was diluted with water, and a colored product which separated was collected and recrystallized from ethanol–water.

The 4-phenylazo derivative (VIa): yellow needles, mp 99–100°, lit.[2] 96°. *Anal.* Calcd for $C_{23}H_{20}ON_4$: N, 15.21. Found: N, 15.02.

The 4-(*p*-chlorophenylazo) derivative (VIb): yellow needles, mp 97–98° (dec). *Anal.* Calcd for $C_{23}H_{19}OClN_4$: N, 13.91. Found: N, 13.55.

The 4-(*p*-tolyl) derivative (VIc): yellow needles, mp 88–89° (dec). *Anal.* Calcd for $C_{24}H_{22}ON_4$: N, 14.65. Found: N, 14.57.

The 4-(*p*-anisyl) derivative (VId): yellow needles, mp 79–80° (dec). *Anal.* Calcd for $C_{24}H_{22}O_2N_4$: N, 14.06. Found: N, 13.92.

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The Nature of the Alkali-Induced Isomerization of 2,3,4,4a,6,6a-Hexahydro-6aα-hydroxy-4aβ,6β,7,9-tetramethyl-3-oxo-1H-5,11-dioxadibenzo[*a,d*]pentalene

D. S. DEORHA[1] AND PADMA GUPTA

Department of Chemistry, University of Rajasthan, Jaipur, India

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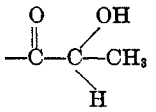
The base-catalyzed isomerization of the hydroxypentalene (III, R = H) appears to involve epimerization at the starred carbon atom. The view is substantiated by the fact that the γ-hydroxy acid (X, R = R_1 = H), derived from acid hydrolysis of carbethoxymethylhydroxypentalene (X, R = H, R_1 = C_2H_5), is converted to the γ-lactone (XII) on being heated with alkali and subsequent acidification. Structures III (R = H) and VIII (R = H), previously suggested for the hydroxypentalene and its alkali isomerized product, are confirmed by obtaining their methyl ethers from γ-hydroxy acid (X, R = R_1 = H) and the γ-lactone (XII), respectively, after subjecting these to appropriate reactions.

Ozonolysis[2a] of the grisene (I) (Chart I) in methyl acetate provided a product of structure II (R = CH_3) while oxidation of the former by osmium tetroxide furnished an alcohol (II, R = H). The later could be methylated to yield a product, identical with the former (II, R = CH_3). These oxidation products (II, R = CH_3, and II, R = H) were assigned[2b] configurations III (R = CH_3) and III (R = H), respectively. Dean, *et al.*,[2b] found that while the latter III (R = H) isomerized in warm alkali, the former (III, R = CH_3) was unaffected. This suggested that the hydroxyl group must be essential for this change. The new isomer gave a methyl ether different from but isomeric with the ozonolysis product (III, R = CH_3) and was so closely similar to the original alcohol (III, R = H) both in chemical and spectroscopic properties that the change was considered stereochemical rather than structural in origin. The view was substantiated and the center involved shown to be that starred in III (R = H) by the fact that neither compound IV nor V was affected by alkali.

An explanation[2b] of the above results was provided by the suggestion that bases would induce β elimination, thus reversing the cyclization which gave ring B of the alcohol (III, R = H). In the resulting glycol (VI, R = H), however, the presence of the tertiary alcoholic group allows a reverse aldol condensation so as to open the remaining heterocyclic ring generating, if only momentarily, an intermediate (VII). This is obviously not likely in compound VI (R = CH_3). There is now present a grouping



$$-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{\diagdown}}{\overset{OH}{\overset{\diagup}{C}}}-CH_3$$

in VII well known to be epimerizable by bases, so that, when the rings close again by reversal of the sequence, the more stable of the two structures (III, R = H, and VIII, R = H) would be favored. The benzene ring eclipses the methyl group at the atom starred in III (R = H) but the resulting repulsion is absent from the epimer (VIII, R = H), so that with VIII (R = H) as the structure of the new isomer, all the facts are satisfactorily explained.

That the isomerization of the alcohol (III, R = H) by alkali is due to the change in the position of methyl group at the starred carbon atom has now been demonstrated. The grisene[3] (IX) on oxidation by osmium tetroxide furnished a product which was similar in spectroscopic properties to the alcohol (III, R = H). By analogy with arguments used for assigning the configuration of dibenzopentalene (II, R = H) as III (R = H), the oxidation product of the grisene (IX) may have the configuration as in X (R = H; R_1 = C_2H_5).

On hydrolysis with sulfuric acid dihydrate, the difuranoid compound (X, R = H; R_1 = C_2H_5) yielded an acid (X, R = R_1 = H) indicating that OH and CH_2COOH in it do not exist on the same side of ring B. Had the two groups been in *cis* configuration, lactonization to form a γ-lactone would have been spontaneous. However, when the acid (X, R = R_1 = H) was warmed with alkali, acidification furnished a neutral solid showing infrared characteristics of a γ-lactone. This is possible only when alkali induces epimerization at the center starred in the acid (X) to place the $-CH_2COOH$ group on the side of the OH group with an opportunity for γ-lactonization. All attempts to obtain the acid (XI, R = R_1 = H) have been unsuccessful. The identical γ-lactone (XII) was obtained from the alkaline hydrolysis of compound X (R = H; R_1 = C_2H_5), followed by acidifica-

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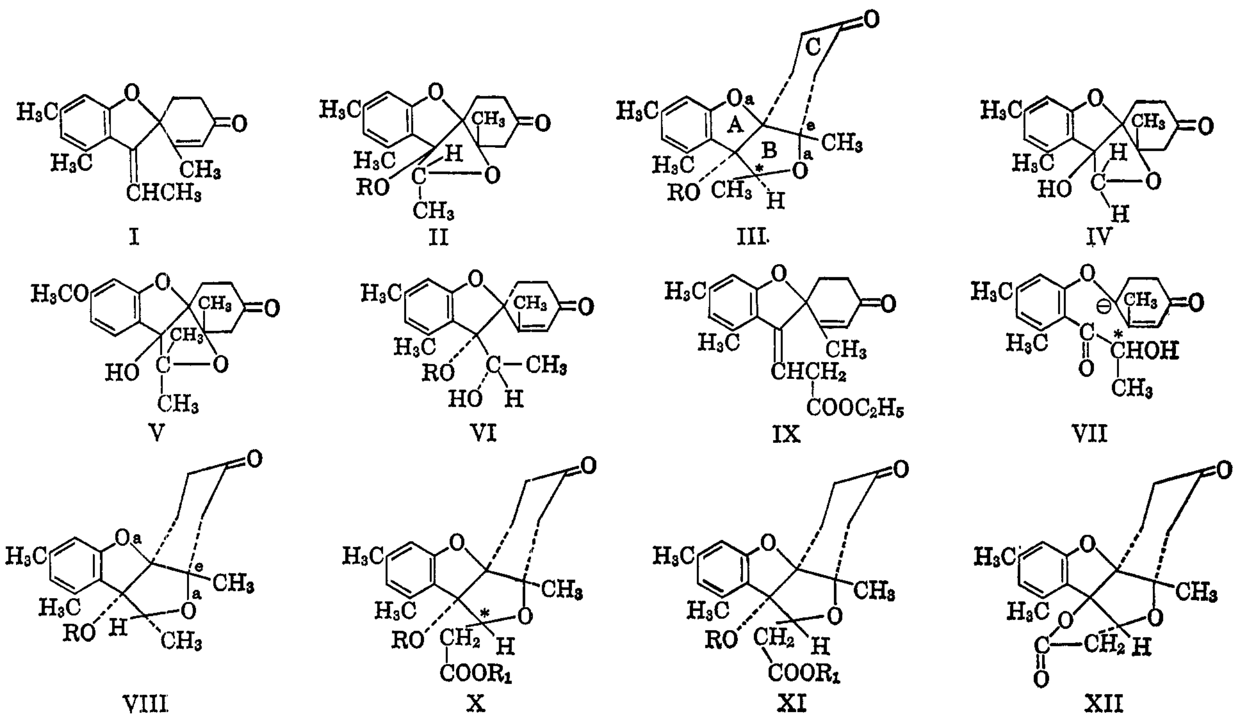
(1) Deceased.

(2) (a) F. M. Dean, T. Francis, and K. Manunapichu, *J. Chem. Soc.*, 4551 (1958); (b) F. M. Dean, D. S. Deorha, J. C. Knight, and T. Francis, *ibid.*, 327 (1961).

(3) D. S. Deorha, unpublished work.

CHART I



tion, showing that hydrolysis is accompanied by epimerization at the starred center.

Methylation of compound XI (R = H; R_1 = Na) in alkali by dimethyl sulfate afforded the ether (XI, R = R_1 = CH_3) which on hydrolysis provided the acid (XI, R = CH_3; R_1 = H). Its decarboxylation afforded a compound identical with one (VIII, R = CH_3) obtained from methylation of the alkali-isomerized product (VIII, R = H) of the alcohol (III, R = H), thus showing that in compound VIII, (R = H) the OH and CH_3 groups are *cis* in position. The demethylation of the methyl ether (VIII, R = CH_3) undertaken with a view to obtain the alcohol (VIII, R = H), however, resulted in intractable tars. The decarboxylation of compound X (R = R_1 = H) afforded a product identical with the one (III, R = H) obtained from the oxidation of the grisene (I) by osmium tetroxide, indicating that in the alcohol (III, R = H) the OH and CH_3 groups are in *trans* configuration. These results thus confirm the view[2b] that the two isomers (III and VIII) differ in the spatial position of methyl group at the starred carbon atom.

In regard to the base-catalyzed isomerization, it may be mentioned that it was not brought about by bases like pyridine or quinoline.

Experimental Section

2,3,4,4a,6,6a-Hexahydro-6aα-hydroxy-4aβ,7,9-trimethyl-6β-(carbethoxymethyl)-3-oxo-1H-5,11-dioxadibenzo[*a,d*]pentalene (X, R = H; R_1 = C_2H_5).—A mixture of 0.5 g of 3-(β-carbethoxyethylidene)-2′,4,6-trimethylgris-2′-en-4′-one,[3] 1 ml of pyridine, and 0.5 g of osmium tetroxide in 30 ml of ether was kept at room temperature for 2 days, when a dark crystalline complex separated. This was collected, washed with ether, and dried in air. A steady stream of sulfur dioxide was passed through a solution of the adduct in 70 ml of 80% ethanol containing 1.0 g of charcoal. After about 45 min, the solution was filtered and the violet filtrate was concentrated to about 10 ml under reduced pressure and then diluted with water. The product was isolated with ether which was washed with water, dried over anhydrous magnesium sulfate, and evaporated. The oily product eventually solidified and crystallized from aqueous ethanol affording 0.2 g (36%) of 4aβ,7,9-trimethyl-6β-(carbethoxymethyl)-5,11-dioxapentalene in colorless plates: mp 144°; λ_{max} 226, 278, 290 mμ (log ϵ 4.13, 3.51, 3.61); ν_{max} 3440 cm^{-1} (OH), 1745 cm^{-1} (ester), 1705 cm^{-1} (ketone).

Anal. Calcd for $C_{21}H_{26}O_6$: C, 67.34; H, 7.00. Found: C, 67.50; H, 7.13.

Its 2,4-dinitrophenylhydrazone separated from ethanol in yellow crystals, mp 220°.

Anal. Calcd for $C_{27}H_{30}N_4O_9$: N, 10.10. Found: N, 9.89.

γ-Lactone (XII) of 2,3,4,4a,6,6a-Hexahydro-6aα-hydroxy-4aβ,7,9-trimethyl-6α-(carboxymethyl)-3-oxo-1H-5,11-dioxadibenzo[*a,d*]pentalene.—Dioxadibenzopentalene (0.3 g) (X, R = H; R_1 = C_2H_5) was heated under reflux with 35 ml of 2 *N* sodium hydroxide and 35 ml of ethanol till the whole dissolved and a drop of the solution on dilution with water did not give turbidity. On dilution with water and acidification, the alkaline solution deposited a solid. This was collected into ether, washed with water, dried over anhydrous sodium sulfate, and recovered by evaporation of the solvent. The residue was taken up in benzene–light petroleum ether (1:1) and left stand for 2 days. The crystalline solid was collected and recrystallized from the same solvents giving 0.1 g (38%) of the γ-lactone in prisms: mp 162°; λ_{max} 286 mμ (log ϵ 3.51); ν_{max} 1786 cm^{-1} (γ-lactone), 1710 cm^{-1} (ketone) (no OH absorption).

Anal. Calcd for $C_{19}H_{20}O_5$: C, 69.50; H, 6.14. Found: C, 69.68; H, 6.25.

Its 2,4-dinitrophenylhydrazone separated from ethyl acetate in yellow needles, mp 210°.

Anal. Calcd for $C_{25}H_{24}N_4O_8$: N, 11.02. Found: N, 11.28.

2,3,4,4a,6a-Hexahydro-6aα-methoxy-4aβ,7,9-trimethyl-6α-(carbomethoxymethyl)-3-oxo-1H-5,11-dioxadibenzo[*a,d*]pentalene (XI, R = R_1 = CH_3).—The preceding lactone (0.5 g) was dissolved in 3 ml of 2 *N* sodium hydroxide solution by warming. To this solution was added 0.5 g of dimethyl sulfate, cooling with water; the mixture was allowed to stay at room temperature for 1 hr. The separated organic material was taken into ether. The ethereal layer was washed with 1 *N* sodium hydroxide and with water, and dried over anhydrous magnesium sulfate. On removing ether, the residue was crystallized from aqueous ethanol to give 0.2 g (35%) of plates: mp 154°; λ_{max} 284, 290 mμ (log ϵ 3.48, 3.52); ν_{max} 1745 cm^{-1} (ester), 1710 cm^{-1} (ketone).

Anal. Calcd for $C_{21}H_{26}O_6$: C, 67.34; H, 7.00. Found: C, 67.16; H, 7.15.

Its 2,4-dinitrophenylhydrazone separated from ethanol in orange-yellow crystals, mp 204°.

Anal. Calcd for $C_{27}H_{30}N_4O_9$: N, 10.10. Found: N, 10.31.

2,3,4,4a,6,6a-Hexahydro-6aα-methoxy-4aβ,7,9-trimethyl-6α-carboxymethyl-3-oxo-1H-5,11-dioxadibenzo[*a,d*]pentalene (XI, R = CH_3; R_1 = H).—The foregoing methoxypentalene (0.5 g) was heated under reflux with 10 ml of 2 *N* sodium hydroxide solution till it dissolved. On cooling and acidification, the alkaline solution deposited a solid which was isolated with ether in the usual way. From ethanol, 0.15 g. (31%) of colorless crystals separated, mp 184°.

Anal. Calcd for $C_{20}H_{24}O_6$: C, 66.64; H, 6.71. Found: C, 66.80; H, 6.54.

2,3,4,4a,6,6a-Hexahydro-6aα-methoxy-4aβ,6α,7,9-tetramethyl-3-oxo-1H-5,11-dioxadibenzo[*a,d*]pentalene (VIII, R = CH_3).—A mixture of 0.5 g of the preceding carboxymethylpentalene, 0.1 g of copper bronze, and 4 ml of quinoline was kept at 220° for 15 min, cooled, diluted with ether, and filtered. Quinoline was removed by means of 2 *N* hydrochloric acid and acidic impurities by aqueous sodium bicarbonate, whereafter evaporation of the dried (anhydrous sodium sulfate) solution gave a solid which crystallized from aqueous ethanol affording 0.1 g (23%) of 2,3,4,4a,6,6a-hexahydro-6aα-methoxy-4aβ,6α,7,9-tetramethyl-3-oxo-1H-5,11-dioxadibenzo[*a,d*]pentalene in colorless needles, mp 159° undepressed on admixture with the compound obtained from methylation of the alkali isomerized product of 2,3,4,4a,6,6a-hexahydro-6aα-hydroxy-4aβ,6β,7,9-tetramethyl-3-oxo-1H-5,11-dioxadibenzo[*a,d*]pentalene,[2b] ν_{max} 1715 cm^{-1} (ketone).

Anal. Calcd for $C_{19}H_{24}O_4$: C, 72.10; H, 7.64. Found: C, 72.24; H, 7.52.

Its 2,4-dinitrophenylhydrazone crystallized from ethanol in yellow needles, mp 224° (lit.[2b] mp 224°).

Anal. Calcd for $C_{25}H_{28}N_4O_7$: N, 11.30. Found: N, 11.07.

2,3,4,4a,6,6a-Hexahydro-6aα-hydroxy-4aβ,7,9-trimethyl-6β-carboxymethyl-3-oxo-1H-5,11-dioxadibenzo[*a,d*]pentalene (X, R = R_1 = H).—A mixture of 0.5 g of the 4aβ,7,9-trimethyl-6aβ-carbethoxymethyl-5,11-dioxapentalene (X, R = H; R_1 = C_2H_5) and 20 ml of sulfuric acid dihydrate was heated at 60° for 15 min. The cooled and diluted mixture was extracted with ether. Removal of ether from the dried (anhydrous sodium sulfate) extract furnished a solid which separated from aqueous methanol affording 0.2 g (43%) of 6β-carboxymethylpentalene (X, R = R_1 = H) in microscopic crystals, mp 206°.

Anal. Calcd for $C_{19}H_{22}O_6$: C, 65.89; H, 6.40. Found: C, 65.70; H, 6.53%.

The acid (100 mg) on heating under reflux for 1 hr with 15 ml of methanol and 15 ml of 1 *N* sodium hydroxide, cooling, and acidification furnished a solid which supplied 0.02 g of a neutral compound from benzene–light petroleum ether (1:1) in prisms. This was identical with the γ-lactone (XII) described above.

2,3,4,4a,6,6a-Hexahydro-6aα-hydroxy-4aβ,6β,7,9-tetramethyl-3-oxo-1H,5,11-dioxadibenzo[*a,d*]pentalene (III, R = H).—6aβ-Carboxymethyl-3-oxo-1H-5,11-dioxadibenzo[*a,d*]pentalene (0.25 g) was decarboxylated under the condition described above for the methyl ether of its isomer. The product crystallized from aqueous methanol to provide 48 mg (21%) of 4aβ,6β,7,9-tetramethyl-5,11-dioxadipentalene in plates: mp 151°, λ_{max} 284 mμ (log ϵ 3.50), ν_{max} 3436 cm^{-1} (OH), 1718 cm^{-1} (ketone).

This was identical with that[2b] obtained by osmium tetroxide oxidation of 3-ethylidene-2′,4,6-trimethylgris-2′-en-4′-one.

Anal. Calcd for $C_{18}H_{22}O_4$: C, 71.53; H, 7.33. Found: C, 71.40; H, 7.49.

Its 2,4-dinitrophenylhydrazone separated from ethanol in yellow needles, mp 220° (lit mp 221°).[2b]

Anal. Calcd for $C_{24}H_{26}N_4O_7$: N, 11.61. Found: N, 11.80.

2,3,4,4a,6,6a-Hexahydro-6aα-methoxy-4aβ,6β,7,9-tetramethyl-3-oxo-1H-5,11-dioxadibenzo[*a,d*]pentalene (III, R = CH_3).—The preceding alcohol (0.1 g) was methylated according to the procedure reported by Dean, *et al.*[2b] The product crystallized from methanol providing 40 mg (36%) of 6aα-methoxy-5,11-dioxapentalene in prisms: mp 128° (lit.[2b] mp 128°); λ_{max} 282, 290 mμ (log ϵ 3.48, 3.51).

Anal. Calcd for $C_{18}H_{21}O_3OMe$: C, 72.10; H, 7.64; OMe, 9.82. Found: C, 72.25; H, 7.80; OMe, 9.60.

This was also obtained by decarboxylation of the substance X (R = CH_3; R_1 = H) according to the procedure described for the preparation of compound VIII (R = CH_3) from the acid (XI, R = CH_3; R_1 = H).

The 2,4-dinitrophenylhydrazone crystallized from ethanol in yellow needles, mp 211°.[2b]

Anal. Calcd for $C_{25}H_{28}N_4O_7$: N, 11.30. Found: N, 11.11.

2,3,4,4a,6,6a-Hexahydro-6aα-methoxy-4aβ,7,9-trimethyl-6β-carbethoxymethyl-3-oxo-1H-5,11-dioxadibenzo[*a,d*]pentalene (X, R = CH_3; R_1 = C_2H_5).—A mixture of 0.3 g of hydroxypentalene (X, R = H; R_1 = C_2H_5), 0.9 g of silver oxide, and 6 ml of methyl iodide in dimethylformamide was shaken for 60 hr. On filtration, the residue was washed with ether–dimethylformamide (1:1). The washings and the filtrate were combined and diluted with ether. The organic layer was washed with aqueous potassium cyanide (to remove silver salts) and water, and dried over anhydrous magnesium sulfate. Evaporation of ether left an oil which crystallized from ethanol affording 0.1 g (32%) of 6aα-methoxy-4aβ,7,9-trimethyl-6β-carbethoxymethyl-5,11-dioxapentalene in prisms: mp 124°; λ_{max} 282, 288 mμ (log ϵ 3.42, 3.49); ν_{max} 1742 cm^{-1} (ester), 1705 cm^{-1} (ketone).

Anal. Calcd for $C_{22}H_{28}O_6$: C, 68.01; H, 7.26. Found: C, 68,20; H, 7.10.

Its 2,4-dinitrophenylhydrazone separated from ethanol in yellow crystals, mp 210°.

Anal. Calcd for $C_{28}H_{32}N_4O_9$: N, 9.86. Found: N, 9.63.

2,3,4,4a,6,6a-Hexahydro-6aα-methoxy-4aβ,7,9-trimethyl-6β-(carboxymethyl)-3-oxo-1H-5,11-dioxadibenzo[*a,d*]pentalene (X, R = CH_3, R_1 = H).—The preceding methoxy ester (0.25 g) (R = CH_3; R_1 = C_2H_5) in 10 ml of boiling ethanol was heated for 30 min with 3 ml of 2 *N* sodium hydroxide. The cooled and diluted solution was acidified by hydrochloric acid to furnish a solid which was taken into ether and thence into aqueous sodium bicarbonate. Acidification of the bicarbonate extract furnished a product which crystallized from methanol to give 80 mg (34%) of plates, mp 164°.

Anal. Calcd for $C_{20}H_{24}O_6$: C, 66.64; H, 6.71. Found: C, 66.40; H, 6.83.

An identical compound was formed if the ester X (R = CH_3; R_1 = C_2H_5) was hydrolyzed by sulfuric acid dihydrate according to the procedure described in the preparation of the acid (X, R = R_1 = H).

Its 2,4-dinitrophenylhydrazone crystallized from ethanol in yellow needles, mp 234°.

Anal. Calcd for $C_{26}H_{28}N_4O_9$: N, 10.36. Found: N, 10.15.

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