165°). The crude anil, however, could be cyclized with sulfuric acid in good yields (80–90%). The benzoquinoline twice recrystallized from petroleum ether (40–60°) formed colorless needles, m. p. 51.5–53°. Material of the same m. p. was obtained laboriously in about 2% yield using the procedure of Reed.[8] The mixed m. p. showed no depression. It was surprising to find that hydrogen fluoride failed to cyclize noticeably 4-(1-naphthylimino)-pentanone-2; hydrolysis to α-naphthylamine took place instead.

Absorption Spectra.—A Hilger quartz spectrograph equipped with a Hilger photometer was used in conjunction with a hydrogen discharge tube as the light source. Ethanol, specially dried over magnesium ethoxide[22] and distilled in an all-glass apparatus, was used as the solvent.

The analytical samples of the benzoquinolines were used. Benzo[f]quinoline (Eastman Kodak Company) was recrystallized from 60–68° petroleum ether, m. p. 90.5–91.5°. Anthracene was sublimed and recrystallized from chloroform and ethanol, m. p. 214.5–215.5°. A pure sample of phenanthrene was prepared by dehydrogenation of pure 9,10-dihydrophenanthrene[23] over 30% palladium-charcoal,[24] followed by recrystallization from ethanol, m. p. 98–99°.

The linear compounds were determined at four concentrations: $M/4000$, $M/10{,}000$, $M/40{,}000$ and $M/200{,}000$. For anthracene a determination was made also at $M/400{,}000$. The angular substances were determined at $M/2000$, $M/10{,}000$, $M/50{,}000$ and $M/200{,}000$. In the figures the abscissas are plotted in fresnel (f) units in accordance with the suggestion of Brode.[25] The log E values observed for anthracene and phenanthrene do not check those of Capper and Marsh,[26] but in the case of anthracene are in agreement with those of Heertjes and Waterman.[27]

The principal maxima are given below. The wave lengths are in ångström units, the intensity in log E (in parentheses), and * indicates inflections.

Anthracene.—3740 (3.75), 3700* (3.55), 3560 (3.9), 3505* (3.75), 3375 (3.70), 3340* (3.58), 3200 (3.43), 3090 (3.05), 2940 (2.75), 2530 (5.30).

2,4-Dimethylbenzo[g]quinoline.—3800 (3.45), 3640 (3.70), 3575 (3.85), 3470 (3.62), 3380 (3.62), 3290 (3.45). 2565 (5.10).

2,4,10-Trimethylbenzo[g]quinoline.—3870 (3.6), 3695 (3.75), 3600 (3.7), 3530 (3.7), 3420 (3.6), 2590 (5.3).

Phenanthrene.—3460 (2.4), 3375 (2.24), 3290 (2.5), 3220 (2.34), 3150 (2.18), 3080 (2.00), 2935 (4.00), 2815 (3.88), 2760 (3.80), 2600 (4.48), 2525 (5.00).

2,4-Dimethylbenzo[h]quinoline.—3480 (3.6), 3310 (3.50), 3160 (3.30), 2980 (4.00), 2870 (4.35), 2790 (4.50), 2700 (4.85).

1,3-Dimethylbenzo[f]quinoline.—3450 (3.65), 3300 (3.48), 3160 (3.24), 2970 (3.95), 2700 (4.60).

Benzo[f]quinoline.—3470 (3.54), 3310 (3.41), 3160 (3.18), 2900* (3.57), 2665 (4.06).

Summary

The preparation and proof of structure of some benzoquinoline derivatives is considered. Particular attention is given to the cyclization of the anil from β-naphthylamine and acetylacetone, which, surprisingly, takes place so as to give a linear benzoquinoline. The latter represents a class of compounds about which little has been known. Some of the properties of this type of substance are considered.

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[22] Fieser, "Experiments in Organic Chemistry," D. C. Heath and Company, 2nd ed. Part II, 1941, p. 359.

[23] Fieser and Johnson, THIS JOURNAL, **61**, 168 (1939).

[24] Zelinsky and Turowa-Pollak, *Ber.*, **58**, 1295 (1925).

[25] W. Brode, "Chemical Spectroscopy," John Wiley and Sons, New York, N. Y., 1939, p. 191.

[26] Capper and Marsh, *J. Chem. Soc.*, 724 (1926).

[27] Heertjes and Waterman, *Bull. soc. chim.*, [5] **7**, 187 (1940).

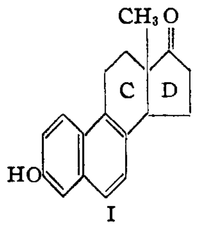
MADISON, WISCONSIN RECEIVED AUGUST 2, 1943

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

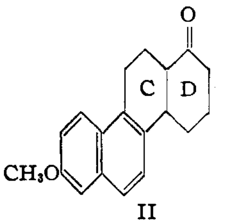
Introduction of the Angular Methyl Group. II.[1] *cis*- and *trans*-8-Methylhydrindanone-1[2]

BY WILLIAM S. JOHNSON

The purpose of this communication is to describe a method for converting decalone-1 (III) into the angularly methylated hydrindanones (IX and X). This process affords a means of arriving at the structure defined by rings C and D (compare formula I) of a number of the steroid hormones, and obviously serves as a model synthesis for the preparation of hormones of the equilenin (I) type from chrysene derivatives like II.[3]



I



II

Considerable attention already has been devoted to 8-methylhydrindanone-1[4–11] but with one exception[11] all of the syntheses have led to one and the same isomer of this compound which, however, can exist in two racemic forms described by *cis* (IX) and *trans* (X) fusion of the rings. The present synthesis affords a means of obtaining each of these diastereoisomers, which is fortunate particularly in view of the fact that the ring C/D

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[1] For the first paper of this series see Johnson, THIS JOURNAL, **65**, 1317 (1943).

[2] This work was assisted in part by a grant from the Wisconsin Alumni Research Foundation.

[3] The unsaturated progenitor (double bond in ring D) of compound II is available by the Robinson-Schlittler synthesis; Robinson and Thompson, *J. Chem. Soc.*, 1739 (1939).

[4] Chuang, Tien and Ma, *Ber.*, **69**, 1494 (1936).

[5] Kon, Linstead and Simons, *J. Chem. Soc.*, 814 (1937).

[6] Linstead, Millidge and Walpole, *ibid.*, 1140 (1937).

[7] Robinson and Walker, *ibid.*, 1160 (1937).

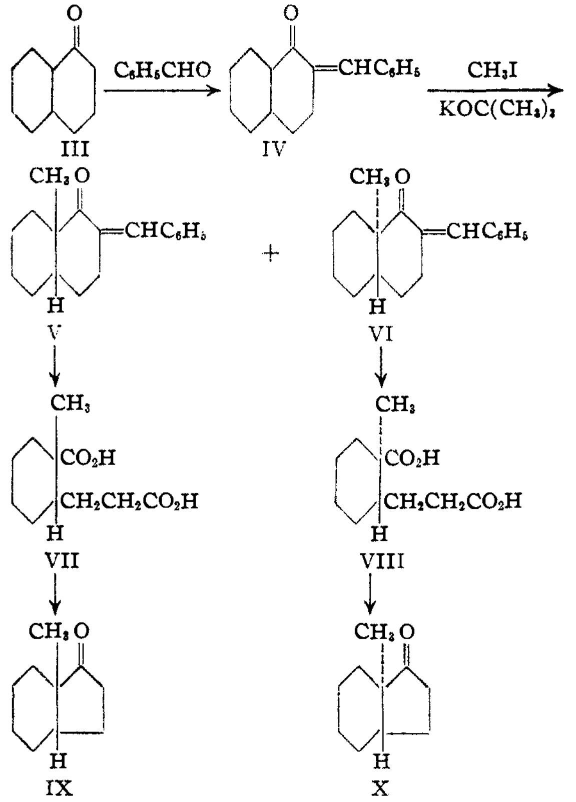
[8] Elliott and Linstead, *ibid.*, 660 (1938).

[9] Burnop and Linstead, *ibid.*, 720 (1940).

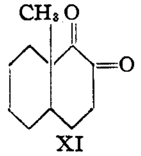
[10] Nenitzescu and Przemetzky, *Ber.*, **74B**, 676 (1941).

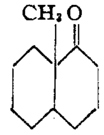
[11] Bachmann and Kushner, THIS JOURNAL, **65**, 1963 (1943).

configuration of the steroids has not yet been established unequivocably.



In a previous communication[1] was described a practicable preparation of the two stereoisomeric forms of 2-benzal-9-methyldecalone-1 from decalone-1 (III → VI). In the present work these benzal derivatives were found to be very susceptible to oxidative degradation by potassium permanganate in acetone solution. With the amount of oxidizing agent calculated to produce the α-diketone XI a mixture of starting material and acidic substances was obtained. None of XI was found even when the reaction was conducted at 0°. This suggests that under the conditions employed, the diketone, if formed, is more sensitive to oxidation than the benzalketone.


XI


XII

When an excess of permanganate was employed the benzal derivatives V and VI were converted into the dibasic acids VII and VIII, respectively, and benzoic acid. For the purpose of preparing the hydrindones it was found unnecessary to isolate these acids. Thus by distillation from a small amount of barium oxide[12] the crude acidic fractions from the oxidation gave the 8-methylhydrindanones IX and X isolated as the semicarbazones in over-all yields of 35 and 55%, respectively. The pure ketones were obtained by steam distillation of these derivatives in the presence of oxalic acid.

From the benzal derivative, m. p. 104°, which formerly[1] was converted to the 9-methyldecalone-1 (XII) of *cis* (probable[8]) configuration, was obtained the well-known[4-11] *cis*-8-methylhydrindanone-1. This relationship between the two homologous ketones is consistent with the previous demonstration[8] that they belong to the same stereochemical series. From the isomeric benzal derivative, m. p. 94°, was produced the stereoisomeric 8-methylhydrindanone-1 (configuration provisionally *trans*) which has been obtained through a different synthesis by Bachmann and Kushner.[11] Their description of the new ketone (which was published since the completion of the present work), is in good agreement with the current findings. A comparison of the two stereoisomeric ketones and derivatives is found in Table I.

TABLE I[a]

8-METHYLHYDRINDANONE-1[b]

	cis[c]	*trans*[c]
B. p. °C.	106	109
B. p. Mm.	20	20
M. p., °C.	34.5–36	...
Semicarbazone, m. p., °C.	224.5–225.5	242–243
Oxime, m. p., °C.	87–88	115–115.5
2,4-Dinitrophenylhydrazone, m. p., °C.	140.5–141	146.5–147 153.5–154[d]

[a] All melting points are corrected. [b] The comparison of melting and boiling points with those which have been reported previously may be found in the experimental part of this paper. [c] Probable configuration. [d] Double melting point.

The difference which has been observed between members of the *cis* and *trans* series with respect to reactivity of the carbonyl group[1] is consistently carried over to the hydrindanones as shown by the fact that the so-called *trans* substance forms the semicarbazone with marked rapidity relative to its stereoisomer. As with the 9-methyldecalones ordinary molecular models fail to show any pronounced difference in degree of hindrance of the carbonyl group. The chemical distinction, however, is quite significant, and if generally applicable, it may prove to be useful in the problem of determining the ring C/D configuration of the steroids.

Experimental Part[13]

***cis*-8-Methylhydrindanone-1 (IX).**—Twelve and one-half grams (a 5% excess) of powdered potassium permanganate was added gradually to a cooled and mechanically stirred solution of 7.20 g. of *cis*-2-benzal-9-methyl-

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[12] The pyrolytic cyclization of the acids VII and VIII was used rather than the Dieckmann method principally because of the simplicity of manipulation. The latter method should be useful, however, particularly when applied to larger molecules. *Cf.* Bachmann, Cole and Wilds, THIS JOURNAL, **62**, 824 (1940).

[13] (a) All melting points are corrected. (b) The configurations of the substances described herein are provisional.

decalone-1[1] (m. p. 99–102°) in 250 cc. of acetone. The rate of addition was controlled so that the temperature was maintained between 2 and 4°. After the addition was complete, stirring was continued for about one hour at 0°; then the solvent was evaporated in a stream of air and replaced by water. This mixture was chilled (ice–salt bath) and stirred mechanically while dilute sulfuric acid (20 cc. of concentrated acid in 20 cc. of water) was added followed by 20 cc. of a saturated solution of sodium bisulfite. The colorless mixture was extracted thoroughly with several portions of ether, and the latter solution was in turn extracted with portions of saturated sodium bicarbonate solution. Evaporation of the ether yielded 0.88 g. of a semicrystalline neutral fraction which consisted mainly of starting material. Acidification of the combined aqueous extracts yielded an oily mixture of the dicarboxylic acid VII and benzoic acid. In one experiment the benzoic acid was removed by steam distillation, leaving *cis*-β-(2-carboxy-2-methylcyclohexyl)-propionic acid (VII) as an oil which solidified on standing, m. p. 93–97°. As reported by Burnop and Linstead, reference 9 (footnote p. 721), recrystallization was difficult. The m. p. of once recrystallized material was 99.5–103°. The pure substance is reported to melt at 108–109°.[9] The mixture of organic acids was extracted with ether, washed with water, saturated salt solution and dried over anhydrous sodium sulfate. Evaporation of the ether left 7 to 8 g. of crude acid fraction which was mixed with 0.35 g. of barium oxide and pyrolyzed according to previous procedures[5,7] in a two-bulb flask at 300–320° for one to two hours. The colorless distillate which had partially solidified (benzoic acid) was dissolved in ether and extracted with a saturated solution of sodium bicarbonate which on acidification yielded benzoic acid. The ether solution was washed with saturated salt solution, dried over anhydrous potassium carbonate and the solvent was removed through a short Vigreux column. The residue which had a strong camphor-like odor was dissolved in 15 to 20 cc. of methanol, 3.0 g. of semicarbazide hydrochloride and 3.0 cc. of pyridine were added, and the mixture refluxed for one hour during which the semicarbazone gradually precipitated. After the addition of a little water and cooling 1.97 g. of material m. p. 221–222.5° (dec.) was obtained. An additional 0.10 g., m. p. 208–215°, was obtained from the mother liquors, making the total yield 35%. A sample of the semicarbazone recrystallized to constant m. p. from methanol formed small colorless blades, m. p. 224.5–225.5° (dec.) (reported m. ps. range from 213°[4,11] to 224–225°[11]).

The free ketone was obtained easily in practically quantitative yield by distillation of an aqueous solution of oxalic acid containing a suspension of the semicarbazone, m. p. 221–222.5° (dec.). The distillate contained the oily colorless ketone which solidified on standing in ice. Ether extraction followed by distillation gave *cis*-8-methylhydrindanone-1 of constant boiling point, 106° (20 mm.); m. p. 34.5–36° (reported m. ps. range from 33–34°[5] to 39.5°[10]). In agreement with the observation of Elliott and Linstead[8] the semicarbazone formed readily only on heating.

The oxime of *cis*-8-methylhydrindanone-1 was prepared in methanol with hydroxylamine hydrochloride and pyridine. The crude product was sublimed at 65–70° (0.1 mm.) and recrystallized twice from aqueous methanol. The colorless crystals melted at 87–88°. Bachmann and Kushner[11] give m. p. 85.5–87°.

Anal. Calcd. for $C_{10}H_{17}ON$: C, 71.81; H, 10.25. Found: C, 71.60; H, 9.92.

The **2,4-dinitrophenylhydrazone** of IX formed short orange needles from methanol, m. p. 140.5–141°.

Anal. Calcd. for $C_{16}H_{20}O_4N_4$: C, 57.82; H, 6.07. Found: C, 57.87; H, 6.19.

***trans*-8-Methylhydrindanone-1** (X) was prepared by essentially the same procedure which is described above for the *cis* isomer. For the oxidation of 16.56 g. of *trans*-2-benzal-9-methyldecalone-1 (m. p. 92–93.5°) 250 cc. of acetone and 31.6 g. (a 15% excess) of potassium permanganate were used. The larger excess of oxidizing agent seemed to improve the reaction; only a negligible amount of neutral material remained. After the addition of the sulfuric acid (50 cc. concentrated acid and 50 cc. water) and the sodium bisulfite solution (50 cc.) the dibasic acid VIII and benzoic acid remained as a colorless precipitate which was filtered, dissolved in sodium bicarbonate solution, filtered, and reprecipitated with hydrochloric acid. The filtrate from this operation was combined with the original filtrate from the oxidation step and worked up by extraction as in the previously described procedure. (This method of working up the organic acids in two fractions seemed desirable because of the low solubility of the dibasic acid VIII in non-polar solvents.) The additional oily acidic material thus obtained was combined with the above solid fraction, and 0.8 g. of barium oxide was added for the pyrolysis. In this preparation the crude distillate from the pyrolysis was treated directly, without removal of the benzoic acid, with 50 cc. of ethanol, 7 g. of semicarbazide hydrochloride and 15 cc. of pyridine. The insoluble semicarbazone began to precipitate after two minutes' heating on the steam-bath. After one hour the mixture was cooled, filtered and washed thoroughly with water; yield 7.39 g. of colorless crystals, m. p. 243–244° (dec.). From the mother liquors was obtained an additional 0.16 g. of good material, m. p. 239–242° (dec.), making the total yield 55%. Hydrolysis of the semicarbazone as described above gave *trans*-8-methylhydrindanone-1 of constant b. p. 109° (20 mm.), $n^{26}\text{D}$ 1.4800, d^{26}_{4} 0.9793, $M\text{D}$ (found) 44.16, $M\text{D}$ (calcd.) 43.99. Bachmann and Kushner[11] report, b. p. 108–109° (20 mm.), $n^{25.8}\text{D}$ 1.4807. The ketone had the characteristic camphor-like odor and reformed the semicarbazone readily at room temperature.

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.89; H, 10.60. Found: C, 78.78; H, 10.66.

The **semicarbazone** of *trans*-8-methylhydrindanone-1 on recrystallization from ethanol formed colorless plates, m. p. 242–243° (dec.) (reported, 234°[11]).

Anal. Calcd. for $C_{11}H_{19}ON_3$: C, 63.13; H, 9.15. Found: C, 62.87, H, 9.01.

The **oxime** was purified by sublimation at 70–80° (0.1 mm.) and recrystallization from aqueous methanol. It formed small colorless plates, m. p. 115–115.5° (reported, 113–115.5°[11]).

Anal. Calcd. for $C_{10}H_{17}ON$: C, 71.81; H, 10.25. Found: C, 72.30; H, 10.21.

The **2,4-dinitrophenylhydrazone** formed orange blades from methanol–ethyl acetate. It melted sharply at 146.5–147° and resolidified as the temperature was raised, remelting at 153.5–154°.

Anal. Calcd. for $C_{16}H_{20}O_4N_4$: C, 57.82; H, 6.07. Found: C, 58.16; H, 6.00.

***trans*-β-(2-Carboxy-2-methylcyclohexyl)-propionic Acid (VIII).**—A sample of the solid reprecipitated acid mixture obtained in the above oxidation was triturated with benzene in which the dicarboxylic acid VIII is relatively insoluble. The latter was filtered, washed with benzene and recrystallized to constant m. p. from aqueous methanol and then once from ethyl acetate. It formed colorless pointed blades, m. p. 179–180°.

Anal. Calcd. for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47. Found: C, 61.80; H, 8.41.

Summary

A method is described for obtaining *cis*- and *trans*-8-methylhydrindanone-1 from decalone-1.

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