ultraviolet and n.m.r. spectra demonstrated that these products have the assigned structure.

Deprotonation of 5,7-Diphenyl-1-anthrazulenium Ion.—When solutions of either the fluoroborate, perchlorate, or trifluoroacetic salts of the 5,7-diphenyl-1-anthrazulenium ion in dichloromethane were added to a cooled solution (−65°) of trimethylamine (5 g.) in 25 ml. of dichloromethane, the color changed from the intense red characteristic of the ion to pale orange. The solutions darkened to a bright red in a few minutes. The ultraviolet spectrum of these solutions which were taken within 5 min. after initial reaction gave the spectrum in Figure 2. Isolation of a polymeric material after evaporation of the solvent gave an identical ultraviolet spectrum.

Anal. Found: C, 89.01; H, 5.91; mol. wt., 1170, 1172.

The analytical data indicates that the polymer chain is short. The low carbon content is explained by the short polymer chains since termination will leave a positive ion which must be accompanied by an inorganic anion which will cause a low carbon analysis.

Indano[5′,6:4,5]-5,7-diphenyltropenium Fluoroborate.—Indane[5′,6′:4,5]-2,7-diphenyltropone (200 mg., 0.575 mmole) was added to a suspension of lithium aluminum hydride (0.2 g. 5.25 mmoles) and allowed to stand for 20 min. Then 20 ml. of a saturated solution of ammonium chloride was added dropwise. The ether layer was isolated and dried over anhydrous magnesium sulfate. The ether was then removed on a rotary evaporator to give an amorphous solid which would not crystallize. This solid was dissolved in 5 ml. of ether and *ca.* 0.5 ml. of fluoroboric acid was added dropwise causing an immediate precipitation of a bright orange solid in quantitative yield. This compound could be recrystallized from acetonitrile, m.p. 218–220° dec.

Anal. Calcd. for $C_{26}H_{21}BF_4$: C, 74.30; H, 5.04. Found: C, 73.98, 73.95; H, 5.13, 5.19.

The ultraviolet spectrum (96% H_2SO_4) had λ_{max} 473 mμ (ε 3800), 327 mμ (ε 64,800), and 249 mμ (ε 24,500); the n.m.r. spectrum (trifluoroacetic acid), τ 0.32 (doublet, the 3,6-hydrogens of the tropenium ion), 0.67 (triplet, the 1-hydrogen of the tropenium ion), 1.34 (singlet, the benzene hydrogens of the indane system), 2.3 (multiplet, the 2,7-phenyl hydrogens), 6.46 (triplet, the α-hydrogens of the five-membered ring), and 7.51 (quintuplet, the β-hydrogens of the five-membered ring).

Acknowledgment.—The author would like to express his indebtedness to the National Science Foundation for Research Grant N.S.F. GP758 which supported this work.

The Preparation of S-(1-Propynyl)-L-cysteine

JOHN F. CARSON AND LOIS BOGGS

Western Regional Research Laboratory,[1] Albany, California

Received September 29, 1964

Pourcelot, *et al.*, reported that simple 2-propynyl sulfides isomerize in base to the corresponding 1-propynyl sulfides. We have found that this reaction takes place with S-(2-propynyl)-L-cysteine (I) which, in the presence of potassium *t*-butoxide in dimethylformamide at 0°, isomerizes to S-(1-propynyl)-L-cysteine (II).

S-(2-Propynyl)-L-cysteine was prepared by reaction of 3-bromopropyne with disodium cysteinate in ethanol. The structure of the compound was established by infrared (sharp absorption at 3290 cm.$^{-1}$ characteristic for a terminal triple bond) and by n.m.r. The proton on the α-carbon appears in the n.m.r. spectrum taken in 0.6 *M* sodium deuterioxide as a quartet centered at τ 6.53 (referred to sodium 3-(trimethylsilyl)-1-propanesulfonate) due to gauche-*trans* spin–spin coupling to the β-protons. The β-methylene protons occur as the AB portion of an ABX multiplet and are centered at τ 7.1. The γ-methylene protons occur as a sharp singlet at τ 6.67. The remaining protons exchange with deuterium of the solvent. Integration confirmed the assignment. In sodium hydroxide solution, the acetylenic proton occurs at *ca.* τ 7.4 as a broad band.

The structure of the isomerized compound II was established by disappearance of infrared absorption at 3290 cm.$^{-1}$ and by n.m.r. In 0.6 *M* sodium deuterioxide with the same reference as before, the n.m.r. spectrum again showed the α-proton as a quartet but slightly shifted downfield to τ 6.43. The protons of the β-carbon gave an ideal eight-line AB portion of an ABX multiplet and were centered at τ 7.05. The protons of the acetylenic methyl group gave a single sharp peak at τ 8.08. Integration confirmed the assignment.

$$HC{\equiv}CCH_2SCH_2CH(NH_2)COOH \longrightarrow$$
$$\text{I}$$
$$[H_2C{=}C{=}CH{-}S.....] \longrightarrow$$
$$CH_3C{\equiv}CSCH_2CH(NH_2)COOH$$
$$\text{II}$$

As Pourcelot, *et al.*,[2] suggested, this type of isomerization may proceed through a series of prototropic changes *via* an allenic intermediate[3] (see preceding equation).

We have been unable to isolate any allenic compounds in this reaction. When dimethyl sulfoxide was substituted for dimethylformamide, only resinous material could be isolated.

We further characterized S-(2-propynyl)- and S-(1-propynyl)-L-cysteines by preparation of crystalline N-2,4,6-trinitrophenyl derivatives and the cyclohexylamine salts of the N-2,4-dinitrophenyl (DNP) amino acids. The latter compounds have large negative molecular rotations in acetic acid in agreement with the general rule[4] that DNP derivatives of L-α-amino acids, except alanine, have negative rotations in acetic acid. The values are also large for the S-substituted cysteines. The trinitrophenyl derivatives of the two new amino acids, however, have small positive rotations in acetic acid.

Attempted reduction of the triple bond of S-(1-propynyl)-L-cysteine (II) with sodium and liquid ammonia led to desulfurization with the production of L-alanine as the only amino acid product.

Experimental

S-(2-Propynyl)-L-cysteine.—The procedure used is an adaptation of the method of Theodoropoulos.[5] To a stirred suspension

(1) A laboratory of the Western Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

(2) G. Pourcelot, P. Cadiot, and A. Willemart, *Compt. rend.*, **252**, 1630 (1961).

(3) Pourcelot, *et al.*,[2] isolated an allenic sulfide by isomerization of a 2-propynyl sulfide carrying a methyl substituent on the α-carbon.

(4) K. R. Rao and H. A. Sober, *J. Am. Chem. Soc.*, **76**, 1328 (1954); J. F. Carson and F. F. Wong, *J. Org. Chem.*, **26**, 4997 (1961).

(5) D. Theodoropoulos, *Acta Chem. Scand.*, **13**, 385 (1959).

of 19.3 g. (0.11 mole) of L-cysteine hydrochloride hydrate in 600 ml. of absolute ethanol there was slowly added 9.7 g. (0.42 mole) of sodium in small pieces. The reaction mixture was kept cool with an ice bath and was maintained under a nitrogen atmosphere. When all the sodium had dissolved and when the evolution of hydrogen had ceased, 25 g. (0.21 mole) of 3-bromopropyne was added and the mixture was stirred at room temperature under nitrogen for 2 hr. The alcoholic suspension was then concentrated *in vacuo* to *ca.* 200 ml. and diluted with 500 ml. of water and 75 ml. of acetic acid. The solution was poured through a column of Amberlite IR-120 (H^+; 500 ml.). The resin was washed with 3 l. of distilled water and the amino acid was eluted with 2 l. of 2 *N* ammonium hydroxide. Concentration of the ammoniacal solution *in vacuo* to 150 ml. followed by refrigeration yielded 10.4 g. of product. An additional 4.6 g. was obtained from the mother liquor by addition of ethanol (85.7% yield).

Recrystallization from aqueous ethanol yielded 13.2 g. (75% yield) of long blades, decomposing over the range from 165–300°, $[\alpha]^{25}D$ −8.5 (*c* 1.17, water).

Anal. Calcd. for $C_6H_9NO_2S$: C, 45.26; H, 5.70; N, 8.80. Found: C, 45.5; H, 5.72; N, 8.73.

The infrared spectrum (potassium bromide disk) showed bands at 3290 (s) (HC≡C), 2050–2100 (w), 1595 and 1625(s) (ionized carboxyl) $cm.^{-1}$.

In paper chromatography, the compound had a relative R_f with respect to alanine of 2.06 with 1-butanol–acetic acid–water (63:10:27) and 2.62 with collidine–lutidine–water (3:1:1).

Cyclohexylamine Salt of N-2,4-Dinitrophenyl-S-(2-propynyl)-L-cysteine.—This compound was prepared by a procedure previously described.[4] The salt was crystallized from acetone–ether (1:2): m.p. 149–150°, $[\alpha]^{26}D$ −134.3 (*c* 0.7664, acetic acid).

Anal. Calcd. for $C_{18}H_{24}N_4O_6S$: C, 50.93; H, 5.70; N, 13.20. Found: C, 50.9; H, 5.68; N, 13.0.

N-2,4,6-Trinitrophenyl-S-(2-propynyl)-L-cysteine.—The procedure of Irreverre, *et al.*,[6] was used. A solution of 0.90 g. of the amino acid and 1.95 g. of sodium 2,4,6-trinitrobenzenesulfonate in 65 ml. of water was stirred for 1 hr. at room temperature while 20% sodium carbonate solution was added to maintain a pH between 7.5 and 8.0. The deep red solution, after standing overnight in the dark, was chilled and acidified with cold 2 *N* hydrochloric acid. The product precipitated as a gum which crystallized on standing, yield 1.67 g. Recrystallization from 25 ml. of 80% methanol yielded 1.20 g. of the pure compound as yellow needles: m.p. 111–112, $[\alpha]^{26}D$ +2.7 (*c* 0.6292, acetic acid).

Anal. Calcd. for $C_{12}H_{10}N_4O_8S$: C, 38.92; H, 2.72. Found: C, 39.0; H, 2.85.

S-(1-Propynyl)-L-cysteine.—To a mixture of 14 g. (0.088 mole) of S-(2-propynyl)-L-cysteine in 900 ml. of dry dimethylformamide cooled in a salt–ice bath, there was added 13 g. (0.116 mole) of potassium *t*-butoxide and the pale amber suspension was stirred for 8 hr. at 0° under anhydrous conditions. A solution of 80 ml. of acetic acid in 2 l. of ice–water was then added slowly with external cooling.

The turbid solution was passed through a column of Amberlite IR-120 (H^+, 470 ml.) after which the resin column was washed with 3 l. of ice water, and the amino acid was then eluted with 2.5 l. of cold 1.7 *N* ammonium hydroxide. Concentration *in vacuo* to *ca.* 100 ml. and refrigeration yielded 5.4 g. A second crop (2.76 g.) was obtained by concentration of the mother liquor to 40 ml., and a third crop (1.0 g.) was obtained by adding 2 volumes of ethanol to the mother liquor (total crude yield 65%). The fractions were chromatographically homogeneous. The combined crops were recrystallized by concentrating a dilute ammoniacal solution *in vacuo* to give 7.95 g. (57%) as coarse needles: m.p. 176°, $[\alpha]^{26}D$ −14.7 (*c* 1.23, 0.25 *N* sodium hydroxide).

Anal. Calcd. for $C_6H_9NO_2S$: C, 45.26; H, 5.70; N, 8.80; S, 20.14. Found: C, 45.1; H, 5.64; N, 8.80; S, 20.4.

In paper chromatography, the compound had a relative R_f with respect to alanine of 2.76 with butanol–acetic acid–water (63:10:27) and 3.76 with collidine–lutidine–water (3:1:1).

In the infrared (KBr pellet) the compound showed typical amino acid absorption between 2200 and 3100, no absorption near 3290 (absence of terminal acetylene), 2050–2100 (w), 1600, and 1625 $cm.^{-1}$ (ionized carboxyl).

Cyclohexylamine Salt of N-2,4-Dinitrophenyl-S-(1-propynyl)-L-cysteine.—The derivative was prepared by a procedure previously described[4] and was crystallized from acetone–ether (1:4): m.p. 124–125° dec., $[\alpha]^{26}D$ −202.4 (*c* 0.7, acetic acid).

Anal. Calcd. for $C_{18}H_{24}N_4O_6S$: C, 50.93; H, 5.70. Found: C, 51.0; H. 5.56.

N-2,4,6-Trinitrophenyl-S-(1-propynyl)-L-cysteine was prepared in the same manner as the isomeric product already described. It was isolated from methanol–water (1:1) as yellow-orange needles: m.p. 89–91° dec., $[\alpha]^{26}D$ +32.1 (*c* 0.7, acetic acid).

Anal. Calcd. for $C_{12}H_{10}N_4O_8S$: C, 38.92; H, 2.72. Found: C, 38.8; H, 2.67.

Reaction of II with Sodium and Ammonia.—To a solution of 4.5 g. (0.0283 mole) of S-(1-propynyl)-L-cysteine in 500 ml. of liquid ammonia cooled in a Dry Ice–acetone bath, there was added 2.0 g. of sodium (0.087 g.-atom) in small portions over 2 hr. The deep blue solution was allowed to stand for an additional 2 hr. and the sodium was then destroyed with ammonium chloride. The ammonia was allowed to evaporate spontaneously and the remaining solid was dissolved in water and passed through a strong cation exchanger. Elution with ammonia and concentration of the eluate to a small volume followed by addition of ethanol yielded 2.52 g. of L-alanine (65.9%). Identity was established by paper chromatography and infrared (potassium bromide disk). L-Configuration was established by preparation of the N-*p*-toluenesulfonyl derivative, $[\alpha]^{27}D$ −15.7 (*c* 2.13, methanol) in agreement with an authentic sample which had $[\alpha]^{25}D$ −15.41.

Instruments.—Infrared spectra were run on a Perkin-Elmer Model 237 and n.m.r. on a Varian Associates A-60 spectrometer.

Acknowledgment.—The authors wish to acknowledge the assistance of Dr. Robert Lundin and Miss Nancy Henderson for determining n.m.r. spectra and for the interpretation; and to Mr. L. M. White and Miss Geraldine Secor for elemental analyses. Reference to a company or product name does not imply approval or recommendation of the product by the U. S. Department of Agriculture to the exclusion of others that may be suitable.

(6) F. Irreverre, K. Morita, A. V. Robertson, and B. Witkop, *J. Am. Chem. Soc.*, **85**, 2824 (1963).