group,[8] to give diphenyl(4-benzoyl-1-butyl)phosphine oxide (III), identified by elemental and infrared analysis.

$$\begin{array}{l} \mathrm{I} + \mathrm{NaOH} \longrightarrow \\ \qquad [C_6H_5{-}CO(CH_2)_4{-}P(OH)(C_6H_5)_3] + NaBr \\ \qquad\qquad \downarrow \\ C_6H_5{-}CO{-}(CH_2)_4{-}P(O)(C_6H_5)_2 + C_6H_6 \\ \qquad\qquad \mathrm{III} \end{array}$$

EXPERIMENTAL[9]

4-Benzoyl-1-bromobutane. This was prepared by a method based upon that of Perkin[10] but greatly simplified.

To an ethanolic sodium ethoxide solution, prepared from 5.0 g. (0.22 mole) of sodium and 75 ml. of dry ethanol, was added with stirring a mixture of 40 g. (0.21 mole) of ethyl benzoylacetate and 42 g. (0.18 mole) of 1,3-dibromopropane. After a refluxing period of 4 hr. there was added a second portion of ethanolic sodium ethoxide solution, prepared with the same quantities of reagents as the initial portion, and refluxing was continued for 16 hr. The reaction mixture was filtered to free it from precipitated sodium bromide, and most of the alcohol was distilled. More sodium bromide precipitated during the removal of the alcohol. Addition of water to the residual mixture resulted in the formation of two liquid layers. The lower layer consisted of crude 3,4-dihydro-5-carbethoxy-6-phenyl-2*H*-pyran. This was treated without resort to purification with 83 ml. of 48% hydrogen bromide (d_4^{24} 1.49). The reaction mixture, which consisted of two layers, began to bubble vigorously (carbon dioxide) after standing a few minutes at room temperature. There were still two layers after one hour's refluxing. On cooling the upper layer solidified and could be separated by suction filtration. This solid (23.8 g.) consisted of crude 4-benzoyl-1-bromobutane. Another 3.1 g. could be recovered from the filtrate by extraction with petroleum ether and evaporation of the latter. The combined crude product was recrystallized from ethanol. The recrystallized product (14.8 g., 36%) had m.p. 52–54°, a lower m.p. than that (61°) reported by Perkin, but was of satisfactory quality for use in the subsequent step.

Triphenyl(4-benzoyl-1-butyl)phosphonium bromide. A mixture of 19.0 g. (0.079 mole) of 4-benzoyl-1-bromobutane and 22.8 g. (0.087 mole) of triphenylphosphine[11] was maintained at 100° for 88 hr., care being taken to screen the reaction mixture from light in view of the light sensitivity of alkyl bromides. The reaction mixture liquefied at first and then gradually resolidified. The crude product was ground under ether, filtered, and washed repeatedly with ether. There was thus obtained 28.2 g. (71%) of white product, m.p. 167° with softening at 163°. The purity of this product is adequate for the intramolecular Wittig olefin synthesis. To obtain a sample for analysis some of the product was recrystallized from ethanol–ether. The m.p. was then 167°.

Anal. Calcd. for $C_{29}H_{28}BrOP$: C, 69.23; H, 5.61; Br, 15.89; P, 6.16. Found: C, 68.97; H, 5.67; Br, 16.2; P, 5.98.

1-Phenylcyclopentene by intramolecular Wittig olefin synthesis. To a hot ethanolic sodium ethoxide solution prepared from 0.50 g. (0.022 mole) of sodium and 60 ml. of dry ethanol was added 10 g. (0.020 mole) of finely powdered triphenyl(4-benzoyl-1-butyl)phosphonium bromide. The solution turned bright orange and then a rust color. Subsequent refluxing for 0.5 hr. caused much sodium bromide to precipitate. This was removed by filtration. The alcohol was stripped from the filtrate by distillation and then the olefinic product was distilled at 121–122°/20 mm., the yield being 0.68 g. (24%). Infrared examination of the residue showed it to contain triphenylphosphine oxide. A redistilled sample of the olefin had m.p. 21–22° and n_D^{27} 1.5720. Bauer reports similar b.p., m.p., and n_D^{25} for 1-phenylcyclopentene prepared by addition of phenyl Grignard reagent to cyclopentanone and dehydration of the resulting 1-phenylcyclopentanol with formic acid.[7] We repeated Bauer's preparation and showed that the products of the two methods had identical infrared spectra.

Diphenyl(4-benzoyl-1-butyl)phosphine oxide. A solution of 10 g. of sodium hydroxide in 50 ml. of water was added to a solution of 1.00 g. (0.00199 mole) of triphenyl(4-benzoyl-1-butyl)phosphonium bromide in 100 ml. of water. A cloudiness resulted upon mixing, and on boiling a light yellow precipitate formed. The odor of benzene was evident during boiling. The precipitate was filtered, washed with water, and dried. It weighed 0.48 g. (65%) and had m.p. 148–149°. It was recrystallized from ethanol-water. The white crystals had m.p. 150–150.5°.

Anal. Calcd. for $C_{23}H_{23}O_2P$: C, 76.20; H, 6.40; O, 8.84; P, 8.55. Found: C, 76.27; H, 6.55; O, 8.83 (by direct analysis); P, 8.35.

The infrared spectrum of the substance corroborated its structure.

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(8) C. W. Fenton and C. I. Ingold, *J. Chem. Soc.*, 2342 (1929).

(9) Temperatures are not corrected.

(10) W. H. Perkin, *J. Chem. Soc.*, **51**, 726 (1887).

(11) Donated by Metal and Thermit Corp., Rahway, N. J.

Electron Exchange Polymers. XVI. The Oxidation Behavior of Dimethyl Ethers of Hydroquinone and Methyl-Substituted Hydroquinones

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In the preparation of monomers derived from vinyl hydroquinone and their subsequent polymerization to poly(vinylhydroquinone)-based electron-exchange polymers[3] the ether link is useful for covering the sensitive hydroquinone hydroxyl group. However, it is then difficult to uncover these groups after the polymer has been prepared. A study of oxidative cleavage of the hydroquinone methyl ethers produced the results reported here.

It has been reported[4] that oxidations of 1,4-dimethoxy-2-substituted benzenes with chromic oxide yield diquinones, and that diquinones are also produced in the oxidation of 2-methoxy-6-[1-propyl]quinone in the presence of hydrochloric

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(1) Present address, Institute for Muscle Disease, New York, N. Y.

(2) Present address, Rohm & Haas Co., Research Laboratories, Bristol, Pa.

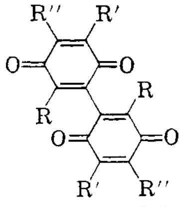
(3) H. G. Cassidy, *J. Am. Chem. Soc.*, **71**, 402 (1949). I. H. Updegraff and H. G. Cassidy, *J. Am. Chem. Soc.*, **71**, 407 (1949). R. Stern, J. English, Jr., and H. G. Cassidy, *J. Am. Chem. Soc.*, **79**, 5792 (1957).

(4) Th. Posternak, W. Alculay, R. Luzzati, and A. Tardent, *Helv. Chim. Acta*, **31**, 525 (1948).

acid.[5] Di- and polyquinones have also been prepared by alkaline oxidation of hydroquinones.[6]

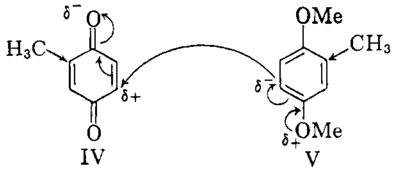
We have oxidized hydroquinone dimethyl ether, and the dimethyl ethers of 2-methylhydroquinone; 2,5-dimethylhydroquinone; 2,3,5-trimethylhydroquinone and 2,3,5,6-tetramethylhydroquinone with ceric sulfate in excess. The mixture was then reduced with titanous chloride. If, instead of completely reducing the mixture, only the excess ceric ion was reduced, it was possible to isolate dimeric quinone from the first three reactions in yields of about 20%, 65%, and 20%, respectively. No dimer could be isolated after oxidation of trimethylhydroquinone dimethyl ether. None was obtained after oxidation of durohydroquinone dimethyl ether, but duroquinone only appeared to be formed, as judged by potentiometric back-titration of the reaction mixture.

The dimeric quinones are of the type:



$\text{I. } R = H; R' = H, R'' = H$
$\text{II. } R = H; R' = H; R'' = CH_3$
$\text{III. } R = CH_3; R' = CH_3; R'' = H$

where I is derived from hydroquinone dimethyl ether; II from toluhydroquinone dimethyl ether; and III from *p*-xylohydroquinone dimethyl ether. The structure of I, reported by Erdtman, Granath, and Schultz,[6] is supported by the finding of only one kind of hydrogen upon NMR examination. The structure II is written as shown because in the NMR we see two different aromatic hydrogens. The methyl substituent cannot, therefore, be in the position *ortho* to the bond joining the two rings—a position inherently unlikely on steric grounds. We place it in the *para* position, rather than the *meta*, because we assume that in the dimerization reaction an oxidized moiety, the quinone, IV, acts as an electrophile relative to an aromatic moiety, V:



IV V

During oxidation of all the diethers except the tetramethyl-substituted diether characteristic colors appear. The solution of diether is initially colorless. It becomes orange, or green, or bluish during the reaction, and at the end becomes quinone-yellow. When the oxidized materials are reduced with titanous chloride, the colors observed at 50% reduction of the organic material are: a slightly green solution, a pink solution, slightly blue, slightly blue, and pale yellow, respectively, for the unsubstituted, mono-, the di-, and the tetrasubstituted diethers. The intensity of the color seems to reach a maximum at the mid-point of the oxidation or of the reduction (except in the case of the tetramethyl substituted compound, where the quinone-yellow increases to complete oxidation). All of the solutions are colorless when fully reduced, and yellow when fully oxidized. (Any slight excess of ceric or titanous ions seems to introduce negligible color.) If the pure dimer is half-reduced, intensely colored, difficulty soluble, quinhydrone can be isolated. Because of the insolubility of these quinhydrones it has not yet been possible to make a clear-cut test of whether their solutions obey Beer's law. Ordinary quinhydrone dissociates in water to a pale yellow solution with less than 5% quinhydrone present.[7] The marked coloration of the solutions of half-reduced biquinones suggests that appreciable interaction of some kind is present. We see five possible sources of color: charge-transfer[8] between two rings, one oxidized and the other reduced, the two being connected by a covalent bond; charge-transfer between paired dimer molecules in solution; resonance across the bond between the rings, with concomitant delocalization of π electrons; semiquinone formation, with each ring in a semiquinone form; complexation with metal ions. Complexation can probably be ruled out, as the pure half-reduced form can be isolated as an intensely colored crystalline material free from ash upon combustion. As the number of methyl substituents on the ring is increased, the likelihood of a contribution from semiquinone is increased. That a contribution of this kind may be present is suggested by the blue tinge observed in the mid-point colors of the mixtures from the oxidation of the more highly substituted diethers; on the other hand, duroquinone when half-reduced does not give visual evidence of semiquinone under the acid conditions used in these experiments.

Scale models indicate that the two rings of I and II may approach coplanarity; but those of III cannot. Thus; any interaction between the rings of III must be other than of the ordinary π-bond type. These dimers give us the opportunity of studying interesting new types of interaction, possibly applicable to higher polymers. When poly(vinylhydroquinone) is oxidized, a pink color

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(5) F. M. Dean, A. M. Osman, and A. Robertson, *J. Chem. Soc.*, 11 (1955).

(6) H. Erdtman, M. Granath, and G. Schultz, *Acta Chem. Scand.*, **8**, 1442 (1954).

(7) L. Michaelis and S. Granick, *J. Am. Chem. Soc.*, **66**, 1023 (1944).

(8) R. S. Mulliken, *J. Am. Chem. Soc.*, **72**, 600 (1950); **74**, 811 (1952). For a review see L. E. Orgel, *Quart. Rev.*, **8**, 422 (1954).

develops to a maximum at the mid-point of the titration, and fades as oxidation proceeds further.[3]

EXPERIMENTAL

Materials. Hydroquinone, hydroquinone dimethyl ether, 2-methyl-, and 2,3,5,6-tetramethylhydroquinone were commercial products which were purified before use; 2,5-dimethylhydroquinone, 2,3,5-trimethylhydroquinone, and the dimethyl ethers of these hydroquinones, except for the 2,3,5,6-tetramethyl diether were prepared according to the methods of Smith and Opie.[9] The diether of 2,3,5,6-tetramethylhydroquinone was prepared by a method which will be reported in another connection.

Potentiometric methods. The experimental methods have been described previously.[10] In all cases the oxidant used was 0.0863*N* ceric sulfate in 0.5*N* sulfuric acid and the reductant was 0.1645*N* titanous chloride in dilute sulfuric acid. The organic substance was dissolved in a mixture of one part by volume of glacial acetic acid with one part of 0.5*N* sulfuric acid ("acetic-sulfuric solution"), using a total of 200 ml. for the sample to be titrated. The titrations were carried out under nitrogen, at 29.65 ± 0.05°. In the oxidative and reductive titrations the potentials read from three platinum electrodes against a standardized calomel electrode agreed within ± 1 mv., and were reproducible within 1 mv. The endpoints calculated from the curves showed the proper stoichiometry.

Oxidation of Hydroquinones. Five hydroquinones were oxidatively titrated. The solutions changed from colorless to yellow as the oxidation progressed, with some of the color being contributed beyond the endpoint by the excess ceric sulfate. The index potentials are correct for 2-electron processes.[11] The calculated E° values, which were essentially constant between 10 and 90% oxidation or reduction, are collected in Table I.

TABLE I

OXIDATION POTENTIALS OF HYDROQUINONE AND METHYL-SUBSTITUTED HYDROQUINONES AND PRODUCTS FROM THE OXIDATION OF THE CORRESPONDING DIETHERS

Substance	E° Red.[a] (Quinone)	E° Ox.[b] (Hydroquinone) ± 1 Mv.	E° Red[b] (Pure Dimer) ±1 Mv.
Hydroquinone	−0.711	−0.6867	.7001
2-Methylhydroquinone	−0.656	−0.6311	.6581
2,5-Dimethylhydroquinone	−0.597	−0.5493	.5700
2,3,5-Trimethylhydroquinone	—	−0.4886	—
2,3,5,6-Tetramethylhydroquinone	−0.466	−0.4563	—

[a] Values obtained by Conant and Fieser for titration in alcoholic hydrochloric acid (1.0*N* in HCl). J. B. Conant and L. Fieser, *J. Am. Chem. Soc.*, **46**, 1858 (1924); L. Fieser, *J. Am. Chem. Soc.*, **52**, 5204 (1930). [b] In acetic-sulfuric solution, average of two runs. The E° values are given in Volts, and are calculated to pH 0, using the glass electrode readings for the experimental values. These hardly changed during a titration.

Oxidation and Back-titration of Diethers. The diether, 0.286 to 0.287 meq., in acetic-sulfuric solution, was treated with five equivalents of ceric sulfate and the ultraviolet absorption at 254 to 257 mμ was examined every five to ten minutes. This spectral region is characteristic of quinone, and complete oxidation of the hydroquinoid nucleus to quinone was assumed when the observed value of this absorption reached a maximum. The solution was then reduced with standard titanous chloride. The reduction was followed electrometrically. A sharp endpoint was obtained as the excess ceric sulfate was reduced, and a second sharp endpoint when the quinone was reduced. Preliminary trials had indicated that five equivalents of ceric sulfate would provide sufficient excess to oxidize the diethers at 29.6° within ten to twenty minutes. It was found that when only one equivalent of ceric sulfate was used per equivalent of diether the oxidation to quinone was not complete. Back-titration of the excess ceric always accounted for less than the (theoretical) four equivalents excess which was initially employed.

Isolation of Oxidation Products. The oxidation product of hydroquinone dimethyl ether was prepared by dissolving 600 mg. (8.68 meq.) of the diether in 150 ml. acetic-sulfuric solution, and adding 500 ml. 0.0863*N* ceric sulfate (43 meq.) slowly, with swirling. The initially colorless solution developed an intense reddish-brown color as the addition of ceric sulfate proceeded. The color intensified to dark brown, then changed to orange, and finally to yellow as the reaction ended. The mixture was allowed to stand about 30 minutes, then was back-titrated with titanous chloride to complete removal of excess ceric ion but not to reduction of quinone. The yellow solution, slightly opaque, was repeatedly extracted with ether. The ether solutions (which contain some acetic acid) were combined, dried sufficiently over sodium sulfate, and reduced in volume at reduced pressure to about 25 ml. About 60 ml. water was added slowly, whereupon shining yellow crystals appeared. On working up the product and solution about 20% of crude product was obtained which could be recrystallized from methanol and acetone to give shiny, needle-like yellow crystals, after further recrystallization, m.p. 192–193° (corr.). The material can also be recrystallized from methanol-ether, and acetic acid–water.

The pure oxidation product (141.8 mg.) was dissolved in 200 ml. acetic-sulfuric solution and titrated to 50% reduction. The dark orange-colored solution was extracted with ether several times, the extracts combined, dried over sodium sulfate, and concentrated to yield shiny, green-black "quinhydrone" crystals. The oxidation products and their products of half-oxidation from the diethers of tolu- and *p*-xylo-*p*-quinones were prepared and isolated in a similar manner. Their properties are gathered below. All wave lengths are in mμ; Ext., extinction, is $E^{1\%}_{1\,\mathrm{cm.}}$ = optical density/$C^{\%}$ *l*, where $C^{\%}$ = g/100 ml., and *l*, the internal length of the cell is 1.00 cm. The u.v. and visible (vis.) spectra were taken in the acetic-sulfuric mixture (see above). None of the dimers, whether fully oxidized or half-reduced, was steam-volatile. In all cases the oxidized dimer formed yellow crystals and the half-reduced dimer, intensely green or green-brown crystals.

Dimer from p-benzoquinone. Oxidized form: m.p., 192–193°; lit. m.p. 192–194°,[6] u.v._{max} 251; Ext. 1.560; vis._{max} 438; Ext. 25; Anal. C, calcd., 67.27, found, 67.32; H, calcd., 2.82, found, 3.07. NMR examination in deuterochloroform (conc. approx. 1%) showed only one kind of quinone hydrogen (chemical shift 3.22 τ).[12] Half-reduced form: m.p., 225–226°; u.v._{max} 255, 295, Ext. 697, 313; vis._{max} 475, Ext. 20.17; Anal. C, calcd., 66.65, found, 67.1; H, calcd., 3.65, found 3.30.

Dimer from tolu-p-quinone. Oxidized form: m.p., 178.5–179.5°; u.v._{max} 260, Ext. 1,101; vis._{max}, 450–440, Ext. 10.7;

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[9] L. I. Smith, *J. Am. Chem. Soc.*, **56**, 472 (1934); L. I. Smith and J. W. Opie, *J. Org. Chem.*, **6**, 427 (1941).

[10] I. D. Robinson, M. Fernandez-Refojo, and H. G. Cassidy, *J. Polymer Sci.*, **39**, 47 (1959).

[11] L. Michaelis and M. L. Schubert, *Chem. Revs.*, **22**, 437 (1938).

[12] We wish to thank Mr. Mark R. Willcott for making this measurement.

Anal. C, calcd., 69.41, found, 69.63; H, calc., 4.16, found 4.45. NMR measurements in deuterochloroform, conc. approx. 1% showed 3 kinds of hydrogens, with chemical shifts at 3.21, 3.22 τ for one H next to carbonyl, one H next to methyl, and 7.86 τ for methyl hydrogens.[12] Ratios of areas under peaks approximately 1:1:3, but the low concentration of the solution made this difficult to determine exactly. Half-reduced form: m.p., 215–215.5°; $\text{u.v.}_{\max}$ 254, 296, Ext., 609, 527; $\text{vis.}_{\max}$ 455, Ext. 27.1; Anal. C, calcd. 68.84, found, 68.56; H, calcd., 5.07, found, 4.77. Mol. wt. (camphor) 234; calcd., 242.

Dimer from p-xylo-p-quinone. Oxidized form: m.p., 149–150°; $\text{u.v.}_{\max}$, 256, Ext. 1,160; $\text{vis.}_{\max}$, 430, Ext. 10.58; Anal. C, calcd., 71.11, found, 70.73; H, calcd., 5.22, found, 4.98. Half-reduced form: m.p., 163–164°; $\text{u.v.}_{\max}$, 246, 288, Ext. 580, 396; $\text{vis.}_{\max}$ 430, Ext. 14.49; Anal. C, calcd., 70.58, found, 70.22; H, calcd., 5.92, found, 6.4.

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16-Methylated Steroids. III. The Synthesis of 9α-Fluoro-16α,17α-dimethyl-4-androstene-11β,17β-diol-3-one

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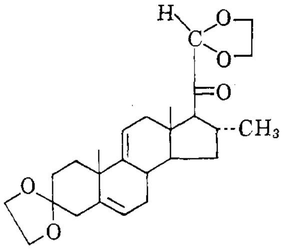
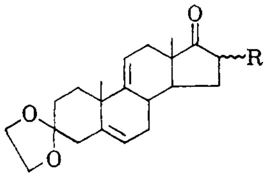
The greatly enhanced anti-inflammatory potency of 16α-methylcorticoids[1–4] prompted us to prepare some 16α-methyl derivatives in the testosterone series. The 16α-methyl analog of 9α-fluoro-17α-methyl-4-androstene-11β,17β-diol-3-one[5] was of particular interest since the parent compound has been utilized clinically as a potent androgenic and anabolic agent.[6] A 2:1 ratio of anabolic to androgenic activity has been demonstrated in animals.[7]

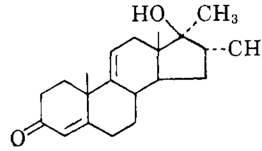
This note describes the partial synthesis of 9α-fluoro-16α,17α-dimethyl-4-androstene-11β,17β-diol-3-one IX from 16α-methyl-4,9(11)-pregnadiene-17α,21-diol-3,20-dione 21-acetate[2] (I). Selective ketal formation of I at C-3 afforded 3-ethylenedioxy-5,9(11)-pregnadiene-17α,21-diol-20-one 21-acetate (II). In addition to II a slightly less polar compound III, $C_{26}H_{36}O_5$ was isolated in 3% yield, by chromatography of the reaction mixture. This compound showed only saturated carbonyl, $\lambda_{\max}$ 5.79 μ, in the infrared. The NMR spectrum[8] indicated two distinct dioxolane functions, τ 5.89 and 5.95. One of these can be assigned to a dioxolane of an aldehyde on the basis of the companion proton at τ 4.84 and the positive Schiff aldehyde test obtained with III after acid treatment. The data are best interpreted on the basis of structure III, 16α-methyl-3,21-bisethylenedioxy-5,9(11)-pregnadiene-20-one. Formation of III may proceed *via* hydrolysis at C-21, Fischer rearrangement[9] to the 21-aldehyde 17,20-diol, followed by dehydration and dioxolanation. The C-17 side chain is presumed to be in the thermodynamically more stable β-configuration.[10]



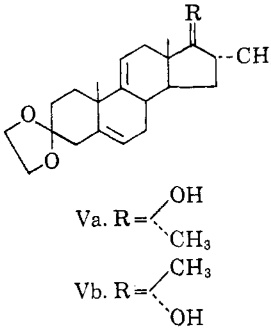
III



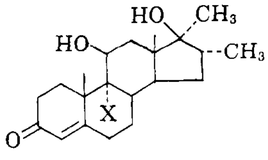
IVa. R = --CH_3
IVb. R = —CH_3



VI



Va. R=
Vb. R=



VII. X = --Br
IX. X = --F

Reduction of II with lithium aluminum hydride followed by periodic acid cleavage afforded 16α-methyl-3-ethylenedioxy-5,9(11)-androstadiene-17-one IVa. An idea of the conformational stability of

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(1) G. E. Arth, D. B. R. Johnston, J. Fried, W. W. Spooncer, D. R. Hoff, and L. H. Sarett, *J. Am. Chem. Soc.*, **80**, 3160 (1958).

(2) G. E. Arth, J. Fried, D. B. R. Johnston, D. R. Hoff, L. H. Sarett, R. H. Silber, H. C. Stoerk, and C. A. Winter, *J. Am. Chem. Soc.*, **80**, 3161 (1958).

(3) E. P. Oliveto, R. Rausser, A. L. Nussbaum, W. Gebert, E. B. Herschberg, S. Tolksdorf, M. Eisler, P. L. Perlman, and M. M. Pechet, *J. Am. Chem. Soc.*, **80**, 4428 (1958).

(4) E. P. Oliveto, R. Rausser, L. Weber, A. L. Nussbaum, W. Gebert, C. T. Coniglio, E. B. Hershberg, S. Tolksdorf, M. Eisler, P. L. Perlman, and M. M. Pechet, *J. Am. Chem. Soc.*, **80**, 4431 (1958).

(5) M. E. Herr, J. A. Hogg, and R. H. Levin, *J. Am. Chem. Soc.*, **78**, 500 (1956).

(6) T. H. McGaback and W. Seegers, *Am. J. Med. Sc.*, **235**, 125 (1958).

(7) S. C. Lyster, G. H. Lund, and R. O. Stafford, *Endocrinology*, **58**, 781 (1956).

(8) NMR Spectra were run on a Varian 60 mc. spectrometer at a concentration of *ca.* 20 mg. in 0.3 ml. deuterochloroform. $\tau = \nu/60 + 3.5$ where ν is the observed band position in c.p.s. relative to benzene as external standard. *Cf.* G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

(9) H. O. L. Fischer, C. Taube, and E. Baer, *Ber.*, **60**, 479 (1927).

(10) A. Butenandt and G. Fleischer, *Ber.*, **70**, 96 (1937); A. Butenandt and L. Mamoli, *Ber.*, **68**, 1847 (1935).