methanol was added and after another 20 min. an additional 10 ml. of the 0.30 *N* base was added.) The resulting solution was acidified to litmus with 2 *N* hydrochloric acid, water was added, and the amorphous material which separated soon crystallized and was collected. Two recrystallizations from acetone–water gave 413 mg. (99%) of IIa (which contained water of crystallization), m.p. 123–126°. A chloroform solution of the product was dried, concentrated, and diluted with carbon tetrachloride to yield 281 mg. of IIa as white plates with m.p. 126–128°; $[\alpha]_D$ +25° (*c* 1.845); $\lambda_{max}^{CHCl_3}$ 2.90 (w, br.) μ.

Anal. Calcd. for $C_{27}H_{48}O_3$: C, 77.08; H, 11.50. Found: C, 77.00; H, 11.49.

Reaction of 5β-Cholestane-3β,5,6β-triol 3,6-Diacetate (IIb) with Potassium Acid Sulfate.—A mixture of 500 mg. (0.994 mmole) of IIb, 150 mg. of powdered potassium acid sulfate, and 5 ml. of acetic anhydride was heated on the steam bath for 1 hr., after which time crushed ice was added to the reaction mixture. After standing for 2.5 hr., the crystallline material was collected and dissolved in methylene chloride. The dried solution was evaporated, and the residue was chromatographed on 25 g. of alumina (Merck, acid-washed). Elution with 40–60% benzene–petroleum ether yielded 308 mg. of semicrystalline material which, upon crystallization from methanol, gave 207 mg. (43%) of cholest-4-ene-3β,6β-diol diacetate (III), m.p. 130–135°, $[\alpha]_D$ −13.5° (*c* 2.07). Recrystallization from methanol gave 170 mg. with m.p. 133–133.5°, λ_{max} 5.74 (s) μ. This material did not depress the melting point of authentic III (m.p. 133–133.5°, $[\alpha]_D$ −13°) prepared by the Darzens' dehydration of 5α-cholestane-3β,5,6β-triol 3,6-diacetate and the infrared spectra of the two samples were identical.

The semicrystalline material (115 mg.) that was eluted with 70% benzene–petroleum ether to 100% benzene mixtures was crystallized from methanol to yield 60 mg. (14%) of 5α-cholestan-3β-ol-6-one acetate (IV) as white rods with m.p. 126–128°, $[\alpha]_D$ −20° (*c* 0.75). Recrystallization from methanol gave 31 mg. with m.p. 128–130°. No depression in melting point was observed upon admixture with authentic IV and the infrared spectra of the two samples were identical.

5β-Cholestane-3β,5-diol-6-one Diacetate (Ib). A.—A mixture of 700 mg. (1.52 mmoles) of 5β-cholestane-3β,5-diol-6-one 3-monoacetate (Ia), 7.5 ml. of acetic anhydride, and 7.5 ml. of glacial acetic acid was warmed on the hot plate until solution was complete. One hundred and forty milligrams of *p*-toluenesulfonic acid monohydrate was added to the cooled solution, which was allowed to remain overnight at room temperature. The flask was then cooled in an ice–water mixture as water was added in portions. The precipitated product was collected, washed with water, and recrystallized from methanol containing a small amount of chloroform to yield 700 mg. (92%) of Ib, m.p. 190–193°. Recrystallization from chloroform–petroleum ether gave 653 mg. of small white needles with m.p. 192–193.5°; $[\alpha]_D$ −26° (*c* 1.25), −23° (*c* 1.30); λ_{max} 5.73 (s) and 5.79 (s, sh) μ.

Anal. Calcd. for $C_{31}H_{50}O_5$: C, 74.06; H, 10.02. Found: C, 74.02; H, 9.88.

B.—A mixture of 300 mg. (0.652 mmole) of Ia, 80 mg. of powdered potassium acid sulfate, and 2.5 ml. of acetic anhydride was heated on the steam bath for 80 min. Crushed ice was added to precipitate the product, which was collected, washed with water, and recrystallized from acetone–petroleum ether to give 285 mg. (87%) of Ib, m.p. 191–193°. No depression of the melting point occurred upon admixture with Ib prepared by method A.

5β-Cholestane-3β,5-diol-6-one Ethylene Ketal (V).—To a solution of 1.000 g. (2.17 mmoles) of the diolone monoacetate (Ia) in 80 ml. of toluene were added 10 ml. of redistilled ethylene glycol and 80 mg. of *p*-toluenesulfonic acid monohydrate. The mixture was boiled under reflux for 6.75 hr. (constant water separation) with magnetic stirring, cooled, stirred for a few minutes after the addition of 1 g. of anhydrous potassium carbonate, and diluted with water. The layers were separated and the aqueous phase was saturated with sodium chloride and extracted twice with ether. The combined organic phases were washed with a saturated saline solution and dried. Evaporation of the solvents gave an oil [λ_{max} 2.79–2.89 (w, br), 5.75 (m, sh), 5.84 (m) μ] which was treated with 10 ml. of 0.34 *N* methanolic potassium hydroxide by warming on the hot plate for 0.5 hr. The cooled solution was diluted with water and extracted three times with methylene chloride. The combined extracts were washed with water and dried. Evaporation of the solvent yielded an orange oil which crystallized slowly (upon seeding with V from another run) from cold 95% ethanol to give 576 mg. (57%) of the ketal (V) as pale yellow crystals, m.p. 136–140°. Recrystallization from methanol yielded 501 mg. of pure V, m.p. 140–142°; $[\alpha]_D$ +23.5° (*c* 1.41); λ_{max} 2.82 (w, br.) μ.

Anal. Calcd. for $C_{29}H_{50}O_4$: C, 75.27; H, 10.89. Found: C, 75.33; H, 10.67.

Hydrolysis of the Ethylene Ketal (V).—A solution of 50 mg. (0.108 mmole) of V and 12 mg. of *p*-toluenesulfonic acid monohydrate in 3 ml. of acetone containing 3 drops of water was allowed to stand at room temperature for 22.5 hr. Three milliliters of water was added, most of the acetone was removed by an air stream, and the resulting suspension was extracted three times with methylene chloride. The dried extracts were evaporated to yield an oil whose infrared spectrum was identical to that of 5β-cholestane-3β,5-diol-6-one.[5a]

The oil was dissolved in 0.5 ml. of glacial acetic acid and 0.5 ml. of acetic anhydride and treated with 10 mg. of *p*-toluenesulfonic acid monohydrate for 21 hr. at room temperature. Crushed ice was added to the green solution and, after precipitation was complete, the product was collected and recrystallized from acetone–petroleum ether to give 45 mg. (83%, calculated from V) of the diolone diacetate Ib,[11] m.p. 190–192°. The mixture melting point with Ib prepared from Ia was 191–192.5°.

Reaction of the Ethylene Ketal (V) with Potassium Acid Sulfate.—A mixture of 143 mg. (0.309 mmole) of V, 50 mg. of potassium acid sulfate, and 4 ml. of acetic anhydride was heated on the steam bath for 70 min. Crushed ice was added to the green solution and, after standing overnight, the orange oil that had separated was redissolved by the addition of *ca.* 25 ml. of acetone. The resulting solution was heated on the steam bath for 1.5 hr., as acetone was added periodically to maintain solution. Cooling, followed by the addition of water and two extractions with chloroform gave an oil whose infrared spectrum [λ_{max} 2.82 (w), 2.89 (w), 5.75 (s), and 5.85 (m) μ] indicated incomplete removal of the ketal group and significant acetylation at C-3. The oil was treated in the manner used for the hydrolysis of the ketal (V) and gave another oil whose infrared spectrum [λ_{max} 2.89 (w), 5.75 (s), and 5.85 (s) μ] was identical with that of Ia.[5a] Upon treatment with 80 mg. of potassium acid sulfate in 2 ml. of acetic anhydride on the steam bath for 1 hr., this material yielded a brown oil which, upon two recrystallizations from methanol, gave 35 mg. (23%) of the diolone diacetate (Ib) as brown crystals, m.p. 185–187° (previous softening).

Acknowledgment.—The author is indebted to Thomas Green and Steven Dressner for technical assistance.

(11) The facile hydrolysis of V and subsequent conversion to Ib indicated that no unusual rearrangement occurred in the formation of V from Ia: *cf.* S. Bernstein, M. Heller, and W. S. Allen, *J. Org. Chem.*, **26**, 1333 (1961).

Heterocyclic Derivatives of 3-Aminopropanethiol

E. CAMPAIGNE AND P. K. NARGUND

Department of Chemistry, Indiana University, Bloomington, Indiana

Received July 22, 1963

2-Aminoethanethiol, 3-aminopropanethiol, and their substituted derivatives[2] are known to protect experi-

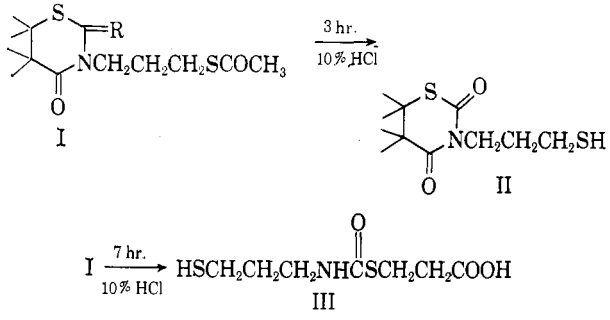
(1) Contribution No. 1156, from this laboratory. This investigation was supported by the U. S. Army Research and Development Command (Contract No. DA-49-193-MD 2096).

(2)(a) D. G. Doherty and W. T. Burnett, Jr., *Proc. Soc. Exptl. Biol. Med.*, **89**, 312 (1955); (b) S. Akerfeldt, *Acta Chem. Scand.*, **14**, 1980 (1960); D. P. Jacobus, B. Ramsay, R. E. Spalding, and D. C. Dittmer, Abstracts of Papers, presented at the 141st National Meeting of the American Chemical Society, Washington, D. C., March, 1962; (c) T. P. Johnston and A. Gallagher, *J. Org. Chem.*, **26**, 3780 (1961), and references cited therein; (d) H. Bretschneider, *Monatsh.*, **81**, 372 (1950); Holmberg and B. Sörbo, *Nature*, **183**, 832 (1959); B. Sörbo, *Acta Chem. Scand.*, **12**, 1990 (1958); (e) A. Kaluszyner, P. Czerniak, and E. D. Bergmann, *Radiation Res.*, **14**, 23 (1961).

mental animals against ionizing radiation. In the course of attempts to synthesize effective drugs with lower toxicity and longer duration of protective action, 3-(β-aminoethyl)-1,3-thiazane-2,4-dione hydrochloride was found to be an active compound.[3] We were therefore interested in synthesizing N-mercaptoalkyl derivatives of 1,3-thiazane-2,4-dione and thiazolidine-2,4-dione, which are derivatives of aminoalkanethiols.

3-(γ-Acetylthiopropyl)-1,3-thiazane-2,4-dione (I, R = O) was obtained in 60% yield by refluxing a mixture of thiolacetic acid and 3-allyl-1,3-thiazane-2,4-dione in carbon tetrachloride over an ultraviolet lamp in a nitrogen atmosphere. 3-(γ-Acetylthiopropyl)thiazolidine-2,4-dione (IV) was prepared in a similar way.

Studies on the acid hydrolysis of (I, R = O) showed that it was possible to effect the complete hydrolysis of the acetylthio group to thiol (II) in 3 hr., but that prolonged hydrolysis resulted in cleavage of the amide linkage of the thiazane ring as well, affording the mercapto acid (III). Mild acid hydrolysis of IV gave 3-(γ-mercaptopropyl)thiazolidine-2,4-dione (V).



It is remarkable that attempts to prepare the anti-Markovnikov thiolacetic acid adducts of 3-allyl-1,3-thiazane-2-thione-4-one (I, R = S) and 3-allylrhodanine with or without benzoyl peroxide as a catalyst and ultraviolet light as a radical promoter failed to give the desired products. The starting thiones were partially recovered in these reactions. It seems that, in some way, the thione moieties are acting to inhibit the free-radical addition reaction, possibly by inhibiting radical formation from thiolacetic acid.

The n.m.r. spectrum of I was in accord with the assigned structure, in particular showing a quartet resonance due to the four ring protons at 6.93 and a singlet resonance for the methyl of the acetyl group at 7.70 τ. The N-methylene protons occurred as a triplet at 6.18, whereas the S-methylene protons were observed as a triplet at 7.22 τ. The methylene protons flanked by the two adjacent methylene groups were seen as a multiplet in the range of 7.88 to 8.42 τ. The n.m.r. spectrum of II showed the quartet of four ring protons at 6.93 and triplet for the N-methylene protons at 6.17 τ. A multiplet due to the middle methylene protons and the thiol proton was present at 8.00 to 8.58, whereas the S-methylene protons appeared as a multiplet at 7.37 to 7.70 τ. The assignment of τ-values for the middle methylene, S-methylene, and thiol protons is supported by the τ-values of 1,3-propanedithiol[4] which shows a triplet resonance for the thiol proton at 8.65, a multiplet for the middle methylene protons at 8.22, and a multiplet for the S-methylene protons at 7.32 τ.

The n.m.r. spectrum of IV was in agreement with the assigned structure, showing a singlet at 5.93 due to the two ring protons and a singlet at 7.70 τ due to the methyl protons of the acetyl group. A triplet for the N-methylene protons was shown at 6.40 and a triplet for the S-methylene protons appeared at 7.05 τ. A multiplet for the methylene protons flanked by the two adjacent methylene groups was observed at 7.97 to 8.33 τ. The structure of V was confirmed by the n.m.r. spectrum, showing a singlet resonance at 5.97 and, in agreement with the spectrum of the thiazanedione, a triplet resonance for the N-methylene protons at 6.33 τ. The multiplet for the middle methylene protons and the thiol was shifted to 7.97 to 8.75, whereas the S-methylene protons were observed as a multiplet in the range of 7.42 to 7.68 τ.[5] The structure of III was confirmed by the infrared spectrum, which showed all the characteristic peaks for the NH, CH, SH (very weak), amide carbonyl, carboxyl carbonyl, and C–N stretches; the first and last, being shifted from their usual positions, are in the characteristic absorptions for monoalkyl dithiocarbamates.[6]

Experimental[7]

3-Allyl-1,3-thiazane-2,4-dione.—The synthesis consisted of two steps: (1) preparation of O-ethyl allylthiocarbamate, and (2) its reaction with β-chloropropionic acid in acetic anhydride to give 3-allyl-1,3-thiazane-2,4-dione.

(1) **Preparation of O-ethyl Allylthiocarbamate.**—Allyl isothiocyanate (59.5 g., Aldrich Chemical Co.) and ethanol (120 ml.) were refluxed for 60 hr. on a steam bath and the excess solvent was removed under reduced pressure. The liquid was distilled and the fraction boiling at 64–65° (0.3 mm.), 71.5 g. (82%), was collected. Vladzimirskaya[8] obtained this compound in 70.7% yield.

(2) **Reaction of O-Ethyl Allylthiocarbamate and β-Chloropropionic Acid.**—A mixture of O-ethyl allylthiocarbamate (145 g., 1 mole), β-chloropropionic acid (108.5 g., 1 mole), acetic anhydride (350 ml.), and 2 drops of concentrated sulfuric acid was refluxed for 4–5 hr., after which the excess acetic anhydride was removed under reduced pressure. The fraction distilling at 108–111° (1.1 mm.) was collected and weighed 100 g. (59%). The infrared spectrum showed by the absence of an NH band at 3–3.1 and C–N stretch at 6.6, and by the presence of amide carbonyl peak at 5.9 and carbamoyl carbonyl peak at 6.15 μ that the product was the ring-closed thiazanedione. The boiling point of 3-allyl-1,3-thiazane-2,4-dione is reported[8] as 82–87° (0.7 mm.).

Anal. Calcd. for $C_7H_9NO_2S$: C, 49.12; H, 5.26; N, 18.71 Found: C, 49.00; H, 5.50; N, 18.67.

β-(Allyldithiocarbamoyl)propionic Acid.—Sodium allyldithiocarbamate, prepared from 28.5 g. (0.5 mole) of allylamine, carbon disulfide, and sodium hydroxide in the usual way, was dissolved in 250 ml. of water, cooled to 0°, and 36 g. (0.5 mole) of β-propiolactone added dropwise, with stirring, at such rate as to keep the temperature below 5°. One-half hour after addition was complete, the solution was acidified with 18% hydrochloric acid, and the oil which separated was extracted with ether, and the ether extracts dried over anhydrous sodium sulfate. Removal of ether left a yellow solid which was recrystallized from

(3) E. Campagine, L. Fedor, and M. C. Wani, Abstracts of Papers, 141st Meeting of the American Chemical Society, Washington, D. C., March, 1962, p. 32N.

(4) High Resolution N.M.R. Spectra Catalog, Varian Associates, Palo Alto, Calif., 1962, Spectrum No. 47.

(5) Proton magnetic resonance spectra were determined in carbon tetrachloride at concentrations between 6–8% w./v. at 25°, using a Varian A-60 spectrometer, and tetramethylsilane as an internal standard.

(6) L. J. Bellamy, "Infrared Spectra of Complex Molecules," 2nd Ed.; Methuen, London, 1960, p. 357.

(7) All melting points are corrected. Analyses were performed by the Midwest Microlab, Inc., Indianapolis, Ind. The assistance of Mr. Rod Hamilton in determination of the n.m.r. spectra is acknowledged.

(8) E. V. Vladzimirskaya, *J. Gen. Chem. USSR*, **32**, 528 (1962).

benzene to give 30 g. (29%) of yellow needles melting sharply at 69.7°, and showing infrared absorption at 5.9 μ.

3-Allyl-1,3-thiazane-2-thion-4-one.—Following the procedure of Gresham,[9] 20.5 g. (0.1 mole) of β-(allyldithiocarbamoyl)-propionic acid was dissolved in 25 ml. of acetic anhydride containing 2 drops of concentrated sulfuric acid, and the mixture stirred for 2 hr. at 55–70°, until the solution became clear. After filtering, the cooled clear solution was poured into 150 ml. of ice water, stirred, and let stand overnight. The oil which separated was extracted with ether, and, after drying over anhydrous sodium sulfate, the ether was removed. The resultant yellow oil, $n^{20}D$ 1.6383, was collected between 145–147° at 0.5 mm., and weighed 12 g. (64%). The presence of a peak at 5.9, but none at 6.1–6.2 μ, confirmed the assignment of amide and carbamoyl CO peaks in 3-allyl-1,3-thiazane-2,4-dione.

Anal. Calcd. for $C_7H_9NOS_2$: C, 44.91; H, 4.81; N, 7.48; S, 34.20. Found: C, 45.05; H, 5.22; N, 7.06; S, 33.30.

3-(γ-Acetylthiopropyl)-1,3-thiazane-2,4-dione (I).—Thiolacetic acid (22.8 g., 0.3 mole, Aldrich Chemical Co.) was added to 3-allyl-1,3-thiazane-2,4-dione (51 g., 0.3 mole) dissolved in carbon tetrachloride (120 ml.), and the mixture was refluxed over a ultraviolet lamp (140-w.) for 22 hr. under a nitrogen atmosphere in a quartz flask. Excess solvent was removed under reduced pressure; distillation of the crude product gave a forefraction boiling in the range of 60–116° (0.3–0.8 mm.) which was discarded and a second fraction, boiling at 195–196° (0.4 mm.) which weighed 42 g. (60%). The infrared spectrum of this fraction showed the amide carbonyl peak at 5.84, carbonyl of the acetyl group at 5.92, and the carbamoyl carbonyl peak at 6.05 to 6.07 μ.

Anal. Calcd. for $C_9H_{13}NO_3S_2$: C, 43.70; H, 5.30; S, 25.90. Found: C, 43.57; H, 5.44; S, 25.61.

3-(γ-Mercaptopropyl)-1,3-thiazane-2,4-dione (II).—A mixture of I (18.4 g.) and 10% hydrochloric acid (300 ml.) was heated with stirring on a steam bath for 3 hr. under nitrogen. At the end of 3 hr. the reaction mixture was cooled and extracted with ether. The ether extract was dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the product distilled at 153–154° (1 mm.) as a pale yellow liquid weighing 11 g. (70%). The infrared spectrum showed thiol absorption at 3.9, amide carbonyl absorption at 5.9, and carbamoyl carbonyl absorption at 6.15 μ.

Anal. Calcd. for $C_7H_{11}NO_2S_2$: C, 40.97; H, 5.37; N, 6.83; S, 31.22. Found: C, 40.69; H, 5.65; N, 6.68; S, 31.40.

β-(3-Mercaptopropylthiocarbamoyl)propionic Acid (III).—A mixture of I (12.1 g.) and 10% hydrochloric acid (150–200 ml.) was heated with stirring on a steam bath for 7 hr. under nitrogen. The reaction mixture was cooled and extracted with ether, and the ether extract dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the solid recrystallized from benzene as colorless needles. It weighed 7 g. (64%) and melted at 100°. The infrared spectrum showed the shifted NH absorption at 3.06,[6] amide carbonyl absorption at 5.95, carbamoyl carbonyl absorption at 6.18, and shifted C–N stretch[6] at 6.6 μ. A very weak peak for thiol was present at 3.91 μ. The compound gave a positive potassium iodide–iodine solution test for free thiol.

Anal. Calcd. for $C_7H_{13}NO_3S_2$: C, 37.65; H, 5.83; N, 6.28; S, 28.70. Found: C, 37.96; H, 6.02; N, 6.27; S, 29.00.

3-Allylthiazolidine-2,4-dione.—This compound was prepared according to the procedure described under 3-allyl-1,3-thiazane-2,4-dione using chloroacetic acid instead of β-chloropropionic acid. It distilled at 81–83° (0.7 mm.) and weighed 125 g. (79.6%). E. V. Vladzimirskaya[10] reports b.p. 81–85° (0.7 mm.). The infrared spectrum of the compound showed, by the presence of amide carbonyl peak at 5.75, the carbamoyl carbonyl peak at 6.0 μ, and the absence of NH and C–N stretches, that the product was ring-closed thiazolidinedione. 3-Allylthiazolidine-2-thion-4-one (3-allylrhodanine, Aldrich) showed a single amide carbonyl peak at 5.75 μ, thus confirming the band assignments for amide and carbamoyl carbonyl peaks.

3-(γ-Acetylthiopropyl)thiazolidine-2,4-dione (IV).—The reaction of the thiolacetic acid and 3-allylrhodanine was carried out according to the procedure described for the preparation of I. The product (40 g., 57%) distilled as a yellow liquid boiling at 162–163° (0.5 mm.) and 168–171° (1 mm.). The infrared spectrum showed two peaks for carbonyl absorptions, one at 5.7 and the other a broad peak at 5.9 and 5.98 μ. The peak at 5.7 is due to amide carbonyl of the thiazolidine ring, but the two carbonyl peaks of the acetyl and carbamoyl groups result in a single broad peak at 5.9 to 5.98 μ.

Anal. Calcd. for $C_8H_{11}NO_3S_2$: C, 41.20; H, 4.72; N, 6.01; S, 27.47. Found: C, 41.60; H, 4.96; N, 5.41; S, 27.59.

3-(γ-Mercaptopropyl)thiazolidine-2,4-dione (V).—A mixture of IV (23.3 g.) and 10% hydrochloric acid (350 ml.) was heated on a steam bath for 3 hr. while stirring under nitrogen. The reaction mixture was then cooled and extracted with three 100-ml. portions of ether. The combined ether extract was dried over anhydrous sodium sulfate and the solvent removed. The yellow liquid boiling at 139–141° (1 mm.) was collected and weighed 13 g. (68%). The compound gave a positive potassium iodide–iodine solution test for thiol. The infrared spectrum showed the amide carbonyl absorption at 5.7 and carbamoyl carbonyl absorption at 5.95–6.0 μ.

Anal. Calcd. for $C_6H_9NO_2S_2$: C, 37.70; H, 4.71; N, 7.33; S, 33.53. Found: C, 37.38; H, 4.83; N, 7.14; S, 33.65.

(9) T. L. Gresham, J. E. Jansen, and F. W. Shaver, *J. Am. Chem. Soc.*, **70**, 1001 (1948).

(10) E. V. Vladzimirskaya, *J. Gen. Chem. USSR*, **32**, 2000 (1962).

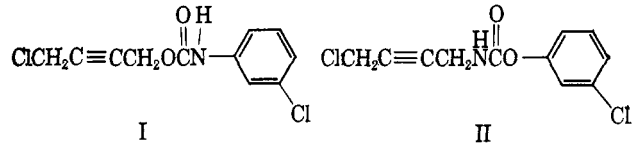
Study of 4-Amino-2-butyn-1-ol and Preparation of the Reverse Carbamate of the Selective Herbicide, Barban

ERIC C. JUENGE[1] AND PAUL SPANGLER[2]

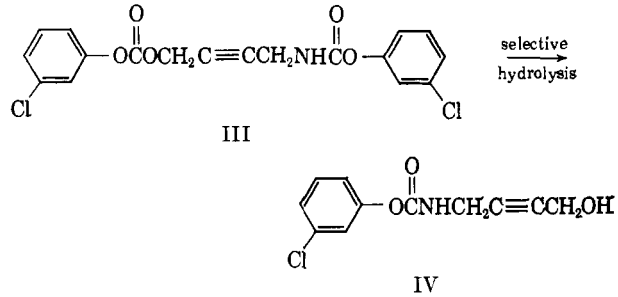
The Department of Chemistry, Kansas State College of Pittsburg, Pittsburg, Kansas, and Spencer Chemical Company, Merriam, Kansas

Received August 1, 1963

The successful preparation of barban, 4-chloro-2-butynyl *N*-(3-chlorophenyl)carbamate (I), and application as a selective herbicide[3,4] suggested the preparation of the reverse carbamate of barban, 3-chlorophenyl *N*-(4-chloro-2-butynyl)carbamate (II), starting with 4-amino-2-butyn-1-ol.



Attempted reaction of 3-chlorophenyl chloroformate with 4-amino-2-butyn-1-ol to initiate the preparation of the reverse carbamate (II) failed when substitution occurred at both amino and hydroxy groups yielding 3-chlorophenyl *N*-[4-(3-chlorophenylcarbonyldioxy)-2-butynyl]carbamate (III). Good yields of the bis-



(1) Kansas State College of Pittsburg, Pittsburg, Kan.

(2) National Science Foundation Undergraduate Research Participant, Kansas State College, Pittsburg, Kan.

(3) T. R. Hopkins, R. D. Neighbors, P. D. Strickler, and L. V. Phillips, *J. Org. Chem.*, **24**, 2040 (1959).

(4) T. R. Hopkins and J. W. Pullen, U. S. Patent 2,906,614 (1959).