[CONTRIBUTION FROM THE PHARMACEUTICAL RESEARCH INSTITUTE, MEDICAL SCHOOL, KEIO-GIJUKU UNIVERSITY]

SANTONIN AND RELATED COMPOUNDS. V. ACETOLYSIS OF 5-BROMO-3-KETO-9-METHYL-Δ^4-OCTAHYDRONAPHTHALENE[1, 2]

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The original objective of the investigation outlined in this paper was the introduction of oxygenated functions at the 5-position in the 9-methyl-3-decalone system. Previous studies in this Laboratory have established (1) that 3-keto-9-methyl-Δ^4-octahydronaphthalene (I) (2) is brominated with N-bromosuccinimide at the 5-position to give II. In the hope that the bromine atom in the 5-bromoketone (II) would be normally replaced by the acetoxyl group, reaction of II with potassium acetate was attempted. After this work had been initiated, Sondheimer, *et al.* (3) and Fieser and Romero (4) simultaneously reported that 6-bromo-Δ^4-3-ketosteroids on treatment with potassium acetate in acetic acid gave, in a low yield, the 2-acetoxyketone, the only product isolated. From these results the initially planned reaction of II was considered unpromising, but it was to our interest to compare the reported acetolysis of steroids with a similar reaction of the simple analog, II.

The crude 5-bromoketone (II), which is unstable even at room temperature, was allowed to react with anhydrous potassium acetate in acetic acid at reflux temperature. The product, after acidic material was separated by alkali wash, was subjected to chromatographic separation on alumina. Each of the main fractions exhibited two ultraviolet absorption maxima in about the same positions (240–248 mμ, 280–281 mμ), being attributed to the Δ^4- and $\Delta^{4,5}$-3-keto hydronaphthalene. Complicated mixtures of 2,4-dinitrophenylhydrazones, obtained from the individual fractions, invariably yielded the extended conjugated dienone (III). It was found that this hydrazone exists in three modifications, but that these are merely polymorphous was shown by mixture melting point determinations and by the ready conversions of two of the forms into the third. In addition to III, the 2,4-dinitrophenylhydrazone of 3-keto-9-methyl-$\Delta^{1,4}$-hexahydronaphthalene (IV), reported by Woodward and Singh (5a), was isolated in a trace amount from only one fraction. It is notable that the cross-conjugated dienone (IV), detected in this acetolysis, was not obtained from 2,4-dibromo-*trans*-9-methyl-3-decalone[3] either with potassium acetate or collidine (1).

In the above separation of the neutral product, the anticipated 5-acetoxyketone (V) was not detected. It has been reported (6) that the 6-acetoxy-Δ^4-3-

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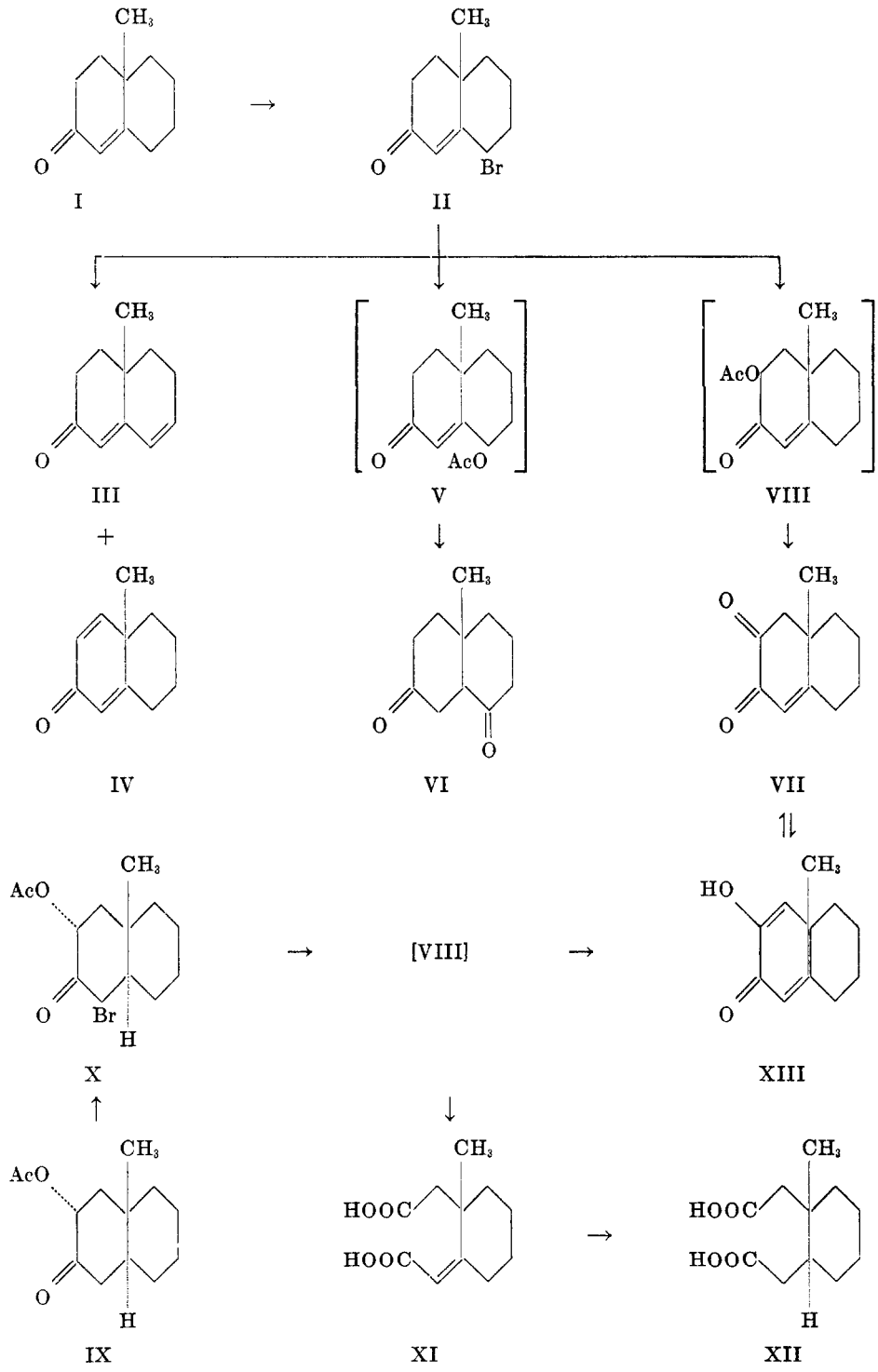
[2] We wish to thank Mr. Ogura in our Laboratory for aid in this experimentation.

[3] After this manuscript had been submitted for publication, it was found that "*cis*-9-methyl-3-decalone" and its transformation products, described in the reference 1, were *trans*-fused, which will be published in the following paper of this series. The present paper has been rewritten in part to take it into account.


CH3
O
I
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III
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VII
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XI
XII
IX

ketosteroids are converted to the 3,6-diketone *via* double bond migration either with acid and alkali. On similar treatment with alkali, some fractions of the neutral product gave the expected 3,5-diketone (VI) (corresponding to the 3,6-diketosteroids), along with III, both of which were isolated as 2,4-dinitrophenylhydrazones. However, the same fractions failed to give VI on acid treatment under the conditions reported for the above 6-acetoxy-ketosteroids. The structure (VI) was assigned for the 3,5-diketone on the basis of the properties (insolubility in alkali and negative test with ferric chloride) and the analytical figures of its bis-2,4-dinitrophenylhydrazone.

The acidic material, separated from the original product, was reacted with hydroxylamine in alkaline solution to give a small amount of a glyoxime of 2,3-diketo-9-methyl-Δ^4-octahydronaphthalene (VII), the structure of which was proved as described below. The formation of the Δ^4-2,3-diketone from II *via* air oxidation is analogous to the result reported (1) that 4-bromo-*trans*-9-methyl-3-decalone[3] with the acetate ion gave the corresponding 2,3-diketone, together with the predominant 2-acetoxyketone[3] (IX). From this it is evident that on acetolysis, the Δ^4-2,3-diketone (VII) is derived from the 2-acetoxyketone (VIII), the possible primary product.

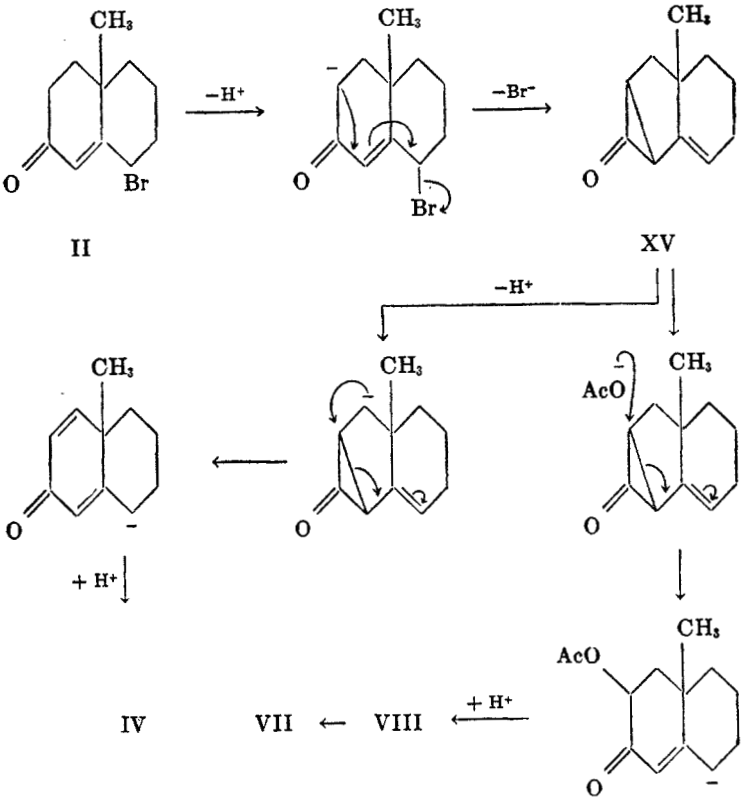
Because of the crudeness of the 5-bromoketone used as starting material, it is necessary to consider the possibility of the formation of IV and VII from the probable impurities in II. If it were so, reaction of the crude II with γ-collidine, which has been reported (1) to give the extended conjugated dienone (III) as the sole product, should yield IV, together with III. Reëxamination of the reaction of II with collidine showed that an oily product formed a complicated mixture of 2,4-dinitrophenylhydrazones, and besides the hydrazone of the predominant III, two unknown derivatives were chromatographically separated, neither of which was identical with the hydrazone of IV. Apparently this demonstrated the formation of IV and VII from II in the acetolysis.

It has been reported (3, 7) that 6-bromo-Δ^4-3-ketosteroids are converted, in satisfactory yield, to the 3,6-diketone on reacting with hydrochloric acid in boiling methanol. On application of this method, the 5-bromoketone (II) gave the 3,5-diketone (VI) in poor yield, and in addition, the Δ^4-2,3-diketone (VII) was isolated as a glyoxime. II with boiling methanol alone gave almost the same result.

In view of the establishment of the structure VII, an alternative route to the Δ^4-2,3-diketone was explored. The acetoxyketone (IX), in which the position of the acetoxyl group has been well established (1), was used as the starting material for this purpose. It was recently reported (8) that 2β-hydroxytestosterone diacetate was epimerized to the 2α-hydroxyl ketone by refluxing the former in potassium acetate-acetic acid solution. Analogously it may be assumed that the acetoxyl group in IX possesses a stable equatorial conformation, and thus, is *trans* to the angular methyl group. Bromination and subsequent dehydrobromination of IX resulted in the formation of an unhomogeneous oil, from which the expected ketone (VIII) could not be isolated as crystalline derivative. Consequently, the crude oily mixture was treated with alkali under the conditions employed for the conversion of the 2-acetoxy ketone (IX) to the corresponding

2,3-diketone (1). From the alkali-soluble fraction of the product, a small amount of Δ^4-2,3-diketone (VII) was isolated in a crystalline state, which formed the glyoxime identical with that obtained from II on acetolysis. In addition to VII, an unsaturated dibasic acid (XI) was obtained which, on catalytic hydrogenation, gave the known saturated *trans*-diacid[3] (XII) (1). VII exhibited ultraviolet absorption maxima at 241 mμ (ϵ 6,180) and 300 mμ (ϵ 5,330), presumably demonstrating the large contribution of the enol form (XIII) to the molecular structure (9).

An explanation has been offered by Fieser and Romero (4) for the formation of the 2-acetoxyketone from 6-bromo-Δ^4-3-ketosteroids on acetolysis, involving the possible formation of the 2-bromoketone *via* migration of the bromine atom. If this explanation is applied to the present reaction of II with potassium acetate, it may be assumed that the cross-conjugated dienone (IV) would be derived from the corresponding 2-bromoketone. In view of the reported result (1) that IV was not obtained from the 2,4-dibromo-3-ketone, this assumption seems unlikely. This opinion finds a support in the recently reported fact (10) that on treatment with the acetate ion 2-bromo-Δ^4-androstene-3,17-dione gave the 2α-acetoxy-androstene-3,17-dione in somewhat lower yield (13%) than that (20%) from the 6-bromo isomer. On the basis of the reaction mechanism involving a cyclopropane intermediate suggested by Loftfield (11), a possible explanation is proposed for the formation of IV and VII from II as follows:



It may be assumed that acetolysis of II proceeds in part through a concerted mechanism,[4] leading to a cyclopropane intermediate (XV). Extraction of a proton at the 1-position from XV by the acetate ion would lead to the cross-conjugated dienone (IV) in a prototropic rearrangement. When an attack by the acetate ion is on the 2-position in XV, the Δ^4-2,3-diketone (VII) would be formed *via* VIII.

EXPERIMENTAL[5]

5-Bromo-3-keto-9-methyl-Δ^4-octahydronaphthalene (II). This was prepared by a slight modification of the method reported (1). 3-Keto-9-methyl-Δ^4-octahydronaphthalene (5 g., I) (2) was treated with 6 g. (1.2 moles) of N-bromosuccinimide in the presence of 0.9 g. of benzoyl peroxide in 140 cc. of boiling carbon tetrachloride. II was also obtained by the bromination of I with bromine (1.1 moles) in carbon tetrachloride by the usual procedure in quantitative yield. Because it was unstable even at room temperature, the product was used for the following step without purification.

Reaction of 5-bromo-3-keto-9-methyl-Δ^4-octahydronaphthalene (II) *with potassium acetate.* To a solution of the 5-bromoketone (II), prepared from 5.0 g. of I, in 80 cc. of glacial acetic acid was added 9.0 g. of anhydrous potassium acetate, and the mixture was refluxed for 4 hours. Potassium bromide (1.9 g., 80%) was filtered off, and the filtrate was concentrated under reduced pressure. After the addition of water, the residue was made alkaline and extracted with ether.

(a) *Neutral products.* The ether extract was washed with water, dried, and evaporated giving a brown viscous oil (4.76 g.). The oil formed a small amount of a semicarbazone, which on repeated recrystallizations from ethanol gave prisms, m.p. 203°, undepressed on admixture with the semicarbazone of 3-keto-9-methyl-$\Delta^{4,5}$-hexahydronaphthalene (III), prepared by the reported method (1). The neutral oil (3.0 g.) was chromatographed on 30 g. of alumina. Representative one of several runs was shown:

Fraction	Solvent (cc.)	Weight, mg.	λ_{max}^{EtOH} mμ (ε)
1–2	Benzene (35)	130	———
3	Benzene (10)	950	248 (11,560), 281 (7,020)
4	Benzene (10)	560	240 (14,700), 281 (6,600)
5	Benzene (10)	140	244 (12,300), 281 (7,840)
6–7	Benzene (30)	115	240 (8,820), 281 (4,800)
8 9	Benzene-chloroform (3:1) (20)	30	———
10–11	Benzene-chloroform (1:1) (20)	40	———
12–14	Chloroform (30)	55	232 (10,280), 275 (infl.)
15–18	Chloroform (50)	50	———
19	Chloroform-methanol (1:1) (20)	405	227 (11,000), 281 (3,900)

The residue (200 mg.) of fraction 3 formed 270 mg. of 2,4-dinitrophenylhydrazone, m.p. 165–185°, which was chromatographed on 5.0 g. of alumina. Each fraction was eluted with 10 cc. of the solvent: Fractions i–vii, carbon tetrachloride; fractions vii-xix, carbon tetrachloride-chloroform (1:1); fraction xx, chloroform.

Fraction i gave 180 mg. of red crystals, m.p. 180–190°, which on recrystallization from

[4] The concerted mechanism for the conversion of II to XV was suggested by a referee, to whom the authors wish to express their appreciation.

[5] All temperatures are uncorrected. Microanalyses were by Miss C. Shibuya, and ultraviolet measurements by Miss M. Suzuki, both of this school.

ethanol afforded red platelets, m.p. 198–200°, the most stable form of 2,4-dinitrophenylhydrazone of III.

Anal. Calc'd for $C_{17}H_{18}N_4O_4$: C, 59.64; H, 5.30; N, 16.37.
Found: C, 59.29; H, 5.21; N, 16.16.

Fractions ii–iii, which were combined, yielded a trace amount of red crystals, m.p. 186–191°, which was recrystallized from ethanol, giving dark red platelets, m.p. 193–195°, the second form of the hydrazone of III. It showed no depression of the m.p. on admixture with the same derivative of III obtained from II by collidine treatment.

Anal. Calc'd for $C_{17}H_{18}N_4O_4$: C, 59.64; H, 5.30; N, 16.37.
Found: C, 59.64; H, 5.82; N, 16.16.

Fractions iv–vii, combined, yielded a trace amount of red crystals, m.p. 175–180°, the third form of the hydrazone of III, which on recrystallization from ethanol gave dark red platelets, m.p. 180–183°. The latter two modifications showed no depression of the m.p. on admixture with the stable form, m.p. 198–200°, and were readily converted to the stable one by prolonged refluxing in ethanol or by seeding.

Fractions viii–xix gave no crystalline products. Fraction xx gave a trace amount of orange-yellow crystals which were not investigated.

To the residue (360 mg.) from fraction 3 in 13 cc. of methanol was added a solution of 290 mg. of potassium hydroxide in 12 cc. of the same solvent, and the whole was refluxed for one hour. The reaction mixture was evaporated under reduced pressure, acidified, and extracted with ether. The ether extract was washed with aqueous sodium bicarbonate, then with 20% sodium hydroxide, and dried over sodium sulfate. Evaporation of the solvent left an oil (260 mg.), λ_{max}^{EtOH} 248 mμ (ε 6,000), 280 mμ (ε 3,350), which gave 60% yield of a bis-2,4-dinitrophenylhydrazone of 3,5-diketo-9-methyldecalin (VI), as orange-yellow crystals, m.p. 235–245°. Recrystallization from a mixture of chloroform and ethanol or benzene alone afforded orange-yellow prisms, m.p. 252–254°.

Anal. Calc'd for $C_{23}H_{24}N_8O_8$: C, 51.11; H, 4.44; N, 20.74.
Found: C, 51.17; H, 4.50; N, 20.73, 20.72.

The mother liquor of recrystallization gave only a deep red tar, from which no crystals could be separated.

To a solution of the residue (390 mg.) from fraction 3 in 14 cc. of methanol was added dropwise 0.3 cc. of conc'd hydrochloric acid with cooling. The solution was refluxed for 5 hours. The reaction mixture was evaporated under reduced pressure, and after the addition of aqueous sodium carbonate, was extracted with ether. Washing with water, drying, and evaporation of the ether extract gave an oil, which was converted to 310 mg. of 2,4-dinitrophenylhydrazone, m.p. 110–120°. The hydrazone mixture was chromatographed on 6 g. of alumina. From the fraction eluted with carbon tetrachloride, two kinds of red platelets, m.p. 183–185° and m.p. 191–194° (both after crystallization from ethanol), undepressed with the corresponding derivatives of the dienone (III), were obtained.

The residue (100 mg.) from fraction 4 gave 100 mg. of a 2,4-dinitrophenylhydrazone mixture, which was chromatographed on 3 g. of alumina as described above. The fraction eluted with carbon tetrachloride afforded the hydrazone of III, m.p. and mixture m.p. 190–194° (after crystallization from ethanol). Evaporation of the fraction eluted with benzene left 8 mg. of red crystals, m.p. 130–173°, which were recrystallized from ethanol giving a few mg. of red platelets, m.p. 133–135°. It showed no depression of the m.p. on admixture with the same derivative, m.p. 133–135°, of 3-keto-9-methyl-$\Delta^{1,4}$-hexahydronaphthalene (IV), prepared by the method of Woodward and Singh (5a). Reported, m.p. 127–129° (5a) and m.p. 133–135° (5b).

By using the procedure described for fraction 3, the residue (560 mg.) of the fraction 4 was treated with 450 mg. of potassium hydroxide to give 290 mg. of a neutral oil, λ_{max}^{EtOH} 240 mμ (ε 7,650), 281 mμ (ε 3,400). The oil (275 mg.) gave 330 mg. of a 2,4-dinitrophenylhydrazone mixture, m.p. 130–168°, which on repeated recrystallizations from a mixture of ethanol and chloroform afforded bis-2,4-dinitrophenylhydrazone, m.p. and mixture m.p. 252–254°, of VI.

A tarry residue from the mother liquor of the recrystallizations was chromatographed on alumina and the elution with carbon tetrachloride gave the 2,4-dinitrophenylhydrazone, m.p. and mixture m.p. 190–194°, of III (after crystallization from ethanol).

In the above chromatographic separations, there must be considered the possibility that the acetoxyl group in V may be secondarily eliminated to yield III during absorption on alumina. To examine this, the residue (140 mg.) from fraction 5 as a benzene solution was allowed to stand with alumina (5 g.) for 3 days. The elution with the same solvent gave 105 mg. of an oil, showing λ_{max}^{EtOH} 240 mμ (ε 10,800), 280 mμ (ε 7,600), almost identical with those of the original fraction. The elution with methanol gave 20 mg. of an oil, λ_{max}^{EtOH} 240 mμ (ε 3,800), 280 mμ (ε 1,600). This result excluded the above possibility.

The combined residues (125 mg.) from fractions 8–11 were treated with potassium hydroxide in methanol as described above. The neutral product (65 mg.) afforded 95 mg. of a 2,4-dinitrophenylhydrazone mixture, m.p. 135–142°, which on recrystallization from ethanol gave a bisdinitrophenylhydrazone, m.p. and mixture m.p. 252–255° of VI. The mother liquor of the recrystallization gave the 2,4-dinitrophenylhydrazone, m.p. and mixture m.p. 193–195°, of III after chromatography.

The alkali-soluble material obtained from each fraction after alkali hydrolysis showed a violet-brown coloration with ferric chloride, showing the presence of an α-diketone (VII). The reaction product of this oil with hydroxylamine showed a brown coloration with a nickel salt, but a glyoxime could not be isolated as crystals.

(b) *Acidic product.* The alkali solution, separated from the original product of II, was acidified and extracted with ether. The ether extract was washed with aqueous sodium bicarbonate, and then with water, and dried over sodium sulfate. Evaporation of the ether left an oil showing a violet-brown coloration with ferric chloride. The oil (170 mg.), combined in several runs, was added to a solution of 230 mg. of hydroxylamine hydrochloride and 300 mg. of potassium hydroxide in 2 cc. of ethanol-water (1:1), and allowed to stand for 5 days. After acidification, the reaction mixture was concentrated under reduced pressure, diluted with water, and extracted with ether. Drying and evaporation of the ether extract gave 55 mg. of an oil which, upon addition of a small amount of ethanol, partly crystallized out. Recrystallization from ethanol gave a glyoxime of 2,3-diketo-9-methyl-Δ^4-octahydronaphthalene (VII), as colorless prisms, m.p. 218–220°. It showed a pink coloration with a nickel salt. There was no depression of the m.p. on admixture with the same derivative of VII prepared by another method described below.

Anal. Calc'd for $C_{11}H_{16}N_2O_2$: C, 63.44; H, 7.74; N, 13.45.

Found: C, 63.11; H, 7.69; N, 13.30.

Reaction of 5-bromo-3-keto-9-methyl-Δ^4-octahydronaphthalene (II) *with methanolic hydrochloric acid.* The crude 5-bromoketone (II), prepared from 0.5 g. of I, was dissolved in 22 cc. of methanol containing 0.6 cc. of conc'd hydrochloric acid. The solution was gently refluxed for 5 hours, and the solvent was evaporated under reduced pressure. The residue was diluted with water and extracted with ether, and the ether extract was washed with aqueous bicarbonate, twice with aqueous sodium hydroxide, and dried. Evaporation of the ether left an oil, which was distilled to give a fraction, b.p. 100–155° at 10 mm. Redistillation gave 295 mg. of a pale-yellow oil, b.p. 110–135° at 3 mm., forming a 2,4-dinitrophenylhydrazone, which on recrystallization from glacial acetic acid gave the bis-hydrazone, m.p. and mixture m.p. 253–255°, of VI in 26% yield (from II).

The alkali solution was acidified and extracted with ether, and the ether extract was dried and evaporated. The residue was distilled to give 100 mg. of an oil, b.p. 135–145° at 8 mm. This oil, exhibiting positive ferric chloride test, gave 5–8 mg. of the glyoxime, m.p. and mixture m.p. 220° of VII in the same manner as described above.

Reaction of 5-bromo-3-keto-9-methyl-Δ^4-octahydronaphthalene (II) *with methanol alone.* A solution of the crude 5-bromoketone (II), prepared from 0.5 g. of I, in 24 cc. of methanol was refluxed for 5 hours, and worked up as described in the preceding experiment. The neutral oil (46% from I), b.p. 132–134° at 6 mm., obtained after two distillations, gave 65%

yield of the bis-hydrazone, m.p. 240–245° of VI. Recrystallization from benzene raised the m.p. to 252–254° (mixture m.p.)

The mother liquor of the recrystallization gave only a deep red tar, from which no crystalline derivative was isolated after chromatography. The alkali-soluble material showed a positive ferric chloride test, but the glyoxime of VII was not isolated.

Reaction of 5-bromo-3-keto-9-methyl-Δ^4-octahydronaphthalene (II) *with γ-collidine.* The reaction was carried out exactly as reported (1). The black oily product was distilled to give a pale yellow oil (42%), b.p. 109–116° at 4 mm., which (400 mg.) was chromatographed on alumina (0.8 g.; 19 cm.). Petroleum benzine eluted 230 mg. of a yellow oil (II), forming the 2,4-dinitrophenylhydrazone, m.p. 183° and m.p. 193–195° (after recrystallization from ethanol). Benzene eluted 50 mg. of an oil, λ_{max}^{EtOH} 240 mμ, 283 mμ, which formed two 2,4-dinitrophenylhydrazones; deep red leaflets, m.p. 182–184°, and deep red prisms, m.p. 198° (both after recrystallization from ethanol). Both hydrazones showed obvious depression of the m.p. on admixture with the same derivative of III. Ethanol eluted 40 mg. of an oil, forming the same hydrazones as were obtained from the benzene elution.

2-Acetoxy-trans-9-methyl-3-decalone (IX). This was prepared from 4-bromo-*trans*-9-methyl-3-decalone (12) according to the method reported (1). The product was a colorless oil, b.p. 135–143° at 5 mm. Reported (1), boiling until 138° at 5 mm. After storage of the oil in the refrigerator for a week, a small amount (2%) of crystals, m.p. 130–140°, separated. Recrystallization from ethanol gave colorless prisms, m.p. 140°, analytical data of which showed it to be one form of IX.

Anal. Calc'd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99.
Found: C, 69.46; H, 8.94.

The *semicarbazone*, obtained in 88% yield from the oil, was recrystallized from ethanol to give prisms, m.p. 187–190°. Reported (1), m.p. 177–178°.

Anal. Calc'd for $C_{14}H_{23}N_3O_3$: C, 59.78; H, 8.24; N, 14.93.
Found: C, 59.99; H, 8.39; N, 15.31.

2,3-Diketo-9-methyl-Δ^4-octahydronaphthalene (VII). To a solution of 1.68 g. of the above 2-acetoxyketone (IX) in 30 cc. of chloroform was added, with stirring, a solution of 1.4 g. of bromine in 10 cc. of the same solvent during 20 minutes and the stirring was continued for additional one hour. The reaction mixture was evaporated under reduced pressure leaving a pale yellow oil (X, quantitative). A solution of the crude bromide in 10 cc. of purified γ-collidine (b.p. 167–170°) was refluxed for 20 minutes, in a nitrogen atmosphere, producing 1.6 g. (quantitative) of collidine hydrobromide. The reaction mixture was worked up in the usual manner (1), and the dark-colored, oily product (1.5 g.), containing VIII, gave no crystalline derivative with ketone reagents. The oil was dissolved in a solution of 0.6 g. of potassium hydroxide in 15 cc. of methanol-water (2:1), and allowed to stand at room temperature for 30 hours. The reaction mixture was acidified and concentrated under reduced pressure, and the residue was extracted with ether. The ether solution was washed with aqueous sodium hydroxide, dried and evaporated, leaving 0.55 g. of a neutral oil which was not investigated. The alkali extract was acidified and extracted with ether. The ether extract was washed with aqueous bicarbonate, dried and evaporated, leaving 0.22 g. of a viscous oil which partly solidified on standing. Crude crystals, m.p. *ca* 138° (60 mg., 4% from IX), separated by addition of a small amount of ethanol, were crystallized from the same solvent to give colorless prisms, m.p. 145–146.5°, λ_{max}^{EtOH} 241 mμ (ε 6,810), 300 mμ (ε 5,330).

Anal. Calc'd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92.
Found: C, 73.95; H, 7.92.

This sample gave blue-violet coloration with ferric chloride. By the procedure described above, the oil, separated from crystals, formed a small amount of the glyoxime, m.p. 220°, showing a pink coloration with a nickel salt.

2-Methyl-2-carboxymethylcyclohexylidene-1-acetic acid (XI). The bicarbonate solution described in the preceding experiment was acidified and extracted with ether. Drying and evaporation of the ether extract gave 300 mg. of a viscous oil, which partly solidified on

standing. One crystallization from ethyl acetate gave 45 mg. (2.7% from IX) of the unsaturated dicarboxylic acid (XI), m.p. 175–178°, which was further recrystallized from the same solvent to colorless prisms, m.p. 196°. This sample decolorized permanganate in sodium carbonate solution.

Anal. Calc'd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60.
Found: C, 62.15; H, 7.69.

Catalytic hydrogenation of the sample over palladium-carbon gave 1-methyl-*trans*-cyclohexane-1,2-diacetic acid (XII), m.p. 195–196° (after recrystallization from ethyl acetate), undepressed with the sample of XII,[3, 6] prepared from *trans*-9-methyl-3-decalone by oxidation with nitric acid (1). When mixed with XII, the unsaturated diacid (XI) showed no obvious depression of the m.p., but the former is stable to permanganate in the carbonate solution, contrary to the latter. It was found that the saturated acid (XII) was prepared in 67% yield from the acetoxyketone (IX) with 30% Perhydrol (hydrogen peroxide) in methanolic potassium hydroxide in the same manner as from 2-acetoxy-3-keto-9-methyl-Δ^1-octahydronaphthalene (1).

SUMMARY

1. Reaction of 5-bromo-3-keto-9-methyl-Δ^4-octahydronaphthalene (II) with potassium acetate afforded the extended and crossed dienones (III and IV) and Δ^4-2,3-diketone (VII). Hydrolysis of the primary product gave 3,5-diketo-9-methyldecalin (VI).

2. A possible mechanism was offered for the acetolysis of II.

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[6] The sample, which was reported (1) to melt at 191.5–192.5°, was found to show the m.p. 195° on reëxamination.