tion of o-, m-, and p-chlorophenylalanine and the dichlorinated phenylalanines was accomplished by treating the appropriate α chlorotoluene with sodium acetamidomalonate in absolute ethanol; the properties of the resulting substituted benzyl acetamidomalonates were in accord with those reported.⁷ The ring-substituted phenylalanines were prepared by acid hydrolysis with boiling 6 N HCl; their physical properties agreed with the reported values and amino acid analysis gave only a single peak (Table II). Previous references to 2,3-, 2.5-, 2,6-, and 3,5-dichlorophenylalanine were not found.

Chlorination of L-Phenylalanine. The halogenations summarized in Table I were carried out as follows. A magnetically stirred solution of 1.65 g (10 mmol) of L-phenylalanine in 200 ml of 6 N HCl was maintained at room temperature while 0.71 g (10 mmol) of chlorine in 125 ml of the same solvent was added over a 10-min period. The reaction was maintained at the stated temperature until the disappearance of the yellow color (15 min) and then stirred for an additional 15 min. Solvent was then removed in vacuo and the crude product was subjected to amino acid analysis (Table I). Tlc on Eastman cellulose sheets No. 6065 (methyl ethyl ketone-pyridine-water-HOAc, 70:15:15:2) gave $R_{\rm fuphe}$ 0.36, $R_{\rm fup}$ 0.44, $R_{\rm fum, p, and 2.3}$ 0.57, $R_{\rm fuphe}$ 3.4 0.64.

Separation of Chlorinated L-Phenylalanines. The separation of 2.0 g (10 mmol) of the isomeric mixture prepared above was attempted using Bio Rad AG 50W cation exchange resin (100–1000 mequiv/mequiv of amino acid) with cross linking from 2 to 8%, a solvent variance from 2 N HCl to 6 N HCl, and the same solvents containing an organic phase (methanol, 2–10%). All attempted variations failed to give an adequate separation or yield of pure IV. The fractions were analyzed by tlc and amino acid analysis. Attempted fractional crystallization also failed.

p-Nitrophenyl-L-alanine Monohydrate (II). The Bergel and Stock¹⁰ procedure was followed (Table III) except that the crude product obtained was recrystallized from water (3 ml/g) four times to give a 40% yield of pure nitro-L-phenylalanine monohydrate (II): mp 240-242° dec (lit.¹⁰ mp 238-241°); $[\alpha]^{26}$ D +7.9 ± 0.2°. (c 1.77, 1.0 N HCl) (lit.¹⁰ $[\alpha]^{26}$ D +9.8 ± 0.2°); nmr {D2O-DCl, 3-(trimethylsilyl)propanesulfonic acid as internal reference] δ 3.48 (d, J = 7.0 Hz, 2 H, -CH₂-), 4.45 (t, J = 7.0 Hz, 1 H, -CHCO₂H), 7.55 (d, J = 7.0 Hz, 2 H, aromatic protons, ortho to -CH₂-), 8.08 (d, J = 7.0 Hz, 2 H, aromatic protons ortho to -NO₂). Anal. (C₉H₁₀N₂O₄, H₂O removed by heating in high vacuum) C, H.

p-Aminophenyl-L-alanine Monohydrate (III). The method of Bergmann¹¹ was used and gave a quantitative yield of pure amino-L-phenylalanine by filtering off the catalyst: mp 242-247° dec (lit.¹¹ mp 235-242°); $[\alpha]^{25}$ D -42.0 ± 0.5° (c 1.5, H₂O) (lit.¹⁴ $[\alpha]^{25}$ D -42°); amino acid analysis gave a single peak (Table II); nmr (D₂O) δ 3.25 (d, J = 7.0 Hz, 2 H, -CH₂-), 4.00 (t, J = 7.0 Hz, 1 H, -CHCO₂H), 7.30 (s, 4 H, aromatic).

p-Chlorophenyl-L-alanine (IV). A solution of 7.23 g (40 mmol) of p-amino-L-phenylalanine in 24 ml of 4.0 N HCl was mechanically stirred at 0° while 2.00 g (40 mmol) of $\rm NaNO_2$ in 6 ml of water was added over a 20-min period. After stirring for 5 min longer, the resulting solution was added to 5.35 g (54 mmol) of CuCl in 24 ml of concentrated HCl at 0° over 20 min. The reaction was quite frothy (a 500-ml flask is adequate for the reaction) with the bubbling continuing as the reaction was heated to 60° for 30 min with vigorous stirring. The resulting mixture was dissolved in 350 ml of water and H₂S was bubbled through the solution until the filtrate was clear. This clear aqueous solution was evaporated in vacuo, the residue was dissolved in H_2O (500 ml) and neutralized (pH 6.5) with 3 N NaOH, and the solution was again evaporated to dryness. Chromatography of the residue on 120 g of silica with CH₃OH-17% NH₃-CHCl₃ (10:1.5:13.5) as eluent gave 7.50 g (86%) of pure IV: mp 241-243° dec (lit.⁷ 236-242°); $[\alpha]^{26}$ _D $-3.9 \pm 0.3^{\circ}$ (c 2.0, 1 N HCl) (lit.⁶ -3.5); $[\alpha]^{26}$ _D $-27.8 \pm$ 0.2° (c 0.4, H₂O); nmr (D₂O-DCl) δ 3.35 (d, J = 6.5 Hz, 2 H, $-CH_2-$), 4.40 (t, J = 6.5 Hz, 1 H, $-CHCO_2$ H), 7.32 (d, J = 8.0 Hz, 2 H, aromatic protons ortho to $-CH_{2-}$), 7.36 (d, J = 8.0 Hz, aromatic protons ortho to -Cl), Anal. (C9H10ClNO2) C, H, N.

Optical Purity of IV. Hydrogenation of 0.603 g (3.02 mmol) of IV in 100 ml of water in the presence of 0.20 g of 10% Pd/C was carried out with hydrogen at 40 psi for 2 hr. After filtering off the catalyst and washing it thoroughly with H₂O, the resulting solution was adjusted to pH 5.50 with 1.0 N NaOH and lyphilized. The rotation of the residue (0.678 g; theory, 0.675 g; 100.5%) was $[\alpha]^{26}D - 33.90 \pm 0.05^{\circ}$ (c 2.0, H₂O), allowing for the presence of NaCl; L-phenylalanine has $[\alpha]^{26}D - 34.13 \pm 0.03^{\circ}$. A series of control experiments using L-phenylalanine and L-phenylalanine hydro-

chloride was performed to ensure that there was no change of optical activity in the L-phenylalanine during the hydrogenation, neutralization, or lyphilization. The amino acid analysis showed only the phenylalanine peak and the total absence of IV in the hydrogenated material.

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Potential Bioreductive Alkylating Agents. 3. Synthesis and Antineoplastic Activity of Acetoxymethyl and Corresponding Ethyl Carbamate Derivatives of Benzoquinones

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A number of benzo- and naphthoquinone derivatives with one or two side chains capable of alkylation after reduction were found (a) to possess inhibitory activity against the growth of transplantable tumors of mice and (b) to cause inhibition of nucleic acid biosynthesis and of the activities of coenzyme Q mediated enzyme systems.¹⁻³ In vivo conversion to an active form is hypothesized to involve reduction, presumably by a pyridine nucleotide-requiring quinone reductase,^{4,5} to a dihydroquinone which spontaneously decomposes to an o-quinonemethide. This extremely reactive intermediate has the capacity to alkylate cellular components. Although no evidence is currently available to support the existence of o-quinonemethide in vivo, chemical evidence has been obtained to substantiate the formation of quinonemethide in the reductive amination of 2,3-dimethyl-5,6-bis(acetoxymethyl)-1,4-benzoquinone by aniline and morpholine.⁶ The theoretical potential of compounds of this type against solid neoplasms has been discussed.²

The proposed action mechanism for bioreductive alkylating agents suggests that the biochemical activation of compounds of this type would be significantly influenced by their oxidation-reduction potentials. Compounds with relatively high (positive) redox potentials should be more susceptible to reduction than derivatives with more negative ones, and thereby the former types of agents might possess greater antineoplastic activity. Since substitution of the quinone ring with electron-donating groups, such as methyl or methoxy, should change the redox potentials of these quinones,⁷ benzoquinones with methyl or methoxy substituents were prepared as potential anticancer agents.

Chemistry. In a previous paper, the synthesis of 2,3dimethyl-5,6-bis(acetoxymethyl)-1,4-benzoquinone by oxidation of the methyl ether of the corresponding dihydroxybenzoquinone (1a) with either fuming nitric acid or AgO/H^+ was reported.¹ Similar approaches were tried for



the preparation of the carbamyl derivative without success, possibly because of instability of the carbamate 1b in the acidic medium. An alternate attempt to aminate compound 2 also failed to give the carbamate. However, the desired carbamate and acetoxymethyl analogs were successfully prepared by the approach shown in Scheme I.

Scheme I



Compound 4a was prepared by either employing the Mannich reaction with 2,3-dimethyl-1,4-dihydrobenzogui-

none (3a), piperidine, and formaldehyde or by treatment of duroquinone with piperidine at room temperature, as described by Cameron, et al.⁸ Using the latter procedure, we have isolated, in addition to the reported major prod-2.3-dimethyl-5.6-bis(piperidinomethyl)-1,4-dihydrouct, benzoquinone (4a), a minor product which was identified as 2,5-dimethyl-3,6-bis(piperidinomethyl)-1,4-dihydroquinone by ir, nmr, and melting point. The reaction mechanism which leads to the formation of 4a by treatment of duroquinone with piperidine has been discussed previously.⁸ The initial piperidine group which enters the duroquinone molecule possibly acts as a base; a favorable internal base catalysis, allowing the formation of the intermediate aminated quinonemethide 9 over other possible intermediates 10 and 11, was suggested to be the dominating factor which accounts for the observed product.



Since the 5,6-bis(piperidino) (major product) and 3,6bis(piperidino) (minor product) derivatives were isolated, and the third isomer, the 2,6-bis(piperidino) analog, was not formed, it appears that, in addition to base catalysis, the internal hydrogen bonding between the enolic hydrogen of the intermediate and the nitrogen of the piperidino group may also contribute to the stabilization of intermediates 9 and 10. Similar hydrogen bonding is impossible with intermediate 11.

Compounds 4b and 4c were prepared in good yield by the Mannich reaction employing the procedure used for the preparation of 4a. Chromic trioxide oxidation of bis(piperidino) compounds 4a-c gave the corresponding phthalaldehyde derivatives 5a-c in about 15-25% vields. Since hydroquinones are generally extremely susceptible to oxidation by even mild oxidizing agents, the resistance of the hydroquinone group in 5a-c to chromic acid oxidation is of interest. This exceptionally great resistance to oxidation may be due to strong internal hydrogen bonding in both the starting material and the product. The relatively simple nmr patterns of these aldehydes make identification relatively straightforward. Sodium borohydride reduction of aldehydes 5a-c, followed by selective oxidation of the hydroquinone with ferric chloride,⁹ gave the corresponding bis(hydroxymethyl)benzoquinone derivatives 6a-c, which were used for reaction without further purification. Acetylation of the alcohol 6a with acetic anhydride gave bis(acetoxymethyl)benzoquinone (7a), which was identical in melting point and ir with the compound obtained through nitric acid oxidation of 1a.¹ Compounds **7b,c** were prepared by a similar procedure. Carbamates 8a-c were synthesized by refluxing the alcohols 6a-c in ethyl isocvanate; these products were not stable and gradually formed black tars after standing at room temperature. Therefore, carbamates were analyzed and tested immediately following purification.

Biological Results. Antineoplastic activity was measured against both Sarcoma 180 and Adenocarcinoma 755





\mathbf{R}_{i}	\mathbf{R}_2	x	Av Δ wt, $\%^b$	$\begin{array}{c} Av\\ \text{survival,}\\ \text{days}\\ \pm \text{ S.E.} \end{array}$	T/C^{c}
Control			+22.0	$14.8 \pm$	
CH_3	\mathbf{CH}_3	$OOCCH_3$	-11.9	$28.7 \pm$	1.9
CH_3	$\mathbf{C}\mathbf{H}_{3}$	$OOCNHC_2H_5$	-4.1	$32.8 \pm$	2.2
OCH_3	\mathbf{CH}_3	$OOCCH_3$	+31.2	$3.4 \\ 13.6 \pm$	0.9
\mathbf{OCH}_3	\mathbf{CH}_3	$OOCNHC_2H_5$	+26.8	0.3^{e} 13.0 ±	0.9
OCH_3	OCH_3	$OOCCH_3$	-4.8	$0.5 \\ 30.0 \pm$	2.0
OCH_3	OCH_3	OOCNHC ₂ H ₅	-1.6	$7.1 \\ 35.8 \pm 7.7$	2.4

^aAdministered once daily at a daily dosage of 5 mg/kg for 6 consecutive days, beginning 24 hr after tumor implantation. ^bAverage weight change from onset to termination of drug treatment. ^cT/C represents the ratio of the survival time of treated to control tumor-bearing animals. ^dReference 1. ^cCorn oil was used instead of 0.9% NaCl as the vehicle for intraperitoneal injection.

ascites cells. The results obtained with the latter neoplasm are presented in Table I. In a manner similar to previously synthesized benzoquinones of this class,¹ the agents described in this report, except for 2-methyl-3-methoxy analogs, were potent inhibitors of Adenocarcinoma 755 but were devoid of inhibitory activity against Sarcoma 180. The extreme sensitivity of Adenocarcinoma 755 to agents of this type essentially prevents this neoplasm from effectively discriminating between agents; this factor coupled with the lack of susceptibility of Sarcoma 180 to benzoquinone derivatives of this class prevented an assessment of the relationship between oxidation-reduction potential and anticancer activity. Recently a number of methyl carbamate derivatives of hydroxymethylbenzoquinones were reported to be inactive against the L-1210 leukemia.¹⁰

Experimental Section

Biological Methods. Antineoplastic Activity. Compounds were tested for antineoplastic activity in BDF_1 mice bearing Adenocarcinoma 755 and in CD-1 mice bearing Sarcoma 180. Complete details of the biological methods have been described earlier.¹¹

Chemical Methods. All melting points were measured on a calibrated Thomas-Hoover capillary melting point apparatus. Analyses were performed by the Baron Consulting Co., Orange, Conn. Spectral data were obtained using a Perkin-Elmer 257 grating ir spectrophotometer and Varian A-60 and A-60A spectrometers. The latter instrument used Me₄Si as an internal standard. Nmr and ir spectra were as expected. Where analyses are indicated only by symbols of elements, analytical results obtained for those elements are within 0.4% of the theoretical values.

2,3-Dimethyl-5,6-bis(piperidinomethyl)-1,4-dihydrobenzoquinone (4a). Duroquinone (10 g, 0.061 mol) was suspended in 50 ml of piperidine and stirred at room temperature for 40 hr. The excess solvent was removed under reduced pressure and the oil crystallized from ligroine (bp 65-90°) to give long colorless needles of the desired product (10 g, 50%), mp 163-165° (lit.⁸ 161-162°). The filtrate was concentrated to a small volume under reduced pressure and kept at 5° overnight to yield pale yellow prisms of 2,5-dimethyl-3,6-bis(piperidinomethyl)-1,4-dihydrobenzoquinone (0.5 g), mp 195-197° (lit.⁸ 198-200°).

2,3-Dimethoxy-5,6-bis(piperidinomethyl)-1,4-dihydrobenzoquinone (4c). 2,3-Dimethoxy-1,4-dihydrobenzoquinone (15 g, 0.088 mol) was dissolved in 280 ml of 95% EtOH containing 28 ml of piperidine and 21 ml of formalin (38%). The dark brown mixture was heated at 80° under nitrogen for 3 hr. The solvent was removed under reduced pressure, and the oily residue crystallized from ligroine (bp 65-90°) to produce large colorless prisms (14 g, 50%), mp 94-96°. Anal. (C₂₀H₃₂N₂O₄) C, H, N.

The same procedure was used for the preparation of 2-methyl-3-methoxy-5,6-bis(piperidinomethyl)-1,4-dihydrobenzoquinone (**4b**) in 35% yield, mp 140–142°. *Anal.* ($C_{20}H_{32}N_2O_3$) C, H, N.

4.5-Dimethoxy-3,6-dihydroxyphthalaldehyde (5c). Amine 4c (6 g, 0.165 mol) in 30 ml of warm AcOH was added slowly to CrO_3 (3 g) in 30 ml of 50% AcOH. The solution was stirred for 5 min and then poured into 200 ml of ice-H₂O. The yellow precipitate which formed was collected, dried, and recrystallized from EtOAc and ligroine (bp 65-90°) to give yellow crystals (0.6 g, 16%), mp 134-136°. Anal. ($C_{10}H_{10}O_6$) C, H.

4-Methoxy-5-methyl-3,6-dihydroxyphthalaldehyde (5b). A procedure identical with that used for 5c was employed. The crude aldehyde was dissolved in dilute NaOH and extracted twice with ether. The aqueous layer was filtered, acidified with concentrated HCl, and extracted three times with equal volumes of CHCl₃. The extracts were combined, washed once with small amounts of H₂O, dried over Na₂SO₄, and evaporated to dryness to give a greenish powder. Recrystallization from EtOAc and ligroine (bp 65-90°) gave yellow crystals in 23% yield, mp 144-146°. Anal. (C₁₀H₁₀O₅) C, H.

4,5-Dimethyl-3,6-dihydroxyphthalaldehyde (5a) was also prepared by CrO_3 oxidation of 2,3-dimethyl-5,6-bis(piperidinomethyl)-1,4-dihydrobenzoquinone (4a) by the procedure used for the preparation of 5b and 5c, mp 162-164° (from EtOH) (lit.⁸ 166-167°).

2,3-Dimethyl-5,6-bis(acetoxymethyl)-1,4-benzoquinone (7a). Aldehyde 5a (0.25 g, 1.25 mmol) was suspended in 20 ml of 50% MeOH. Sodium borohydride powder was added in small portions with stirring until a clear solution was obtained. The MeOH was evaporated under reduced pressure at room temperature, the aqueous solution was cooled in an ice bath, and the acidity of the solution was adjusted to pH 5-6 with $1 N H_2SO_4$. Ferric chloride (1 g in 5 ml of H_2O) was added and the mixture was stirred at room temperature for 1 hr. The mixture was extracted several times with ether. The ether extracts were combined, dried over Na_2SO_4 , and evaporated to dryness to yield the crude alcohol 6a. The alcohol was suspended in C₆H₆ (10 ml) containing 1 ml of pyridine and 1 ml of Ac₂O. The mixture was stirred at room temperature overnight and then heated on a steam bath for 30 min. The solution was cooled, washed with dilute HCl several times and once with H₂O, dried over Na₂SO₄, and evaporated to dryness. The oil was crystallized from C₆H₆ and ligroine (bp 65-90°) to yield yellow needles (50 mg), mp 91-93° (lit.¹ 91-93°).

2-Methyl-3-methoxy-5,6-bis(acetoxymethyl)-1,4-benzoquinone (7b) was prepared in 60% yield by the procedure used for the synthesis of compound 7a. The product was a yellow oil. For elemental analysis, the sample was purified by molecular distillation. Anal. ($C_{14}H_{16}O_7$) C, H.

2,3-Dimethoxy-5,6-bis(acetoxymethyl)-1,4-benzoquinone (7c) was prepared by the same method from aldehyde 5c in 60% yield, mp 53-54°. Anal. ($C_{14}H_{16}O_8$) C, H.

2,3-Dimethyl-5,6-bis(hydroxymethyl)-1,4-benzoquinone Bis-(ethylcarbamate) (8a). The crude alcohol 6a (0.3 g), obtained by NaBH₄ reduction of aldehyde 5a, was refluxed in 15 ml of ethyl isocyanate for 5 hr. The excess ethyl isocyanate was evaporated to dryness, and the residue was recrystallized from EtOAc and ligroine (bp 65-90°) to give yellow crystals (0.45 g, 88%), mp 129-130° dec. Anal. (C₁₆H₂₂N₂O₆) C, H, N.

2-Methyl-3-methoxy-5,6-bis(hydroxymethyl)-1,4-benzoquinone bis(ethylcarbamate) (8b) was obtained in 33% yield using the same method, mp 118-119° dec (from EtOAc and ligroine). Anal. ($C_{16}H_{22}N_2O_7$) C, H, N.

Identical methodology was employed to form 2,3-dimethoxy-5,6-bis(hydroxymethyl)-1,4-benzoquinone bis(ethylcarbamate) (8c) in 34% yield, mp 103° dec. Anal. ($C_{16}H_{22}N_2O_8$) C, H, N.

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Heterocyclic Steroids. 5.¹ Sulfur, Selenium, and Tellurium 5α -Androstane Derivatives and Their 7α -Methylated Congeners[†]

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As part of a continuing program in the preparation of ring A modified androgens, the preparation of some additional sulfur, selenium, and tellurium derivatives was undertaken.

The 7α -methyl steroids 8-10 were obtained by treatment of 7α -methyl-1,4-dibromo-1,4-seco-2,3-bisnor- 5α androstan-17 β -ol acetate (2)² with Na₂Se, Na₂Te, and Na₂S₂, respectively, in refluxing ethanol. This sequence was taken from our previous preparation³ of 4-7, and the details of the preparation of these compounds are given in the Experimental Section. The 17α -alkyl thiasteroid 11 was prepared by Oppenauer oxidation of 7α -methyl-2thia-A-nor- 5α -androstan- 17β -ol² to give ketone 12 which on treatment with MeMgBr gave 11. A similar sequence gave the 19-nor derivatives 14 and 15.

A thiasteroid containing a six-membered A ring (13) was produced by esterification of 17β -hydroxy-1,2-seco-Anor-5 α -androstane-1,3-dioic acid⁴ followed by formation of the C-17 tetrahydropyranyl ether. Reduction of the last compound with LiAlH₄ gave 3, which was converted to the dimesylate and then to 13 using Na₂S.

The data from the biological testing are given in Table I.[#] As described in our previous work,^{2,3} the activity of the heterocyclic androstane derivatives rises in the order S \sim Se < Te < S-S, and the introduction of the 7 α -methyl group enhances the activity of A-nor thiasteroids. By contrast, the present results show that the introduction of the 7 α -methyl group into the Se, Te, and S-S derivatives does not raise activity.

The activity of the six-membered thiasteroid 13 is most interesting. This compound would be isosteric with a



seven-membered carbocyclic ring containing a Δ^2 double bond. Compound 13 has only about one-fifth the androgenic activity of testosterone, but the levator ani response is nearly as high as that of testosterone. In this respect, it is quite similar to the corresponding 2-oxa analog.⁵ All of these data are in harmony with our postulate³ of the importance of an A ring, equivalent in size to a six-membered or larger carbocyclic ring, flattened in the vicinity of C-2 and C-3, for androgenic-myotrophic activity.



Experimental Section**

2-Selena-*A***-nor-5** α **-androstan-17** β **-ol** (4). To a solution of 0.4 g of 1⁷ in 100 ml of refluxing EtOH there was added a tenfold excess of Na₂Se. Heating was continued for 24 hr when tlc indicated complete conversion of the dibromide to the product. The solution was poured into 600 ml of H₂O, acidified to pH 3, and extracted with Et₂O three times. The Et₂O extract was washed with NaHCO₃ and H₂O, dried (Na₂SO₄), and evaporated to give 0.25 g of 4 as a white solid. Several recrystallizations from Et₂O-hexane gave the analytical sample: mp 157–159°; M+ 328; *m/e* 328 (M⁺), 248.2142 (M⁺ - Se); nmr 0.75, 0.83 ppm (C-18 and C-19). *Anal.* (C₁₇H₂₈OSe-H₂O) C, H.

2-Selena-A-nor-5\alpha-androstan-17\beta-ol Acetate (5). A solution of 0.1 g of 4 in 4 ml of pyridine and 2 ml of Ac₂O was kept overnight at 25°, poured into 100 ml of ice-H₂O, acidified with HCl, and extracted with Et₂O. The Et₂O was washed several times with H₂O, dried (NaSO₄), and evaporated to give an oil, which was crystallized from hexane to give the analytical sample: mp 92-94°. Anal. Calcd for C₁₉H₃₀O₂Se·H₂O: C, 58.91; H, 8.26. Found: C, 58.82; H, 7.77.

2-Telluria-A-nor- 5α -androstan-17 β -ol (6). A refluxing solution of 0.3 g of 1 in 100 ml of refluxing EtOH containing tenfold excess of Na₂Te was allowed to react and worked up as described for 4.

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[‡]Taken in part from the Ph.D. Thesis of G. Gaare, University of California, San Francisco, Calif., 1972.

^{\$}This paper is dedicated to my postdoctoral professor, Alfred Burger (1955-1957).

⁼Pharmacological tests were performed at the Endocrine Laboratories, Madison, Wis., using essentially the method of Hershberger, et al.⁶

^{**}Melting points were determined with a Thomas-Hoover apparatus equipped with a corrected thermometer. Microanalyses were performed by the Microanalytical Department, University of California, Berkeley, Calif. Mass spectra were obtained by Mr. William Garland or Dr. Robert Weinkam on a MS-902 high-resolution instrument. Where analyses are indicated only by symbols of the elements or functions, analytical results obtained for those elements or functions were within $\pm 0.4\%$ of the theoretical values.