plain the absence of much fine structure in the compounds III, as compared to 2,2'-binaphthyl[8]: All of them show an intense absorption at about 240 mμ (log ϵ 5.00) and after some inflections a much lower second maximum (log ϵ 2.78 to 3.00) at approximately 320 mμ. Compound I has a very pronounced fine structure; its spectrum consists of two absorption regions: six high-intensity bands between 290 and 350 mμ and five low-intensity bands between 390 and 430 mμ.

Experimental

3,3'-Dihydroxymethyl-2,2'-binaphthyl (III, R = CH_2OH), prepared from 3,3'-dicarbomethoxy-2,2'-binaphthyl (III, R = $COOCH_3$) and lithium aluminum hydride in 96% yield, crystallized from isopropyl alcohol in colorless needles of m.p. 230° (literature[6] 228–229°); ultraviolet spectrum (in alcohol): 234 mμ (log ϵ 5.16); inflections at 280 mμ (4.19) and 293 mμ (3.76); 320 mμ (2.75).

Pinacol (VI) of 3-Methyl-2-decalone (V).—The mixture of 198 g. of 3-methyl-2-decalone (V),[7] 21 g. of aluminum turnings, 8.5 g. of mercuric chloride and 180 ml. of dry benzene was refluxed for 1 hr. with stirring. At room temperature 60 ml. of water and 180 ml. of benzene were added gradually, and the content of the flask was refluxed for 1 hr. more. The product was filtered while still hot, and the solid phase washed with 200 ml. of hot benzene. Evaporation of the benzene *in vacuo* gave 130 g. (65%) of a viscous oil, which was used directly for the next step.

3,3'-Dimethyl-2,2'-di-3,4,5,6,7,8,9,10-octahydronaphthyl (VII).—The mixture of 100 g. of VI and 20 g. of dehydrated alum was heated at 160–170° for 4 hr. and extracted with hot benzene. The solution was dried and distilled, b.p. 170–175° (0.2 mm.), yield 60 g. (67%); ultraviolet spectrum (in alcohol): inflection at 250 mμ (log ϵ 3.46).

Anal. Calcd. for $C_{22}H_{34}$: C, 88.5; H, 11.5. .Found: C, 87.8; H, 11.3.

3,3'-Dimethyl-2,2'-binaphthyl (III, R = CH_3).—In an atmosphere of nitrogen, 10 g. of VII was heated at 300–330° with 7 g. of 10% palladium–charcoal for 12 hr. The product was extracted with a mixture of benzene and ether and the residue of the solution triturated with petroleum ether and recrystallized from butyl alcohol; prisms of m.p. 144°, yield 6.5 g. (68%); ultraviolet spectrum (in alcohol): 233 mμ (log ϵ 5.10); 290 mμ (4.13); 321 mμ (2.98).

Anal. Calcd. for $C_{22}H_{18}$: C, 93.6; H, 6.4. Found: C, 93.9; H, 6.6.

The compound gave an addition product with 2 moles of **1,3,5-trinitrobenzene**; from isopropyl alcohol, yellow needles of m.p. 140°.

3,3'-Dibromomethyl-2,2'-binaphthyl (III, R = CH_2Br).—(a) A solution of 5 g. of III (R = CH_2OH) in 600 ml. of benzene was prepared at 50°; after addition of 2 drops of pyridine, 10 g. of phosphorus tribromide was added with stirring and the mixture kept at 50° for 2 hr. Cold water was added and the benzene layer washed with sodium bicarbonate solution and water, dried and concentrated; from benzene–petroleum ether colorless needles of m.p. 172° (lit.[6] 165–166°), yield 6.1 g. (87%); ultraviolet spectrum (in ethanol): 238 mμ (5.01); inflection at 300 mμ (3.76); 331 mμ (2.98).

Anal. Calcd. for $C_{22}H_{16}Br_2$: C, 60.0; H, 3.7. Found: C, 60.3; H, 4.0.

(b) The solution of 2.8 g. of 3,3'-dimethyl-2,2'-dinaphthyl (III, R = CH_3) in 100 ml. of carbon tetrachloride was refluxed for 6 hr. with 3.6 g. of NBS and a trace of benzoyl peroxide. The product was filtered and the solution concentrated; from benzene–petroleum ether, m.p. 172°, yield 3.5 g. (75%).

9,10-Dihydro-2,3,6,7-dibenzophenanthrene (VIII).—The reaction between lithium phenyl and the dibromo compound III (R = CH_2Br) was carried out in the same manner as described by Badger, *et al.*[6] VIII was obtained in 37% yield from benzene, m.p. 137–138° (lit.[6] 140–141°); ultraviolet spectrum (in alcohol): 231 mμ (4.63); 264 (4.68); 276 (4.48); 279 (4.49); 319 (3.82).

Anal. Calcd. for $C_{22}H_{16}$: C, 94.7; H, 5.3. Found: C, 94.3; H, 6.0.

2,3,6,7-Dibenzophenanthrene (I).—In an atmosphere of nitrogen, 0.5 g. of VIII and 0.5 g. of palladium–charcoal (10%) were heated at 350° for 4 hr. The product was extracted with hot benzene and the residue of the solution recrystallized from the same solvent; yellow needles of m.p. 257°, yield 0.45 g. (90%); ultraviolet spectrum (in alcohol): 260 mμ (4.83); 305 (4.70); 318 (4.90); 333 (4.57); 343 (4.34); 349 (4.42); 360 (4.28); 380 (2.70); 392 (2.57); 403 (2.78); 415 (2.45); 427 (2.76).

Anal. Calcd. for $C_{22}H_{14}$: C, 95.0; H, 5.0. Found: C, 94.8; H, 5.4.

The dipicrate, prepared in benzene solution and recrystallized from benzene, formed orange-red needles of m.p. 184°, as indicated in the literature.[9]

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(8) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," No. 309, John Wiley and Sons, New York, N. Y., 1951. The main absorption bands of 2,2'-binaphthyl are 254 mμ (log ϵ 4.95) and 305 mμ (4.25).

(9) E. Clar and F. John, ref. 1.

JERUSALEM, ISRAEL

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

cis-Hydroxylation of a Synthetic Steroid Intermediate with Iodine, Silver Acetate and Wet Acetic Acid

BY R. B. WOODWARD AND F. V. BRUTCHER, JR.[1]

RECEIVED AUGUST 23, 1957

Iodine, silver acetate and wet acetic acid oxidize the 6,7-double bond of *dl-anti-trans*-4,4a,4b,5,8,8a-hexahydro-1,8a-dimethyl-2(3H)phenanthrone (I) to give, after hydrolysis, a β-*cis*-glycol IVc in 71% yield and an α-*cis*-glycol in 2.5% yield. This reagent offers a method for producing in quantity the opposite *cis*-glycol stereoisomer compared with that derived from osmium tetroxide hydroxylation.

During recent steroid total synthesis work,[2] osmium tetroxide was used with success in *cis*-hydroxylating *dl-anti-trans*-4,4a,4b,5,8,8a-hexahydro-1,8a-dimethyl-2(3H)phenanthrone (I). Since this reagent possesses certain undesirable characteristics, we later developed a new *cis*-hydroxylation technique which has the unique feature of producing the opposite *cis*-glycol stereoisomer compared with that derived from osmium tetroxide. This paper describes our reagent and discusses its mechanism of hydroxylation.

We have found that when I is treated in acetic acid with iodine (1.05 equivalents), silver acetate (2.25 equivalents) and water (1.0 equivalent) and finally heated at 90–95° for three hours, oxidation

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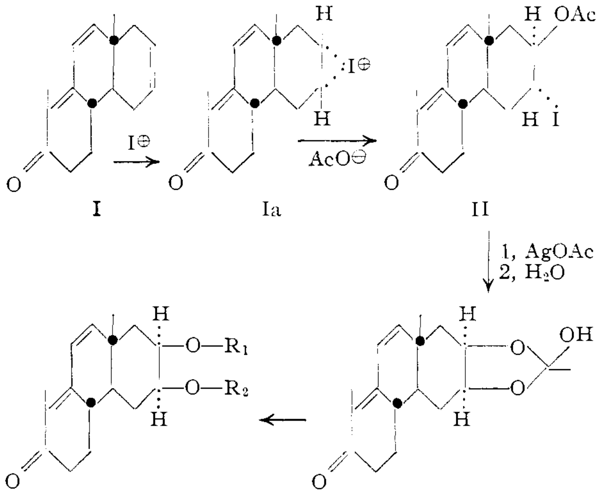
(1) Dept. of Chemistry, University of Pennsylvania, Phila. 4, Pa.

(2) R. B. Woodward, F. Sondheimer, D. Taub, K. Heusler and W. M. McLamore, THIS JOURNAL, **74**, 4223 (1952).

of the 6,7-double bond occurs to give, after hydrolysis with potassium hydroxide, the β-*cis*-glycol IVc, m.p. 184–185°, in 71% over-all yield; IVc was shown by mixed melting point determination and infrared spectra to be identical with the minor β-*cis*-glycol derived from osmium tetroxide oxidation of I[2]. Conversion of IVc to its acetone derivative proceeded smoothly and in good yield. Scrutiny of the mother liquors from the silver acetate–iodine oxidation of I yielded 2.5% of the α-*cis*-glycol, m.p. 156–157°, the major product from osmium tetroxide oxidation.[2]



IVa, $R_1 = H, R_2 = Ac$
IVb, $R_1 = Ac, R_2 = H$
IVc, $R_1 = R_2 = H$

That the β- rather than the α-*cis*-glycol is the major product of the silver acetate–iodine oxidation becomes manifest from examination of the mechanism of the reaction. Many years ago, the reaction of silver salts and iodine[3] in ether or benzene was shown by Simonini[4] to give an active complex intermediate, $(RCOO)_2AgI$, which could be isolated. Birckenbach[5] later established that reaction of equimolecular amounts of silver acetate and iodine in ether at −80° yielded a filtrate which added IOAc to cyclohexene to give the acetate of *trans*-2-iodo-1-cyclohexanol. Finally, in a well known series of experiments, Prevost[6] demonstrated that in benzene solution the complex reacted with olefins to give the *trans*-dicarboxylates.

With regard to our procedure, α-attack by I^+ from IOAc yields Ia, which is then opened *trans* through β-attack of acetate ion to give the *trans*-iodoacetate II, formulated as the diaxial isomer.[7] α-Attack of I^+ is favored since the angular methyl group at carbon 8a hinders the β-side.

The subsequent replacement reaction of II with silver acetate and wet acetic acid at 90–95° is well understood in view of Winstein's elucidation[8] of the remarkable effect of water on the reactions of neighboring acetoxyl groups. Under the controlling influence of water, II yields *cis*-orthoacetate III, which opens to give a mixture of two hydroxy acetates IVa and IVb. Saponification completes the sequence. It is seen that β-attack of acetate ion fixes a β-orientation for the *cis*-glycol, since throughout the replacement sequence oxygen remains on the β-side. On the other hand, predominant attack by osmium tetroxide on the less hindered side must give α-*cis*-glycol.

After its development, our silver acetate–iodine method was employed successfully on 1-(2,3-dimethylphenyl)-cyclohexene in 56% yield[9] and on a tetracyclic synthetic steroid[10] in 67% yield. It has been reported recently,[11] however, that the oxidation of anhydromethyltetrahydroberberine-A was unsuccessful due to internal neighboring group participation. The silver acetate–iodine reagent has found use recently with 5α,22a-spirost-2-ene[12] as a method of obtaining the opposite *cis*-glycol compared with osmium tetroxide oxidation.

Experimental[13]

***dl-anti-trans*-4,4a,4b,5,8,8a-Hexahydro-1,8a-dimethyl-6β,-7β-dihydroxy-2(3H)phenanthrone (IVc)**.—Ten grams (0.0438 mole) of *dl-anti-trans*-4,4a,4b,5,8,8a-hexahydro-1,8a-dimethyl-2(3H)phenanthrone[2] (I) was dissolved in 200 ml. of glacial acetic acid (analytical reagent, 99.5%) in a three-neck flask equipped with reflux condenser and thermometer. After addition of 16.43 g. (0.0986 mole) of silver acetate, 11.69 g. (0.0461 mole) of finely powdered iodine was added in small portions to the vigorously stirred reaction mixture over a 0.5 hour period at room temperature. When all of the iodine had been consumed (0.5 hour), 19.70 ml. of aqueous glacial acetic acid (0.0438 mole of water, prepared by dilution of 2.0 ml. of water up to 50 ml. with glacial acetic acid) was added. The reaction mixture was then heated at 90–95° for three hours with vigorous stirring. At the end of this time it was cooled, treated with excess sodium chloride, and filtered free from insoluble salts. The precipitate was thoroughly washed with hot benzene. The filtrate was evaporated at the water-pump, taken up in methanol, filtered, neutralized with several ml. of a methanolic potassium hydroxide solution, and then treated with 3.1 g. of potassium hydroxide dissolved in methanol. Hydrolysis was allowed to proceed overnight under nitrogen at room temperature. In the morning, the reaction product was neutralized carefully with dilute hydrochloric acid at ice-bath temperature. Methanol was removed at the water-pump and then under oil-pump vacuum to give a crystalline residue which weighed 12.20 g. The crude glycol was dissolved in a large volume of ethyl acetate which was then concentrated until solid separated, at which time the solution was cooled gradually to ice-bath temperature attendant with the separation from solution of a large mass of fine needles. After filtration there remained 7.48 g. (65%) of β-*cis*-glycol IVc, m.p. 184–185°. A second crop of β-*cis*-glycol, 0.71 g. (6%), m.p. 181–183°, was obtained from the mother liquors making the over-all yield 71%. After several recrystallizations from ethyl acetate the β-*cis*-glycol melted at 184.6–185.2° (fine needles), λ_{max}^{alc} 290 mμ (ε 26,986). When this β-*cis*-glycol was mixed with the minor β-*cis*-glycol from osmium tetroxide oxidation (isomer B[2]) no depression of the melting point was observed. The two infrared spectra were identical. The mother liquors after removal of 2 crops of β-*cis*-glycol were seeded with α-*cis*-glycol (isomer A[2]) and 0.283 g. of α-*cis*-glycol was ob-

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(3) J. Kleinberg, *Chem. Revs.*, **40**, 381 (1947).

(4) A. Simonini, *Monatsh.*, **14**, 81 (1893).

(5) L. Birckenbach, J. Goubeau and E. Berninger, *Ber.*, **65**, 1339 (1932).

(6) C. Prevost, *Compt. rend.*, **196**, 1129 (1933); **197**, 1661 (1933); C. Prevost and J. Wiemann, *ibid.*, **204**, 700 (1937).

(7) D. H. R. Barton and R. C. Cookson, *Quart. Revs.*, **10**, 44 (1956).

(8) S. Winstein and R. E. Buckles, THIS JOURNAL, **64**, 2780, 2787 (1942); S. Winstein, H. Hess and R. E. Buckles, *ibid.*, **64**, 2796 (1942); S. Winstein and R. M. Roberts, *ibid.*, **75**, 2297 (1953).

(9) D. Ginsburg, *ibid.*, **75**, 5746 (1953).

(10) L. B. Barkley, M. W. Farrar, W. S. Knowles, H. Raffelson and Q. E. Thompson, *ibid.*, **76**, 5014 (1954). More recently, the Monsanto group reports 74% of IVc by this procedure (*cf.* W. S. Knowles and Q. E. Thompson, *ibid.*, **79**, 3212 (1957)).

(11) P. B. Russell, *ibid.*, **78**, 3115 (1956).

(12) C. Djerassi, L. B. High, T. T. Grossnickle and R. Ehrlich, *Chemistry & Industry*, 474 (1955).

(13) All melting points are uncorrected.

tained in 2.5% yield with m.p. 156–157°. No depression of the melting points of the two glycols was observed on admixture. The infrared spectra of the two α-*cis*-glycols were identical.

dl-anti-trans-**1,6a,7,7a,10a,11,11a,11b-Octahydro-4,6a,-9,9-tetramethylphenanthro[2,3][1,3]dioxol-3(2H)one.**—A solution of 7.59 g. (0.029 mole) of IVc in 760 ml. of acetone (dried over potassium carbonate) was shaken vigorously with 38 g. of anhydrous copper sulfate for 48 hr. The salt was filtered off and the filtrate shaken with 20 g. of anhydrous potassium carbonate for 0.5 hour. The filtered solution was evaporated at the water-pump. After heating at 50° under oil-pump vacuum, the residue (8.77 g.) solidified. Recrystallization from benzene–low boiling petroleum ether gave 7.86 g. (90% yield) of acetonide, m.p. 151–153° as short needles. From the mother liquors, 0.34 g. of acetonide, m.p. 146–150°, was obtained, making the over-all yield 94%. Several crystallizations from benzene–low boiling petroleum ether gave material melting at 155.0–155.8°, $\lambda_{\max}^{\text{alc}}$ 289 mμ (ε 25,609).

Anal. Calcd. for $C_{19}H_{26}O_3$: C, 75.46; H, 8.67. Found: C, 75.13; H, 8.63.

PHILADELPHIA 4, PA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

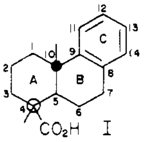
Rearrangements and Oxidations of Tricarbocyclic Diterpenes[1]

BY ERNEST WENKERT AND BILL G. JACKSON

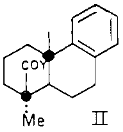
RECEIVED JUNE 3, 1957

A deisopropylation product of dehydroabietonitrile is described. Its stereochemistry is elucidated and its link with podocarponitrile established. The biogenetic consequences in the tricarbocyclic diterpene field are discussed. Possible mechanisms of chromic acid oxidation of ketones are portrayed in the light of certain steric effects observed in these investigations.

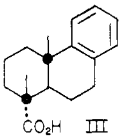
In connection with investigations on the synthesis of tricarbocyclic diterpenes,[2] especially resin acids, it became of importance to acquire the two C-4 epimers of compound I. The isomer (II, Y = OH) derivable from podocarpic acid has been produced most recently,[3] while no compound with the stereochemistry of III is known. However, a compound I with unspecified configuration has been obtained from dehydroabietic acid by acid-catalyzed removal of its isopropyl group.[4] Because of the possibility of arriving at structure III from this source, this reaction was reinvestigated.



I

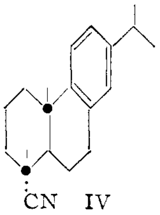


II

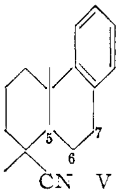


III

Deisopropylation of dehydroabietonitrile (IV) under the stimulus of aluminum chloride in benzene solution led to a mixture of products from which a crystalline $C_{17}H_{21}N$ compound, present in the largest amount (39%), could be isolated readily. Its 4.50μ nitrile band in the infrared and its 265 mμ (log ε 2.95), 272 mμ (log ε 2.93) ultraviolet absorption maxima, characteristic of a tetralin chromophore[2,4] in contrast to the 268 mμ (log ε 2.84), 272 mμ (log ε 2.86) maxima of the starting material IV, suggested that it was a stereoisomer of V. Basic hydrolysis converted V into a carboxylic acid whose melting point, 159–160°, compared favorably with that reported (159–160°) for the deisopropylation product of dehydroabietic acid.[4]



IV



V

Chromic acid oxidation of the nitrile V yielded three crystalline products, two ketones and one acid. One of the two neutral products was a $C_{17}H_{19}ON$ monoketone whose carbonyl group was conjugated with the benzene ring, as indicated by its 5.94 μ infrared band and its typical α-tetralone absorption at 250 mμ (log ε 4.03). The second compound, a yellow $C_{17}H_{17}O_2N$ substance, had all the spectral properties characteristic of an α-diketone. Hence the oxidation had led to a 7-ketone and a 6,7-diketone.[5]

Despite repeated recrystallizations, the diketone refused to yield a sharp melting point, a fact of no small concern until it was discovered that for this compound a melting point was a poor criterion of purity. It appeared that below the apparent melting point the yellow diketone slowly changed to a white substance, presumably the enol, and the mixture gave a wide melting range. However, the crystallinity and constant specific rotation of the diketone were good tests of its homogeneity. Tautomerization to the enol, an unstable compound which on standing was transformed slowly to a gummy yellow material, was a consequence not only of mild pyrolysis but also of alumina chromatography. The initial diketone gave a quinoxaline which was different from the derivative formed by the enol or the diketone resulting from the latter. Thus the original diketone must have had the same configuration at C-5 as its desoxy precursor V, while ketonization of its enol had led to a C-5 epimer.

Most recently the first 6,7-diketonic diterpene, xanthoperol (VI), was isolated from a natural

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(1) Presented to the Symposium of the Chemical Society on "Recent Advances in the Chemistry of Terpenoid Compounds," Glasgow, Scotland, July 11–12, 1957.

(2) E. Wenkert and T. E. Stevens, THIS JOURNAL, **78**, 2318, 5627 (1956).

(3) E. Wenkert and B. G. Jackson, *ibid.*, **80**, 217 (1958).

(4) W. E. Parham, E. L. Wheeler and R. M. Dodson, *ibid.*, **77**, 1166 (1955).

(5) The structure and chemistry of the acid oxidation product will be reported at a later date.