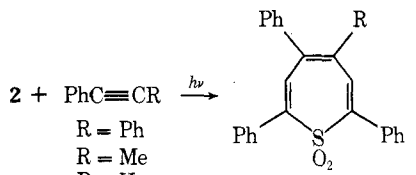
ing of **5** in tetralin yielded 1,2,4,5-tetraphenylbenzene, which is identical (melting point, ir and nmr spectra) with the authentic sample prepared from 3,4-diphenyl-4-hydroxycyclopent-2-en-1-one with diphenylacetylene.[17] Hydrogenation of **5** over Pd/C resulted in the uptake of 3 molar equiv of hydrogen and gave 2,4,5,7-tetraphenylthiacycloheptane 1,1-dioxide. The thermal decomposition to the benzene derivative and sulfur dioxide and ready catalytic hydrogenation to hexahydrothiepin 1,1-dioxide are characteristic with thiepin 1,1-dioxide.[13] These results, in addition to the spectral properties, support the contention that the photoproducts of **2** with diphenylacetylene, methylphenylacetylene, and phenylacetylene are **5**, **6**, and **7**,[18] respectively.



5, R = Ph
6, R = Me
7, R = H

Irradiation of a mixture of **2** and dimethyl acetylenedicarboxylate in benzene resulted in the recovery of the starting materials, whereas photolysis of **2** and 2- or 3-hexyne in benzene gave a polymeric material. Irradiation of a mixture of 3,5-diphenyl-4*H*-thiopyran 1,1-dioxide and diphenylacetylene did not furnish thiepin 1,1-dioxide derivative. The nature of the substituents, both in 4*H*-thiopyran-4-one 1,1-dioxide and acetylenes, seems to be important in the formation of thiepin 1,1-dioxide. Careful study of the ultraviolet spectra of a mixture of **2** and diphenylacetylene in benzene or cyclohexane showed no specific interaction in the ground state, although **2** was expected to function as an electron acceptor in a charge-transfer complex, as has been observed in the case of *p*-quinones.[20]

Experimental Section

Melting points were not corrected. The infrared spectra were recorded on a JASCO DS-402G spectrophotometer. The ultraviolet spectra were obtained with a Hitachi 124 spectrophotometer and the nmr spectra were measured with a JEOL PS-100 spectrometer. The mass spectra were recorded on a Hitachi RMU-6L spectrometer. The molecular weights were determined by a Hitachi 115 molecular weight measuring apparatus.

2,6-Diphenyl-4*H*-thiopyran-4-one 1,1-dioxide[21] was prepared by the oxidation of 2,6-diphenyl-4*H*-thiopyran-4-one with hydrogen peroxide. Arylacetylenes commercially available were used, after purification by distillation or recrystallization.

Irradiation of 2 with Arylacetylenes. A mixture of **2** (0.3 g) and arylacetylene (1.2–3.0 g) in benzene (300 ml) was irradiated under nitrogen for 4 hr using a 300-W medium-pressure mercury lamp equipped with a Pyrex filter. After removal of the solvent, the residual solid was chromatographed on silica gel with cyclohexane–benzene to yield a colorless solid, which was recrystallized from *n*-hexane to give the thiepin 1,1-dioxides. The spectral and physical data of the photoproducts are summarized in Table I.

Thermolysis of 5 in Tetralin. A solution of **5** (0.1 g) in tetralin (3 ml) was refluxed for 3 hr. The reaction mixture was chromatographed on silica gel and eluted with cyclohexane–benzene to give a colorless solid. This solid was recrystallized from ligroin to furnish 1,2,4,5-tetraphenylbenzene in 63% yield: mp 274–275°; mmp 272–275°; nmr ($CDCl_3$) δ 7.25 (s, 20 H), 7.57 (s, 2 H).

Anal. Calcd for $C_{30}H_{22}$: C, 94.13; H, 5.89. Found: C, 94.20; H, 5.80.

Catalytic Hydrogenation of 5. Catalytic hydrogenation of **5** (0.06 g) in ethyl acetate (50 ml) with 10% Pd/C was carried out at room temperature under 15 atm for 50 hr. After removal of the solvent under reduced pressure, preparative thin layer chromatography of the residual solid afforded 2,4,5,7-tetraphenylthiacycloheptane 1,1-dioxide in 60% yield: mp 308–310°; ir (KBr) 1585, 1480, 1435, 1280, 1125, 755, 690 cm^{-1}; nmr ($CDCl_3$) 3 1.2–2.6 (m, 8 H), 7.0–8.0 (m, 20 H).

Anal. Calcd for $C_{30}H_{28}O_2S$: C, 79.61; H, 6.24. Found: C, 79.48; H, 6.28.

Acknowledgment. We thank Dr. R. Mukherjee for his help in preparation of the manuscript.

Registry No. 2, 41068-60-4; **5,** 42867-24-3; **6,** 42867-25-4; **7,** 42867-26-5; diphenylacetylene, 501-65-5; methylphenylacetylene, 673-32-5; phenylacetylene, 536-74-3; 2,6-diphenyl-4*H*-thiopyran-4-one, 1029-96-5; 1,2,4,5-tetraphenylbenzene, 3383-32-2; 2,4,5,7-tetraphenylthiacycloheptane 1,1-dioxide, 42867-28-7.

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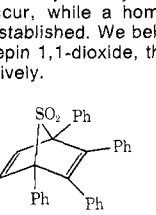
(18) A referee pointed out the possibility **8** for the structure of **5**. It seems, however, unlikely that **8** is stable at room temperature, since the 7-thiabicyclo[2.2.1]hepta-2,5-diene derivative, never isolated, was proposed only as a reaction intermediate.[19] Moreover, cycloaddition of **5** with tetracyanoethylene or dimethyl acetylenedicarboxylate did not occur, while a homo-Diels–Alder reaction of norbornadiene is well established. We believe that the photoproduct has the structure of thiepin 1,1-dioxide, though the structure **8** cannot be ruled out conclusively.



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The Synthesis of 2-Methylproline and 2-Methylornithine

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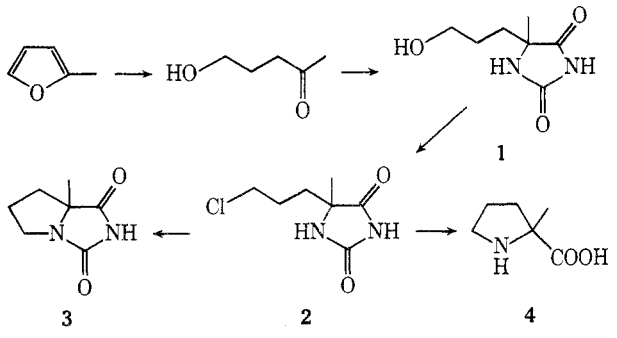
Interest in analogs of the natural amino acids has increased at a rapid rate since du Vigneaud, *et al.*,[1] first re-

ported the synthesis of deaminooxytocin. These amino acid derivatives are substituted into biologically active peptides to modify the activity of the peptide. To this end we have been interested in the synthesis of 2-methylamino acids as substitutes for the naturally occurring amino acids.[2] Our present interest in 2-methylornithine is related to the report by Bodanzky, *et al.*,[3] that a suitably protected ornithine moiety can be readily converted to arginine. This latter amino acid has been shown to be essential in the amino acid sequence of angiotensin and related hypertensive peptides.

The first synthetic route, shown in Scheme I, is based in part on the synthesis of ornithine by Gaudry.[4] Reduc-

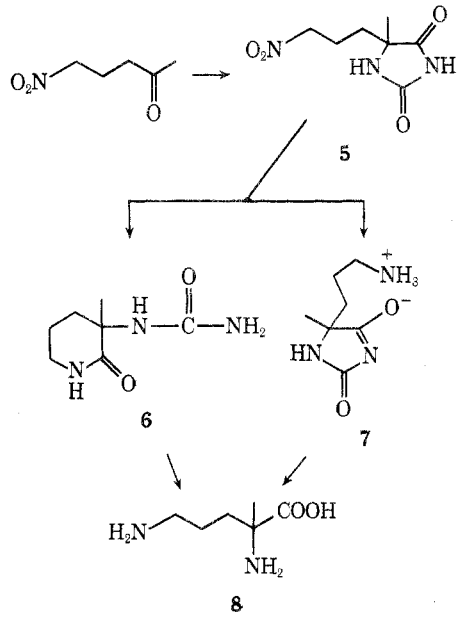
Scheme I



tion of 2-methylfuran[5] and conversion of the 5-hydroxy-2-pentanone to 5-(3-hydroxypropyl)-5-methylhydantoin (1) by the method of Bucherer[6] took place in reasonable yield. Hydantoin 1 was readily converted, in good yield, to the chloro derivative 2 with pyridine–thionyl chloride. Attempts to form 5-(3-aminopropyl)-5-methylhydantoin by amination of 2 resulted in cyclization to 5-methyl-1,5-trimethylenehydantoin (3), a precursor of 2-methylproline (4). Both 2 and 3 were hydrolyzed to 2-methylproline (4).

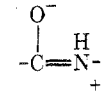
Failure of the Gaudry route in which the nitrogen is inserted at the hydantoin stage of the synthesis with the resultant cyclization led us to investigate an alternate path to 2-methylornithine as shown in Scheme II. This method

Scheme II



introduced the ornithine ω nitrogen at the ketone level. 5-Nitro-2-pentanone[7] was converted to 5-methyl-5-(3-nitropropyl)hydantoin (5) in reasonable yield. Acid or base hydrolysis of 5 gave 2-methylglutamic acid as the only product.[8] Catalytic reduction of 5 gave two characterizable products, 6 and 7, that had the same elemental analysis. Mass spectra indicated a molecular weight of 171 for both, which is correct for the reduction of the nitro function. Compound 6 (mp 235–236°) was identified as 3-methyl-3-ureidopiperidone. 6 gave a positive test with Ehrlich's reagent (lemon-yellow color) which is characteristic of the ureido moiety. Kurhajec[9] reported formation of 3-ureidopiperidone from the reduction of 5-(2-cyanoethyl)hydantoin. Infrared data for the lactam urea 6 and *N*-methylurea show comparable bands [ν_{max} (KBr) 3660, 3365, 3285, 3191, 1670, and 1575 cm^{-1} for 6 *vs.* 3425, 3330, 1650, and 1575 cm^{-1} for *N*-methylurea]. The nmr data for 6 are also consistent with the lactam urea structure in which the methylene protons on the carbon adjacent to nitrogen are found at δ 3.1, two secondary amide protons at δ 6.1 and 7.3, and two primary amide protons at δ 5.4. Exchangeability of the four amide protons was observed on the addition of D_2O.

Compound 7 (mp 175–177°) was assigned a zwitterionic structure. Schauenstein and Perko[10] report that enolization occurs between N-3 and C-4 of hydantoins while Seth Paul and Demoen[11] prefer a mesomeric structure



for the N–C bond. The nmr spectra of 7 indicated an ammonium ion at δ 4.5 and two of the methylene protons at δ 2.5. Exchangeability of the protons at δ 4.5 was confirmed with D_2O. A sample of 5,5-dimethylhydantoin had characteristic hydantoin carbonyl absorption at 1762 and 1700 cm^{-1}, while the sodium salt had strong absorption at 1575 cm^{-1}, similar to the carbonyl absorption of 7. Phenyl isothiocyanate reacts with 7 to give a single product that has the correct elemental analysis for the phenylthiourea derivative of 7 and has carbonyl absorption at 1760 and 1700 cm^{-1}. Base hydrolysis and acid work-up of 6 and 7 gave 2-methylornithine sulfate (8) as the only product. The resolution of the 2-methylamino acids and their incorporation into peptide analogs will be reported later.

Experimental Section

Melting points were determined with a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Atlantic Microlab, Atlanta, Ga., and were within ±0.4% of the theoretical values.[12] The ir spectra were recorded with a Perkin-Elmer 237B spectrophotometer and nmr spectra were determined using a Perkin-Elmer R-20A spectrometer with the chemical shifts (δ) given in parts per million downfield from TMS. Mass spectra were obtained with a Du Pont Model 490 mass spectrometer. Thin layer chromatograms were developed on Eastman 6060 silica gel plates with fluorescent indicator. Solvent systems used were (A) 1-butanol–acetic acid–water–pyridine (15:3:12:10); (B) 1-butanol–acetic acid–water (65:15:22); (C) pyridine–isoamyl alcohol–water (35:30:30); (D) ethanol–benzene (2:3); (E) 2-propanol–benzene (1:9). R_f values are reported as solvent system (R_f).

5-(3-Hydroxypropyl)-5-methylhydantoin (1). To 56.5 g (0.55 mol) of 5-hydroxy-2-pentanone dissolved in 1 l. of 60% EtOH was added 163 g (1.7 mol) of wire brushed ammonium carbonate (ACS). The solution was stirred and warmed to 55°, at which time 29.5 g (0.59 mol) of aqueous sodium cyanide was added over a period of 5 min. The mixture was stirred at 55° for 24 hr. The condenser was removed and the temperature was brought to 90° for 3 hr to remove excess ammonium carbonate. After cooling, the pH was adjusted to 5 with concentrated HCl. (Caution! HCN is generated by the acidification.) Reduction in the volume to 300 ml and cooling to 4° overnight gave 50 g of clear crystals, mp 143–145°. Evaporation of the filtrate to dryness and extraction of the solid residue with 75 ml of hot absolute EtOH gave an additional 10 g of hydantoin (yield 73%). An analytical sample was obtained after two crystallizations from absolute ethanol: mp 144–146°; ir

(Nujol) 3375, 3315, 3250, 1762, and 1725 cm^{-1}; nmr (CD_3OD) δ 1.4 (s, 3 H, C-CH_3), 1.7 (m, 4 H, CCH_2CH_2-), 3.5 (t, 2 H, OCH_2-); homogenous in solvent systems B (0.44) and C (0.54). *Anal.* ($C_7H_{12}N_2O_3$) C, H, N.

5-(3-Chloropropyl)-5-methylhydantoin (2). To 5 g (0.029 mol) of **1** and 2.52 g (0.032 mol) of pyridine, cooled to 0° and protected from moisture, was added 2.19 ml (0.03 mol) of thionyl chloride in 10 ml of $CHCl_3$ over a 1-hr period. The solution was stirred for an additional 3 hr, at which time the reaction had warmed to room temperature. The temperature was then raised to 55° for 30 min. After removal of the chloroform *in vacuo* the resulting viscous oil was dissolved in 10 ml of H_2O and extracted with ether (4 × 20 ml). The ether was dried over $MgSO_4$ and evaporated *in vacuo* to yield 4 g of solid (73%). An analytical sample was obtained by crystallization from benzene: mp 127–129°; ir (KBr) 3300–3100 (br), 1750, 1700, and 1425 cm^{-1}; nmr (CD_3OD) δ 1.4 (s, 3 H, CCH_3), 1.8 (m, 4 H, CCH_2CH_2-), 3.5 (t, 2 H, $ClCH_2$-); homogenous in solvents systems B (0.60) and E (0.36). *Anal.* ($C_7H_{11}ClN_2O_2$) C, H, Cl, N.

5-Methyl-1,5-trimethylenehydantoin (3). A 500-ml Parr hydrogenation bottle was charged with 1.7 g (0.009 mol) of **2**, 8.6 g (0.09 mol) of ammonium carbonate, and 20 ml of 30% aqueous NH_3. The bottle was securely stoppered and stirred for 16 hr at a temperature of 40°. Solvent was then removed *in vacuo* and the resulting oil was dissolved in dilute HCl and applied to a strong cation exchange resin (Amberlite IRC 120, H^+ form). The column was washed with 4 *N* NH_4OH and the eluent was taken to dryness. The white solid, 0.68 g (50%), was crystallized from H_2O to give an analytical sample: mp 129–131°; ir (KBr) 3175, 3060, 1745, 1700–1675, and 1375 cm^{-1}; nmr (CD_3OD) δ 1.4 (s, 3 H, CCH_3), 2.0 (m, 4 H, CCH_2CH_2C), 3.4 (m, 2 H, NCH_2), 4.9 (s, 1 H, NH); homogenous in solvent systems A (0.64), B (0.58), and C (0.59). *Anal.* ($C_7H_{10}N_2O_2$) C, H, N.

Compound **3** was obtained in 80% yield by refluxing **2** with 2 mol of NaOMe for 3 hr and then neutralizing and extracting the cyclized product from an aqueous solution with ether.

2-Methylproline (4). A glass liner bottle for a high-pressure reaction apparatus was charged with 2 g (0.01 mol) of **2**, 6.3 g (0.02 mol) of $Ba(OH)_2 \cdot 8H_2O$, and 50 ml of H_2O. The solution was shaken for 30 min at 160° and then allowed to slowly return to room temperature. The pH was adjusted to 2 with 6 *N* H_2SO_4 and after filtering the $BaSO_4$ the filtrate was applied to a strong cation exchange resin (Amberlite IRC 120, H^+ cycle). Elution with 4 *N* NH_4OH and evaporation of solvent gave 1.2 g (90%) of a white solid, mp 252–258°. Crystallization from MeOH-Et_2O gave an analytical sample: mp 263–264.5°; ir (KBr) 3450, 3200, and 1600 cm^{-1}; nmr (CD_3OD) δ 1.6 (s, 3 H, CCH_3), 1.9 (m, 4 H, CCH_2CH_2C), 3.3 (m, 2 H, $-NCH_2$); homogenous in solvent systems A (0.29), B (0.09), and C (0.14). *Anal.* ($C_6H_{11}NO_2$) C, H, N.

5-Methyl-5-(3-nitropropyl)hydantoin (5). The procedure and equipment were the same as for **1**. The quantities used were 30 g (0.23 mol) of 5-nitro-2-pentanone, 96 g (1 mol) of ammonium carbonate, 12.25 g (0.25 mol) of sodium cyanide, and 450 ml of 60% EtOH. Work-up gave a 20-g (43%) crude yield of **5**. Two crystallizations from absolute EtOH gave an analytical sample: mp 125–127°; ir (KBr) 3100 (br), 1750, 1700, and 1545 and 1385 cm^{-1} (NO_2); nmr (DMSO-d_6) δ 1.28 (s, 3 H, CH_3), 1.7 (m, 4 H, CCH_2CH_2C), 4.6 (t, 2 H, NCH_2), 8.0 (s, 1 H, NH), and 10.4 (s, 1 H, NH), homogenous in solvent systems A (0.70), B (0.60). *Anal.* ($C_7H_{11}N_3O_4$) C, H, N.

Reduction of 5-Methyl-5-(3-nitropropyl)hydantoin (5). A 500-ml Parr hydrogenation bottle was charged with 4 g (0.02 mol) of **5**, 0.25 g of platinum oxide (Adams catalyst), and 75 ml of anhydrous methanol. The solution was shaken for 18 hr at 45 psi and room temperature. Catalyst was removed by filtration and the methanol was evaporated *in vacuo*. The resulting white solid was crystallized from a minimum amount of hot methanol to give 2.45 g (72%) of 5-(3-aminopropyl)-5-methylhydantoin (**7**), mp 171–174°. Recrystallization gave an analytical sample, mp 175–177°. The filtrate from the first crystallization was reduced in volume and the precipitate **6** collected, 0.32 g (9%), mp 225–227°. Recrystallization of **6** from methanol gave an analytical sample, mp 235–236°. The elemental analysis and molecular weight of **6** and **7** were identical. A reduction time of 2 hr gave 60% of **6** and none of **7**. The analytical data for **6** and **7** follow. **6** had mp 235–236°; ir (KBr) 3460, 3365, 3285, 3190, 1670, 1590, and 1230 cm^{-1}; nmr (DMSO-d_6) δ 1.3 (s, 3 H, CCH_3), 1.8 (m, 4 H, $-CCH_2CH_2C$), 3.1 (m, 2 H, NCH_2-), 5.4 (s, 2 H, NH_2), 6.1 (s, 1 H, NH), 7.3 (s, 1 H, NH); mass spectrum molecular ion at *m/e* 171; homogeneous in solvent systems A (0.50), B (0.30), C (0.35). *Anal.* ($C_7H_{13}N_3O_2$) C, H, N. **7** had mp 175–177°; ir (KBr) 3250, 1575 (br), 1390 cm^{-1}; nmr (DMSO-d_6) δ 1.2 (s, 3 H, CCH_3), 1.5 (m, 4 H, CCH_2CH_2C), 2.5 (t, 2 H, NCH_2), 4.1 (br, 3 H, NH_3); mass spectrum molecular ion at *m/e* 171; homogenous in solvent systems A (0.42), B (0.14), C (0.12). *Anal.* ($C_7H_{13}N_3O_2$) C, H, N.

2-Methylornithine Sulfate (8). The hydrolysis procedure was the same as described for 2-methylproline (**4**). The quantities for a typical hydrolysis were 1 g (0.006 mol) of **6** or **7**, 3.78 g (0.012 mol) of $Ba(OH)_2 \cdot 8H_2O$, and 50 ml of H_2O. The pH of the hydrolysis mixture was adjusted to 1.7 with H_2SO_4 and the $BaSO_4$ was removed by filtration and washed with hot H_2O. The combined filtrates were adjusted to pH 6.5 with saturated $Ba(OH)_2$ to remove excess H_2SO_4. Again the $BaSO_4$ was removed by filtration and the combined filtrates were evaporated *in vacuo*. The oily residue was redissolved in hot H_2O and crystallization was facilitated with absolute EtOH and 3 ml of dilute HCl to yield 0.73 g (50%) of product, mp 212–215°. Recrystallization gave an analytical sample: mp 216.5–217.5°; ir (KBr) 3300–2500, 1725, 1580, and 1325 cm^{-1}; nmr (D_2O) δ 1.6 (s, 3 H, $-CCH_3$), 1.95 (m, 4 H, $-CCH_2CH_2C$), 3.1 (t, 2 H, NCH_2); homogenous in solvent systems A (0.18) and C (0.05). *Anal.* ($C_6H_{16}N_2O_6S$) C, H, N, S.

Registry No. **1**, 42856-68-8; **2**, 42856-69-9; **3**, 42856-70-2; **4**, 42856-71-3; **5**, 42856-72-4; **6**, 42856-73-5; **7**, 42856-74-6; **8** sulfate, 42856-75-7; 5-hydroxy-2-pentanone, 1071-73-4; 5-nitro-2-pentanone, 22020-87-7.

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(12) Satisfactory analytical data (±0.4%) were reported for compounds **1–8**.

Photoinduced Addition of Isopropyl Alcohol to α,β-Unsaturated Lactones[1]

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Photoinduced addition of isopropyl alcohol to the double bond adjacent to a carbonyl group has been reported of several ketones[2] and a lactone.[3] The product has been invariably found to be a β adduct. No quantitative study has been made, however, except for the case of 2-cyclopentenone,[2a] where the quantum yield for the photoinduced addition was merely estimated from disappearance of 2-cyclopentenone in dilute solution (0.01 *M*). In the present experiment, the direct excitation of α,β-unsaturated γ-lactones in isopropyl alcohol was found to afford the corresponding adducts with such high quantum yields that the reaction can be used for large-scale preparation.

When 2(5*H*)-furanone (**1**) in isopropyl alcohol was internally irradiated with a 30-W low-pressure mercury lamp, a single product was obtained after distillation of the