mol. wt., 342. Found: C, 38.52; H, 4.15; mol. wt. (a molecular weight was determined from the ultraviolet absorption spectrum of the picrate at 3880 Å.[4]), 341.

2-(β-Phenylethylimino)-5-hydroxyhexahydropyrimidine.—Four grams of 2-nitrimino-5-hydroxyhexahydropyrimidine and 7 g. of β-phenylethylamine were boiled in an Erlenmeyer flask for a few minutes, whereupon a vigorous evolution of ammonia occurred. The resulting viscous sirup was cooled to room temperature and 200 ml. of 20–40° petroleum ether added. An oil separated which solidified upon cooling. Recrystallization from ethanol–water gave colorless crystals of free 2-(β-phenylethylimino)-5-hydroxyhexahydropyrimidine (2.4 g., yield 44%, m.p. 179.3–182°).

Anal. Calcd. for $C_{12}H_{17}N_3O$: C, 65.75; H, 7.76; N, 19.20. Found: C, 65.75; H, 7.55; N, 19.17.

(4) K. Cunningham, W. Dawson and F. S. Spring, *J. Chem. Soc.*, 2305 (1951).

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A New Type Mercuration Reaction

BY W. E. ROSEN, J. B. ZIEGLER AND A. C. SHABICA

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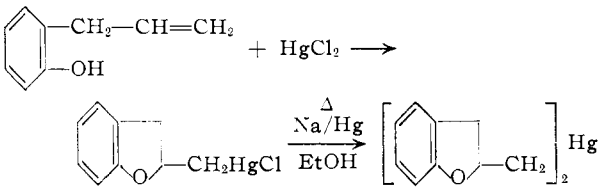
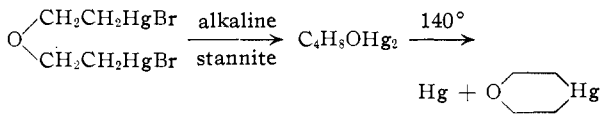
The direct formation of dialkylmercury compounds from mercury salt addition products to olefins has never been established and indirect formation has been reported in only a few cases.[1] Adams[2] reduced the *o*-allylphenol derivative with sodium amalgam

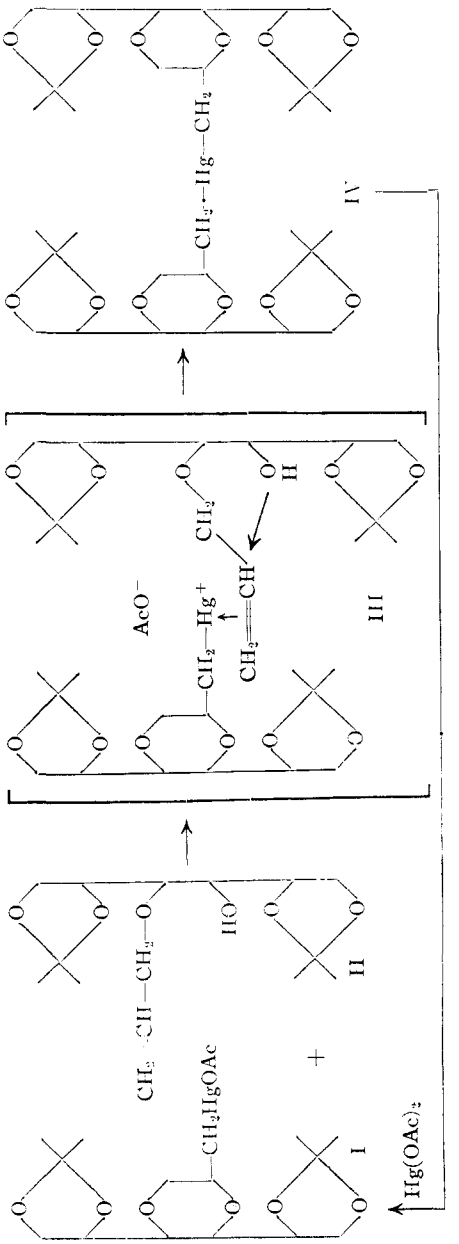


and Sand[3] used alkaline stannite solution to form an intramolecular dialkylmercury compound



These conversions have been successful only with the halides, and have never been carried out either in the absence of reducing agents or under mild conditions. 3-Allyl-1,2;5,6-diisopropylidene-D-mannitol (II) has been mercurated with mercuric acetate to give the acetoxymercurial 2-acetoxymercurimethyl-5,6-bis-(2,2-dimethyl-1,3-dioxolan-4-yl)-*p*-dioxane (I).[4]

In examining the mother liquors from this reaction, a small amount of the diorganomercurial, bis-[5,6-bis-(2,2-dimethyl-1,3-dioxolan-4-yl)-2-*p*-dioxanylmethyl]-mercury (IV), was isolated. The formation of IV, even in small amounts, suggested that the first-formed acetoxymercurial I was capable of reacting further with 3-allyl-1,2;5,6-diisopropylidene-D-mannitol (II). One reasonable mechanism would involve the formation of an intermediate complex III of the olefin and the polarized (or ionized) acetoxymercuric compound, arbitrarily indicated in the flow sheet as a π-complex. Intramolecular attack of the oxygen of the 4-hydroxyl group to form a stable dioxane ring might provide the driving force. When a solution containing equimolar amounts of I and II was shaken at room temperature, compound IV was isolated in 20% yield. Recycling recovered starting material I several times permitted an increase in total yield to 51% (69% conversion yield).



The assigned structure IV is supported by the

(1) A. M. Birks and G. F Wright, THIS JOURNAL, **62**, 2412 (1940), inferred the presence of an R_2Hg type compound in the reaction of mercuric acetate with benzalacetophenone, but were unable to isolate such a product. Further, the reduction of 2-methoxyalkylmercuric halide by hydrazine hydrate has been postulated to proceed through mercuri-bis-2-methoxyalkane [G. F Wright, *Can. J. Chem.*, **30**, 268 (1952)].

(2) R. Adams, F. L. Romans and W. N. Sperry, THIS JOURNAL **44**, 1781 (1922).

(3) J. Sand, *Ber.*, **34**, 2910 (1901). The referee has kindly informed us that some recent Russian work has shown that the product is actually dimeric.

(4) L. H. Werner and C. R. Scholz, THIS JOURNAL, **76**, 2701 (1954).

observation that the acetoxymercurial I can be regenerated by refluxing with mercuric acetate; it is known that "the general equilibrium between mixed and simple organometallic compounds is observable with mercurials: $2RHgX \rightleftarrows R_2Hg + HgX_2$."[5]

The scope and limitations of the addition of a mercurated olefin to another olefin has not been defined, except that no addition product was isolated in a room temperature reaction (dioxane, 2 days) of I with cholesteryl acetate or with cholestenone. However, mercuration of cholesterol with mercuric acetate itself proceeds in fairly low yield even at elevated temperatures, the product being isolated not as the acetoxymercurial, but as 6-chloromercuricholesterol.[6,7] No acetoxymercuri-compound was isolable when a dioxane solution of mercuric acetate was allowed to stand five days with cholesteryl acetate or cholestenone.

Experimental

Isolation of Bis-[5,6-bis-(2,2-dimethyl-1,3-dioxolan-4-yl)-2-*p*-dioxanylmethyl]-mercury (IV) from Mercuration of 3-Allyl-1,2;5,6-diisopropylidene-D-mannitol.—Mercuration of 3-allyl-1,2;5,6-diisopropylidene-D-mannitol (II) with mercuric acetate under anhydrous conditions has been shown to give a crystalline mercurated derivative (I).[4] Evaporation of the mother liquors left a sirup which was partitioned between ether and water; the ether-soluble fraction deposited 2.0 g. (1%) of crude IV on very slow evaporation of an ether–methanol solution. Recrystallization from methanol afforded fine, white glistening needles, m.p. 152–152.2°, $[\alpha]^{25}D$ +27° (chf.).

Anal. Calcd. for $C_{30}H_{50}O_{12}Hg$ (803.31): Hg, 24.97. Found: Hg, 25.48, 24.75.

The infrared spectrum was consistent with the proposed structure and was very similar to that of the iodomercury compound[4] corresponding to I. Attempted molecular weight determination by the Rast method would not give consistent results with any solvent; the compound seemed to decompose.

Preparation of IV by Addition of I to II.—A solution of 2.98 g. (5.3 millimoles) of 2-acetoxymercurimethyl-5,6-bis-(2,2-dimethyl-1,3-dioxolan-4-yl)-*p*-dioxane (I), m.p. 110.5–111.5° and 1.60 g. (5.3 millimoles) of 3-allyl-1,2;5,6-diisopropylidene-D-mannitol (II), $n^{23}D$ 1.4577, in 30 cc. of dioxane was vigorously shaken at room temperature for 21 hours. After the solvent was removed at reduced pressure, the residue was taken up in ether, filtered and diluted with methanol. The concentrated solution deposited a small amount of low melting (51–56°) white solid before very slowly yielding the diorganomercury addition product IV. Spontaneous evaporation over several days afforded 0.55 g. (13%) of white needles, m.p. 142–147°, which melted at 150–152° after one crystallization from methanol; mixed melting point and comparison of infrared spectra established its identity with the diorganomercury compound isolated from the mercuration mother liquors. After an additional 0.31 g. (7.3%) of crude product was obtained from the mother liquors, the solvent was removed and the residue taken up in isopropyl ether. Seeding with I encouraged the crystallization of 0.69 g. of starting acetoxymercurial (I), m.p. 107–110°. The yield of addition product based on unrecovered I (conversion yield) is therefore 26% (17% pure and 9.5% crude). An added trace of acetic acid had no effect on the addition reaction.

When the same procedure was followed with larger quantities of I and II,[8] except that a small volume of ether was used on the crude residue, the more ether-soluble IV dissolved, whereas starting I did not dissolve and was recovered on filtration. By recycling recovered I four times with fresh II, a total yield based on I of 51% (69% conversion yield) of crude product was obtained; two crystallizations from methanol gave an 85% recovery of pure IV, m.p. 150–152°.

Conversion of IV to I.—When 1.00 g. of IV was refluxed for two hours with 0.40 g. (equimolar amount) of mercuric acetate in 15 ml. of methanol, 1.12 g. of pure I, m.p. 111–113° plus 0.14 g. of slightly impure I, m.p. 107–109°, was isolated. This represents an 80% yield of pure I (90% total yield) based on reaction of *both* halves of IV.

Acknowledgment.—The authors are indebted to Dr. L. H. Werner for stimulating discussions, and to Mr. Louis Dorfman and staff for the microanalyses and for the determinations of infrared spectra and optical rotation.

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(5) Henry Gilman in Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., Vol. I, 1943, p. 551.

(6) W. Merz, *Z. physiol. Chem.*, **154**, 225 (1926).

(7) R. H. Levin and M. A. Spielman, THIS JOURNAL, **62**, 920 (1940).

(8) Experiment by Mrs. Margaret Petroski.

Microbiological Converison of Steroids. I. Introduction of the 11β-Hydroxyl Group into C_{21} Steroids

BY G. M. SHULL AND D. A. KITA

RECEIVED JULY 19, 1954

The introduction of hydroxyl groups into the steroid nucleus by microörganisms has been reported in several papers; however, only two examples of 11β-hydroxylation have appeared.[1] This type of hydroxylation is of particular interest in the synthesis of adrenal cortical hormones such as 17α-hydroxycorticosterone (hydrocortisone) and corticosterone. We wish to report the introduction of the 11β-hydroxyl group into several C_{21} steroids by means of the fungus *Curvularia lunata*.[2]

Experimental

Curvularia lunata[3] was grown for two days in shake flasks at 28° on a malt extract–sucrose–salts medium.[4] One hundred ml. of the resulting growth was used to inoculate 2000 ml. of the same medium contained in a fermenter equipped with a submerged aerator. The inoculated medium was agitated at 1700 r.p.m. and aerated at the rate of 0.5 volume of air per volume of medium per minute for 22 hours in a 28° water-bath. Fifty grams of damp mycelium (12.5 g. dry weight), obtained by filtration of the resulting broth, was added to 2000 ml. of water and 0.5 g. of steroid contained in a similar fermenter. After the mycelium-steroid suspension had been agitated (in the manner described above) for the period indicated, it was extracted with chloroform. The extract was qualitatively examined by means of paper chromatography to determine the number of transformation products. The solvent system described by Zaffaroni and Burton[5] and modifications of those described by Bush[6] were used in the paper chromatography. The compounds discussed below were isolated from the extract by silica gel partition chromatography in which ethanol was the stationary phase and methylene chloride the mobile phase.

(1) D. R. Colingsworth, M. P. Brunner and W. J. Haines, THIS JOURNAL, **74**, 2381 (1952); D. R. Colingsworth, J. N. Karnemaat, F. R. Hanson, M. P. Brunner, K. M. Mann and W. J. Haines, *J. Biol. Chem.*, **203**, 807 (1953); F. R. Hanson, K. M. Mann, E. D. Nielson, H. V. Anderson, M. P. Brunner, J. N. Karnemaat, D. R. Colingsworth and W. J. Haines, THIS JOURNAL, **75**, 5369 (1953); H. C. Murray and D. H. Peterson, U. S. Patent 2,602,769 (July 8, 1952).

(2) G. M. Shull, D. A. Kita and J. W. Davisson, U. S. Patent 2,658,-023 (November 3, 1953).

(3) This culture has been deposited with the Fermentation Division of the Northern Regional Research Laboratory, Peoria, Illinois, and is maintained in their culture collection as NRRL-2380.

(4) G. Smith, "Industrial Mycology," 3rd ed., Edward Arnold and Co., Ltd., London, 1946, p. 173.

(5) A. Zaffaroni and R. B. Burton, *J. Biol. Chem.*, **193**, 749 (1951).

(6) I. E. Bush, *Biochem. J.*, **50**, 370 (1952).