gave 5.75 g of the isocyanate, λ 2300 cm^{-1} (NCO). A solution of this isocyanate in 15 ml of methanol was stirred overnight and the solvent was removed under vacuum to yield the methyl carbamate, λ 1750 cm^{-1} (C=O). A solution of the carbamate in 100 ml of BuOH containing 11.2 g (0.2 mol) of KOH was heated at reflux overnight, then cooled and acidified with 4 *N* aqueous HCl. The acidic solution was concentrated under vacuum and the residue was twice recrystallized (H_2O) to give 1.8 g (29%) of **12**, λ 3300 cm^{-1} (NH_3), nmr (D_2O) δ 1.8 (m, 13 H), 2.75 (t, 2 H), 7.2 (m, 4 H).

Anal. Calcd for $C_{16}H_{21}N \cdot HCl \cdot {}^1/_2H_2O$: C, 70.18; H, 8.46; N, 5.12; Cl, 12.95. Found: C, 70.44; H, 8.46; N, 5.07; Cl, 12.94.

Registry No.—**1**, 23716-45-2; **2**, 32497-39-5; **4**, 39253-61-7; **5**, 23716-46-3; **6**, 32497-41-9; **7**, 23718-15-2; **8**, 32497-43-1; **9**, 23716-47-4; **10**, 32497-42-0; **11**, 23716-48-5; **12**, 23716-49-6; ethyl ethoxymethylenecyanoacetate, 94-05-3; α-tetralone, 529-34-0; 6-methoxy-α-tetralone, 1078-19-9.

A New Synthesis of α-Amino Acids[1]

KAZUO MATSUMOTO,* MAMORU SUZUKI, AND MUNEJI MIYOSHI

Research Laboratory of Applied Biochemistry, Tanabe Seiyaku Co. Ltd., 962 Kashima-cho, Higashiyodogawa-ku, Osaka, Japan

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A number of methods for the practical chemical synthesis of α-amino acids exist,[2] among which the amination of carboxylic acids figures prominently. For example, amination of α-halogen acids[3] and unsaturated esters[4] and reductive amination of α-keto acids[5] is frequently employed. Recently, Inouye, *et al.*, reported the amination of sodiomalonate by chloramine[6] and Yamada, *et al.*, have described a similar amination of α-lithiated carboxylic acid salts by various aminating reagents.[7] However, the carboxylation of the α-carbon atom of amines has not been reported previously.

Within the framework of our studies on the synthesis of amino acids, we have studied the reaction of isocyano compounds with various electrophiles.[8–10] In the present paper, we wish to report a new synthesis of α-amino acids by α-carboxylation of isocyano compounds, which are easily prepared from the corresponding amines.[11]

(1) Synthesis of Amino Acids and Related Compounds. 4. Part 3: ref 10. The present study was presented at the 22nd Meeting of the Kinki Branch of the Pharmaceutical Society of Japan, Hyogo, Nov. 12, 1972.

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(11) After the work described in this note was completed, we became aware of a report by W. Vaalburg, J. Strating, M. G. Woldring, and H. Wynberg, *Syn. Commun.*, **2**, 423 (1972), who prepared α-phenylglycine by the same method.