[CONTRIBUTION FROM THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, DEPARTMENT OF CHEMISTRY]

Hydro Di-(4-hydroxyphenyl)-methane Compounds: Octa- and Dodecahydro-Derivatives

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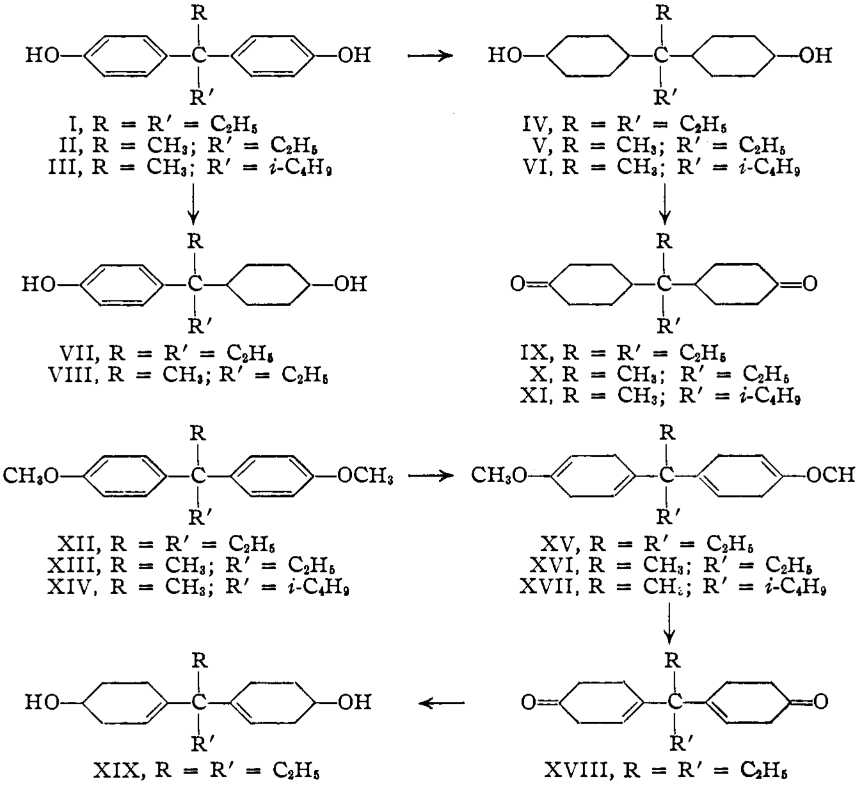
The geometrical resemblance of synthetic estrogens of the stilbestrol type to the natural hormones was early appreciated, and, more recently, precise relationships between the molecular dimensions of natural and synthetic estrogens have been discovered.[2] In view of these findings, and the large number of known synthetic substances with estrogenic activity for which these relationships apply,[3] it is notable that few series of non-steroidal compounds analogous to the androgenic hormones have been investigated.[4,5]

As a preliminary attempt to embody some of the space and polar group characteristics of the natural androgens in a simple molecule, a series of diketones of the general types IX–XI and XVIII have been synthesized.



I, $R = R' = C_2H_5$
II, $R = CH_3$; $R' = C_2H_5$
III, $R = CH_3$; $R' = i\text{-}C_4H_9$

IV, $R = R' = C_2H_5$
V, $R = CH_3$; $R' = C_2H_5$
VI, $R = CH_3$; $R' = i\text{-}C_4H_9$

VII, $R = R' = C_2H_5$
VIII, $R = CH_3$; $R' = C_2H_5$

IX, $R = R' = C_2H_5$
X, $R = CH_3$; $R' = C_2H_5$
XI, $R = CH_3$; $R' = i\text{-}C_4H_9$

XII, $R = R' = C_2H_5$
XIII, $R = CH_3$; $R' = C_2H_5$
XIV, $R = CH_3$; $R' = i\text{-}C_4H_9$

XV, $R = R' = C_2H_5$
XVI, $R = CH_3$; $R' = C_2H_5$
XVII, $R = CH_3$; $R' = i\text{-}C_4H_9$

XIX, $R = R' = C_2H_5$

XVIII, $R = R' = C_2H_5$

The starting material for the synthesis of the diketone IX was diethyldi-(4-hydroxyphenyl)-methane (I), prepared by the method described by Reid and Wilson.[6] The diphenol was hydrogenated under high pressure in the presence of active Raney nickel catalyst to a stereoisomeric mixture of the diols IV (97% yield) from which a pure isomer was isolated by fractional crystallization. The diketone IX was obtained on chromic acid oxidation in 74.5% yield from the crude IV (72.8% over-all).

The homologous diketones X and XI were prepared by similar procedures. The methylethyl diol V was obtained from II as a mixture of isomers in 79% yield, and the diketone X in 80% yield. The methyl isobutyl diketone (XI) was prepared in 71.5% over-all yield from III, but the product was difficultly purified.

By stopping the hydrogenation after absorption of 3 to 4.5 molar equivalents of hydrogen, it was found possible to obtain low yields of the hexahydro derivatives VII and VIII. The diethyl homolog VII was obtained in this way as a single pure isomer in 21% yield. One isomer of VIII was similarly obtained in 9.7% yield.

Synthesis of the octahydro derivative XVIII proceeded through the dimethyl ether XII, obtained from I in quantitative yield by treatment with dimethyl sulfate. In contrast to results obtained by Birch,[7] who reported that hexestrol dimethyl ether was not reduced by sodium–alcohol in liquid ammonia with or without admixed solvents (ether, ethylenediamine), we have found that the corresponding dimethyl ether XII was reduced to the unsaturated enol XV in 42% yield by use of sodium–alcohol in liquid ammonia diluted with ether (no XV was isolated from a similar reaction without ether). The unsaturated diketone XVIII is obtained in 69.4% yield by carefully controlled

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[1] Bristol Laboratories Fellow, 1947–1948.

[2] F. W. Schueler, *Science*, **103**, 221 (1946).

[3] A thorough review is that of Masson, *Rev. Can. Biol.*, **3**, 491 (1944).

[4] Schoeller, Inhoffen, Steinruck and Höss, U. S. Patent 2,392,864 (Jan. 15, 1946) [*C. A.*, **40**, 3233 (1946)]; Ungnade and Ludutsky, THIS JOURNAL, **69**, 2629 (1947); Wilds and McCormack, *ibid.*, **70**, 884 (1948); **70**, 4127 (1948).

[5] Wilds, Shunk and Hoffman, *ibid.*, **71**, 3266 (1949).

[6] E. Reid and E. Wilson, *ibid.*, **66**, 967 (1944).

[7] A. J. Birch, *J. Chem. Soc.*, 430 (1944); Birch and Mukherji, *Nature*, **163**, 766 (1949).

acid hydrolysis in a two phase system. It seems probable that the double bonds are β,γ to the carbonyl groups since the ultraviolet absorption spectrum fails to show the strong maximum at 2200–2500 Å. characteristic of α,β-unsaturated ketones.[8] Hydrogenation of XVIII over platinum oxide activated with ferrous chloride affords a 43% yield of a non-ketonic substance with the properties expected for structure XIX.

The enol ethers XVI and XVII in homologous series were obtained by the procedure described for XV. The over-all yields from the corresponding phenols were 20 and 41%, respectively.

Acid hydrolysis of the enol ethers or acid treatment of the unsaturated ketone XVIII under vigorous conditions designed to induce rearrangement to the respective α,β-unsaturated ketones has not led to the isolation of any crystalline product. Basic reagents, such as dilute alkali hydroxides, result in the formation of a green, water-soluble dye, from which no pure product has been isolated.

All of the ketonic products IX–XI and XVIII and the enol ethers XV–XVII were tested for androgenic activity by bioassay in immature male rats. None of these compounds showed androgenic or estrogenic activity in the doses tested, although a slight diminution of testicular weight and increase in pituitary weight was observed in the case of several of the compounds. We are indebted to Dr. W. W. Westerfeld of the College of Medicine, Syracuse University, for carrying out the bioassays.

Experimental[9]

Diethyldi-(4-hydroxycyclohexyl)-methane (IV).—Diethyldi-(4-hydroxyphenyl)-methane (I), m. p. 204–205°, was prepared using essentially the procedure of Reid and Wilson.[6]

A solution of 10.16 g. (0.04 mole) of I in 150 ml. of commercial absolute ethanol containing 3 g. of Raney nickel catalyst, prepared according to the method of Pavlic and Adkins,[10] was shaken for fifteen hours at 190–195° under 4300 p. s. i. hydrogen pressure, during which time a pressure drop corresponding to the absorption of 0.24 mole (6 molar equivalents) of hydrogen took place. The catalyst was removed by filtration through Filter-Cel. The colorless solution was concentrated to dryness at 50° under reduced pressure, leaving 10.32 g. (97%) of white pulverulent residue, m. p. 124–144°. This material was sufficiently pure for use in the preparation of IX.

A portion (0.250 g.) of the crude product, after three recrystallizations from ethyl acetate, yielded 0.025 g. of one of the three possible isomeric diols in pure form as small, colorless prisms, m. p. 178–179°. Further recrystallization failed to alter the melting point.

Anal. Calcd. for $C_{17}H_{32}O_2$: C, 76.06; H, 12.02. Found: C, 75.81; H, 11.98.

Repeated recrystallization of a second portion of the crude product from benzene resulted in the isolation of a small quantity of ethylated hexahydrodiethyldi-(4-hydroxyphenyl)-methane as irregular prisms, m. p. 153–155°.

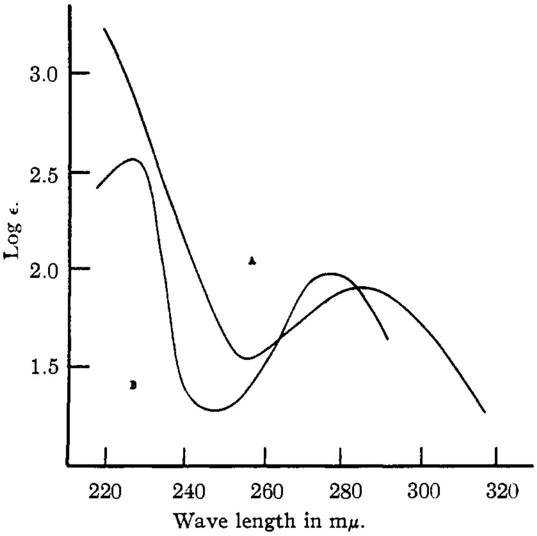

Fig. 1.—Curve A, diethyldi-(4-keto-1-cyclohexenyl)-methane in 95% ethanol; λ_{max} = 285 mμ (log ϵ_{max} = 1.92); λ_{max} = <218 mμ (log ϵ_{max} = >3.2). Curve B, diethyldi-(4-ketocyclohexyl)-methane in 95% ethanol; μ_{max} = 277 mμ (log ϵ_{max} = 2.01); μ_{max} = 226 mμ (log ϵ_{max} = 2.57).

Anal. Calcd. for $C_{19}H_{36}O_2$: C, 78.87; H, 10.41. Found: C, 78.47; H, 10.60.

Methylethyldi-(4-hydroxycyclohexyl)-methane (V).—Methylethyldi-(4-hydroxyphenyl)-methane (II), m. p. 126–127°, was prepared by the method of Reid and Wilson,[6] who reported a melting point of 124°. The diphenol II (10.0 g., 0.041 mole) was reduced by the method described for IV. The white powdery residue obtained by trituration of the crude reduction product with 75 ml. of ether amounted to 7.9 g. (79%), m. p. 120–145°, and was sufficiently pure for use in the preparation of X.

A 0.250-g. portion of the crude residue was extracted with two 5-ml. portions of hot ether, and the residue was recrystallized from acetone, yielding 0.05 g. of one of the three isomeric diols of V as stubby colorless needles, m. p. 158–159°. An analytical sample was obtained by two recrystallizations from acetone; the melting point was constant at 163°.

Anal. Calcd. for $C_{16}H_{30}O_2$: C, 75.41; H, 11.89. Found: C, 75.40; H, 11.78.

Diethyl-(4-hydroxyphenyl)-(4-hydroxycyclohexyl)-methane (VII).—A solution of 50.0 g. (0.20 mole) of I in 300 ml. of commercial absolute ethanol containing 8 g. of Raney nickel catalyst[10] was shaken at 180–185° under 3000 p. s. i. hydrogen pressure until a pressure drop equivalent to the absorption of 0.85 mole (4.25 mole equivalents) of hydrogen had been observed. The catalyst was removed by filtration through Filter-Cel, and washed with two 5-ml. portions of ethanol. On cooling, the filtrate deposited small colorless irregular prisms. The solid collected by filtration amounted to 11.03 g. (21.4%); m. p. 183–189°. Two recrystallizations from methanol yielded one of the two possible isomers of VII in analytical purity, m. p. 193–194°.

Anal. Calcd. for $C_{18}H_{22}O_2$: C, 77.82; H, 9.99. Found: C, 77.88; H, 9.94.

Methylethyl-(4-hydroxyphenyl)-(4-hydroxycyclohexyl)-methane (VIII).—Methylethyldi-(4-hydroxyphenyl)-methane (II) (112.6 g.) was hydrogenated as described in the preparation of VII. The crude glassy product (107.1 g.) obtained from the reduction mixture was taken up in 300 ml. of ether and extracted with three 200-ml. portions of 12% aqueous potassium hydroxide solution. The basic

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[8] L. K. Evans and A. E. Gillam, *J. Chem. Soc.*, 815 (1941).

[9] All melting points are corrected. We are indebted to Mr. S. M. Nagy, Mrs. Louise W. Spencer and Mr. Philip H. Towle for the micro-analyses.

[10] Pavlic and Adkins, THIS JOURNAL, **68**, 1471 (1946).

extracts were combined, washed with ether, and allowed to crystallize overnight. The colorless platelets collected by filtration amounted to 29.7 g. after one recrystallization from the minimum amount of water. A solution of 26.05 g. of the crude potassium salt in 80 ml. of water was acidified to *p*H 5 with 8.6 ml. of 6 *N* hydrochloric acid. The free phenol was extracted with ether, dried over anhydrous magnesium sulfate and the solution concentrated to dryness. On recrystallization from benzene, the phenolic product was obtained as 10.62 g. of colorless needles (9.7%), m. p. 133–135°. Two recrystallizations from benzene yielded analytically pure VIII, m. p. 136°.

Anal. Calcd. for $C_{16}H_{24}O_2$: C, 77.38; H, 9.74. Found: C, 77.61; H, 9.45.

Diethyldi-(4-ketocyclohexyl)-methane (IX).—A solution of 2.66 g. (0.01 mole) of IV in 100 ml. of benzene and 18 ml. of methyl ethyl ketone was added rapidly (2–4 drops per sec.) to a well stirred ice-cold oxidizing solution consisting of 10.45 g. (0.035 mole) of sodium dichromate dihydrate, 22.5 ml. of concentrated sulfuric acid, 12.5 ml. of glacial acetic acid and 200 ml. of water. Ten minutes after completion of the addition the mixture was brought to 30°, and allowed to react at that temperature with vigorous stirring for five hours. The reaction mixture was then extracted with 150 ml. of ether and the amber solvent layer washed with 20 ml. of water, two 20-ml. portions of 5% aqueous sodium hydroxide and then with water until the washes were neutral. After drying over anhydrous magnesium sulfate for several hours, the solvent was removed under reduced pressure. The residue crystallized spontaneously as short needles, m. p. 77–82°, and amounted to 2.50 g. A portion (1.78 g.) of this crude material yielded 1.39 g. (74.5%) of pure IX, m. p. 87–88° on one recrystallization from 20 ml. of cyclohexane. An analytical sample obtained from cyclohexane as colorless rosettes melted at 87–88°.

Anal. Calcd. for $C_{17}H_{28}O_2$: C, 77.22; H, 10.67. Found: C, 77.35; H, 10.72.

Methylethyldi-(4-ketocyclohexyl)-methane (X).—The oxidation of crude V (3.00 g., 0.012 mole) was carried out exactly as described for IX. The yield of pure X, m. p. 114–116°, obtained in two crops on recrystallization of the crude product from acetone–water was 2.37 g. (79.9%). An analytical sample was recrystallized from ether–ethanol as small colorless prisms, m. p. 114–116°.

Anal. Calcd. for $C_{16}H_{26}O_2$: C, 76.75; H, 10.46. Found: C, 76.45; H, 10.51.

Methylisobutyldi-(4-ketocyclohexyl)-methane (XI).—Methylisobutyldi-(4-hydroxyphenyl)-methane (III), m. p. 154–155°, was prepared by the method of Reid and Wilson,[6] who reported the melting point as 153°.

Hydrogenation of III (10 g., 0.0365 mole) was carried out as described in the preparation of IV. The crude methylisobutyldi-(4-hydroxycyclohexyl)-methane (VI) was obtained as 8.7 g. of an intractable glass, which slowly crystallized from benzene solution as an impure mixture, m. p. 120–130°, which was not further purified.

A portion of the crude glass VI (2.0 g.) was oxidized by the procedure described for IX. The unpurified diketone (XI), m. p. 56–65°, was obtained as 1.69 g. of white powder (71.5% from III), which was soluble in all common organic solvents. Two recrystallizations from acetone–water with rejection of the first small portions yielded large colorless platelets in several crops, m. p. 64–67°. The total recovery was 0.71 g. (42%).

Anal. Calcd. for $C_{18}H_{30}O_2$: C, 77.75; H, 10.86. Found: C, 78.20; H, 11.08.

Diethyldi-(4-methoxyphenyl)-methane (XII).—To a solution of 20.5 g. (0.08 mole) of diethyldi-(4-hydroxyphenyl)-methane (I) in 50 ml. of methanol at gentle reflux was added simultaneously at one drop per second 18.9 ml. (0.20 mole) of dimethyl sulfate (previously washed with 20 ml. of ice-water and 6 ml. of saturated aqueous sodium bicarbonate solution) and a solution of 12.2 g. of potassium hydroxide in 20.2 ml. of water. Rapid stirring was maintained throughout the addition, which required about twenty minutes. An oil layer separated after about two-thirds of the reagents had been added. The reaction mixture was refluxed for an additional sixty minutes, then diluted with 50 ml. of water and extracted with two 50-ml. portions of ether. The solvent layer was washed with 20 ml. of saturated sodium bicarbonate solution, then to neutrality with two 20-ml. portions of water. The solvent layer was concentrated under reduced pressure to a light yellow oil, which could be crystallized by scratching under methanol–water; 22.68 g. (99.5%), m. p. 48–50°. Recrystallization from methanol yielded an analytical sample, m. p. 49–50°.

Anal. Calcd. for $C_{19}H_{24}O_2$: C, 80.24; H, 8.51. Found: C, 80.09; H, 8.68.

Diethyldi-(4-methoxy-1,4-cyclohexadienyl)-methane (XV).—Liquid ammonia (400 ml.) was collected in a 500-ml. round-bottomed flask, cooled to −70° in an acetone–Dry Ice-bath and protected with a potassium hydroxide drying tube. The ammonia was blown with a stream of dry air into an insulated 1 l. three-necked flask, fitted with stirrer and a potassium hydroxide tube. A solution of 9.17 g. (0.032 mole) of XII in 195 ml. of dry ether and 44.8 ml. (46.1 g., 0.77 mole) of ethanol was added rapidly to the stirred ammonia to form a clear solution, to which was immediately added 14.7 g. of sodium (0.64 mole) in large pieces during a period of fifteen minutes. The resulting deep-blue solution was stirred for forty minutes, at which time the reaction mixture became colorless. The insulation was removed and excess ammonia allowed to evaporate for thirty minutes. After hydrolysis of the white slurry with 100 ml. of water the ether layer was separated and the aqueous phase further extracted with two 50-ml. portions of ether. The combined solvent layers were washed with five 20-ml. portions of water to neutrality. Distillation of the solvent under reduced pressure yielded 7.82 g. of the crude enol ether, as a colorless powder, m. p. 83–89°. Recrystallization from 200 ml. of methanol afforded 3.88 g. (42%) of XV as colorless platelets, m. p. 109–116°, sufficiently pure for the preparation of XVIII. A sample for analysis, recrystallized from methanol, melted at 113–115°.

Anal. Calcd. for $C_{19}H_{28}O_2$: C, 79.12; H, 9.78. Found: C, 79.36; H, 9.74.

Methylethyldi-(4-methoxy-1,4-cyclohexadienyl)-methane (XVI).—Methylethyldi-(4-hydroxyphenyl)-methane (II) (4.37 g., 0.018 mole) was methylated as described in the preparation of XII. Methylethyldi-(4-methoxyphenyl)-methane (XIII) was obtained as 3.84 g. of a light yellow oil, which was reduced with sodium–ethanol in liquid ammonia, as described for XV, without further purification. The tetrahydro derivative (XVI) was initially obtained as 3.53 g. of yellow oil, which separated as 0.95 g. (20% over-all) of crisp solid from 25 ml. of methanol at 5°. Recrystallization from methanol yielded 0.625 g. of XVI (66% recovery) as colorless rectangular platelets, m. p. 70–72°. An analytical sample was recrystallized from methanol, m. p. 72–73°.

Anal. Calcd. for $C_{18}H_{26}O_2$: C, 78.79; H, 9.55. Found: C, 78.44; H, 9.85.

Methylisobutyldi-(4-methoxy-1,4-cyclohexadienyl)-methane (XVII).—Methylisobutyldi-(4-hydroxyphenyl)-methane (III) (8.14 g., 0.03 mole) was methylated as described for XII. The methylisobutyldi-(4-methoxyphenyl)-methane (XIV) was obtained as 8.11 g. of a colorless viscous oil. This crude material (7.45 g., 0.025 mole) was reduced as described in the preparation of XV, yielding 7.30 g. of a white waxy solid which crystallized from 75 ml. of methanol at 5° as 3.34 g. (41% over-all) of nearly cubical prisms of XVII, m. p. 70–74°. One recrystallization from methanol yielded pure XVII, m. p. 75–76°, with 72.5% recovery. An analytical sample crystallized from methanol had a melting point of 75–76°.

Anal. Calcd. for $C_{20}H_{30}O_2$: C, 79.42; H, 10.00. Found: C, 79.29; H, 9.97.

Diethyldi-(4-keto-1-cyclohexenyl)-methane (XVIII).—To a well-stirred solution of 3.90 g. (0.0135 mole) of XV in

67.5 ml. of toluene at 5° was added at two drops per second an ice-cold solution of 27 ml. of concentrated sulfuric acid in 67.5 ml. of water. After thirty minutes the reaction mixture was brought to 30°, and stirred at that temperature for forty-five minutes. The well-stirred solution was then gently refluxed for one hour. After cooling, the solvent layer was separated and the aqueous portion extracted with two 30-ml. portions of ether. The combined solvent layers were washed with 10 ml. of water, two 10-ml. portions of saturated sodium bicarbonate solution, then with small portions of water to neutrality. After drying over anhydrous calcium sulfate for two hours and then over anhydrous magnesium sulfate, the solvent was distilled at 60° under reduced pressure. A yellow oil setting to a mass of yellow crystals was obtained. After trituration with 10 ml. of petroleum ether (b. p. 30–60°) and storage overnight, XVIII was obtained, 2.48 g. (69.4%), m. p. 89–92°. An analytical sample, m. p. 92–93°, was recrystallized from ligroin (b. p. 60–90°).

Anal. Calcd. for $C_{17}H_{24}O_2$: C, 78.42; H, 9.29; mol. wt., 260.4. Found: C, 78.37; H, 9.31; mol. wt. (Rast, using camphor), 258.

Diethyldi-(4-keto-1-cyclohexenyl)-methane (XVIII) was found unstable on long standing even at 0°, and reacts immediately with dilute basic solutions to produce a brilliant green water-soluble dye, which is decolorized on acidification.

Diethyldi-(4-hydroxycyclohexenyl)-methane (XIX).—A solution of 0.260 g. (0.001 mole) of XVIII in 3 ml. of glacial acetic acid containing 0.016 g. of ferrous chloride dihydrate and 0.050 g. of prereduced Adams platinum catalyst was stirred in a microhydrogenator under one atmosphere of hydrogen pressure. After two hours and ten minutes 0.002 mole of hydrogen had been absorbed, and hydrogen uptake had practically ceased. After removal of the catalyst by filtration, the solvent was removed under reduced pressure, leaving a yellow oil (0.320 g.) that crystallized spontaneously. A portion of this crude material (0.225 g.) was triturated with 3 ml. of petroleum ether (b. p. 30–60°) and the slightly greenish residue was extracted with 10 ml. of boiling cyclohexane. The residue was recrystallized from 3 ml. of benzene. The long hair-like needles that separated from the cyclohexane and benzene solutions proved to be identical, and thus the product is one of the isomers of XIX, m. p. 140–142°. The total yield was 0.080 g. (43%). An analytical sample, after decolorization and recrystallization from benzene, melted sharply at 144°.

Anal. Calcd. for $C_{17}H_{28}O_2$: C, 77.22; H, 10.67. Found: C, 77.11; H, 10.60.

Diethyldi-(4-hydroxy-1-cyclohexenyl)-methane reduces potassium permanganate in acetone, and does not give the green coloration in base characteristic of XVIII.

Summary

Several series of 4,4′-dihydroxy and diketo derivatives of hydrogenated dialkyldiphenylmethane have been synthesized for pharmacological testing.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

The Alkaline Cleavage of Desyl Thioethers

BY SYLVIA TEICH[1] AND DAVID Y. CURTIN

S-Desylthioglycolic acid (I) has been found to undergo ready cleavage when treated with boiling

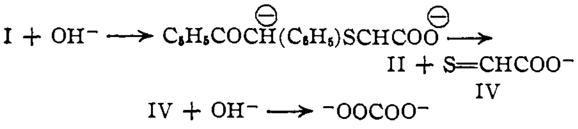
$$C_6H_5COCH(C_6H_5)SCH_2COOH \longrightarrow C_6H_5COCH_2C_6H_5 + HOOCCOOH$$

dilute aqueous sodium hydroxide.[2] The products isolated were desoxybenzoin and oxalic acid (as the calcium salt). The reaction has been extended to a number of related compounds.[2,3]

The mechanism proposed[2,3a] has involved as the initial step a displacement by hydroxyl ion on sulfur to give the conjugate base of desoxybenzoin (II) and a sulfenic acid derivative (III). III has been presumed to be converted to oxalate ion through a sequence of reactions which have not been further elucidated.

$C_6H_5COCHC_6H_5^-$ $HOSCH_2COO^-$
II III

An alternative path for the reaction could involve the initial removal of a proton from the carbon α to the carboxyl group by hydroxyl ion, this step either accompanied or followed by the elimination of the conjugate base of desoxybenzoin (II) as shown.



$$I + OH^- \longrightarrow C_6H_5CO\overset{\ominus}{C}H(C_6H_5)SCHCO\overset{\ominus}{O} \longrightarrow II + \underset{IV}{S{=}CHCOO^-}$$

$$IV + OH^- \longrightarrow {}^-OOCOO^-$$

That such a proton-removal is not impossibly slow even though it leads to a di-negatively charged ion is indicated by a study of the base-catalyzed racemization of the optically active α-phenylmercaptophenylacetic acid anion (V). The racemization has been reported[4] to have a

$C_6H_5CH(SC_6H_5)COO^-$
V

half-time of five hours when carried out at 100° with an aqueous solution only 0.100 molar in V and 0.042 molar with respect to hydroxyl ion. Evidence has been found by other workers that the sulfur atom in a sulfide can help to stabilize a negative charge on an adjacent carbon.[5]

We felt that the examination of the behavior toward alkali of certain compounds related to desylthioglycolic acid might aid in the choice

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(2) Behagel and Schneider, *Ber.*, **68**, 1588 (1935).

(3) (a) Behagel and Ratz, *Ber.*, **72**, 1257 (1939); (b) Holmberg, *Arkiv. Kemi. Minerol. Geol.*, **12A**, No. 9 (1939); (c) Schönberg and Iskander, *J. Chem. Soc.*, 90 (1942); (d) Behagel and Müller, *Ber.*, **68**, 2164 (1935).

(4) Ramberg and Hedlund, *Arkiv. Kemi. Mineral. Geol.*, **12A**, No. 12 (1936).

(5) Gilman and Webb, THIS JOURNAL, **62**, 987 (1940); Rothstein, *J. Chem. Soc.*, 1550, 1553, 1558 (1940); Woodward and Eastman, THIS JOURNAL, **68**, 2229 (1946).