[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Dimerization of 6-Methoxy-3,4-dihydronaphthalene

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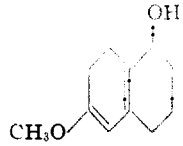
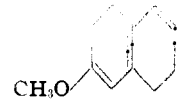
On dehydration of 6-methoxy-1,2,3,4-tetrahydro-1-naphthol (I) with aqueous hydrobromic acid, Long and Burger[1] obtained a crystalline *substance*, $C_{11}H_{12}O$, m. p. 73–74°, which was formulated as 6-methoxy-3,4-dihydronaphthalene (II). Our interest in II as a possible intermediate in the synthesis of oestrone, or allied substances, prompted us to reinvestigate this reaction.

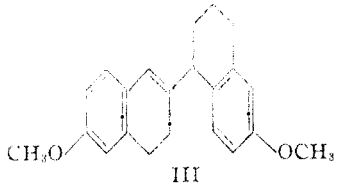


I

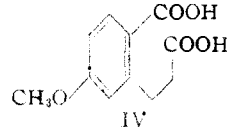


II

In this communication it is shown that the above substance is in fact a dimer of II, *viz.*, 2-(6-methoxy-1,2,3,4-tetrahydro-1-naphthyl)-3,4-dihydro-6-methoxynaphthalene (III).



III



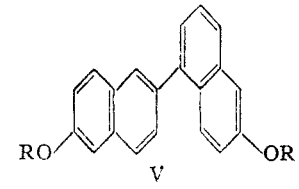
IV

Since neither the dehydration product obtained by the earlier investigators, nor our material, even after a number of recrystallizations, gave concordant analyses for the formula $C_{11}H_{12}O$, we carried out a chromatographic fractionation of the recrystallized substance on alumina. Over 90% of material was recovered, which on one further recrystallization melted at 75.5–77°, and analysis of which left no doubt that the empirical formula of the substance was $(C_{11}H_{12}O)_n$.

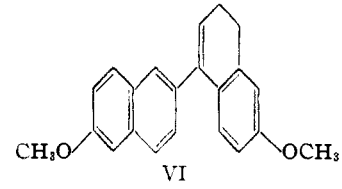
Quantitative titration of the dehydration product with perbenzoic acid indicated one double bond for a molecular weight of 320, and from the oxidation mixture, a crystalline *oxide*, $C_{22}H_{24}O_3$, m. p. 127–128.5°, was obtained. These observations indicated clearly that the original product had the dimeric formula, $C_{22}H_{24}O_2$ (320), and this conclusion was substantiated by direct molecular weight determinations on the material (290, 333) and on the above oxide (322, 326).

Oxidative degradation of the dimer with permanganate led to the isolation, in small quantity, of a dibasic acid, m. p. 201.5–203°, neutralization equivalent 112.6, undoubtedly β-(2-carboxy-4-methoxyphenyl)-propionic acid[2] (IV), and a *dehydro-compound*, $C_{22}H_{22}O_2$, m. p. 107.5–108.5° (VII, *vide infra*). The latter substance was subsequently obtained relatively smoothly and in better yield by the chromic acid oxidation of the dimer. Attempts to obtain products resulting from simple oxidative scission at the (presumable) double bond were unsuccessful.

Dehydrogenation of the dimer with sulfur, or better, catalytically over palladium-charcoal catalyst, gave a *hexadehydro-compound*, $C_{22}H_{18}O_2$, m. p. 91–92°, which was shown by synthesis to be 6,6′-dimethoxy-1,2′-binaphthyl (V, R = CH_3). Condensation of the Grignard reagent

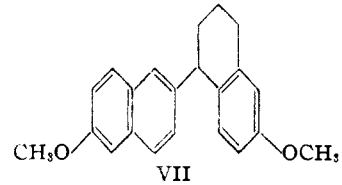


V



VI

from 2-bromo-6-methoxynaphthalene[3] with 6-methoxy-α-tetralone gave directly the dihydrobinaphthyl (VI), m. p. 126°. Catalytic dehydrogenation of VI gave the 6,6′-dimethoxy-1,2′-dinaphthyl (V, R = CH_3), identical in all respects with the hexadehydro compound from the dimer. Further, hydrogenation of the Grignard product (VI) gave a dihydro derivative (VII), which proved to be identical with the de-



VII

hydro compound, m. p. 108°, obtained by direct permanganate or chromic acid oxidation of the dimer.

These observations establish the structure of the dimer as III. The identity of the synthetic binaphthyl with that obtained from the dimer affords conclusive proof of the nature of the carbon skeleton of the latter. The identity of the synthetic substance VII with the dehydro compound from the dimer confirms the skeletal structure,[4]

(1) Long and Burger, *J. Org. Chem.*, **6**, 854 (1941).

(2) The prior preparation of this acid has been reported, without details, by Johnson and Anderson, abstracts of papers presented at the Atlantic City Meeting of the A. C. S., September, 1941, p. 13.

(3) Franzen and Staubel, *J. prakt. Chem.*, **103**, 369 (1922).

(4) Since all of the reactions used in establishing this identity were carried out under mild conditions, this proof of the nature of the carbon skeleton is possibly preferable to that involving the high temperature dehydrogenations. However, the work as a whole demonstrates that no rearrangement takes place during the latter reaction.

and further provides evidence in favor of the $\Delta^{1,2}$-position of the double bond, as opposed to the *a priori* alternatively possible positions, $\Delta^{2,1'}$, $\Delta^{2,3}$, or $\Delta^{1',2'}$. In this light, the failure to obtain products corresponding to simple oxidative fission at the double bond of the dimer is a consequence of the facility with which dihydronaphthalenes pass into the fully aromatic condition. Confirmation of the conjugation of the double bond with one of the aromatic rings is further provided by the absorption spectrum of the dimer (Fig. 1), which is strongly reminiscent of that of the (chromophorically) similarly constituted anethole, $CH_3OC_6H_4CH{=}CHCH_3$,[4a] and markedly different from that of a simple disubstituted anisole.

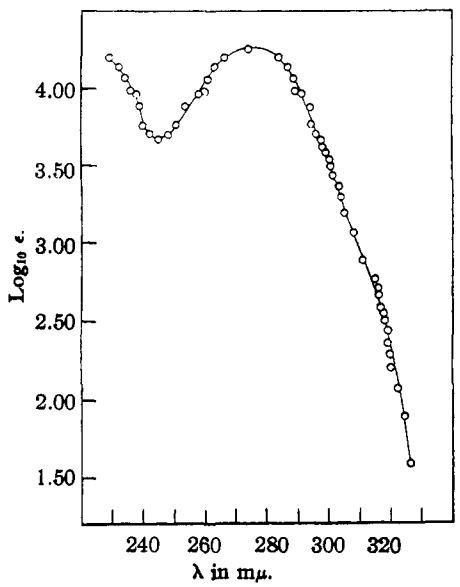
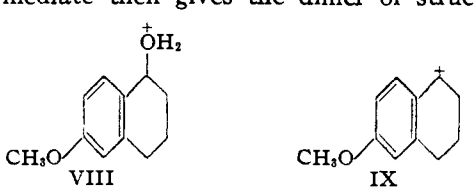
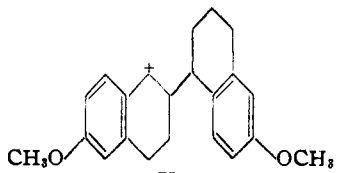


Fig. 1.—Absorption spectrum of 6,6′-dimethoxy-1,2,3,3′,-4,4′-hexahydro-1,2′-binaphthyl in ethanol; $\lambda_{max.}$ = 274 mμ. log ε = 4.25.

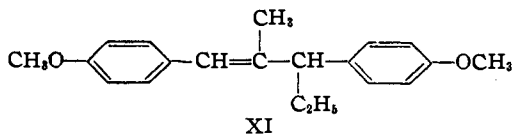
We turn now to a discussion of the mechanism by which the dimer is produced by the action of acid on 6-methoxy-α-tetralol. Loss of water from the conjugate acid (VIII) of the tetralol will give a carbonium ion (IX) (or its equivalent) which may (a) lose a proton with the formation of 6-methoxy-3,4-dihydronaphthalene (II) *and* (b) attack the latter product at the double bond (polarized in the sense $\overset{\curvearrowright}{\underset{1}{C}{=}\underset{2}{C}}$) to give the dimeric species (X). Loss of a proton from the latter intermediate then gives the dimer of structure





X

III. A similar mechanism may be envisaged for the observed dimerization of anethole, in the presence of acidic reagents, to XI.[5]



XI

For the rest, we are concerned with a number of incidental observations made in the course of our experiments. The attack of perbenzoic acid on the dimer need not *a priori* have given an oxide: not infrequently, ketonic, or other isomeric, products are obtained with this reagent. In order to ascertain the structure of our *compound*, $C_{22}H_{24}O_3$, m. p. 127–128.5° (*vide supra*), we determined the ultraviolet absorption characteristics of the substance (Fig. 2). The spectrum shows a considerable resemblance in general form to isosafrole oxide,[6] and differs markedly, on the other hand, from that of 6-methoxy-α-tetralone. The conclusion would seem to be justified that our substance is a true oxide, of the structure XII.

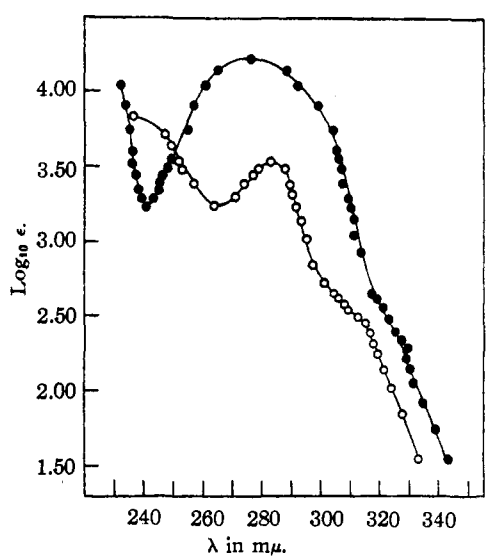


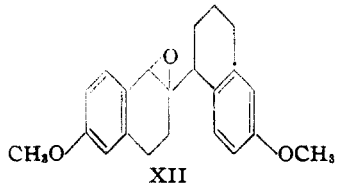
Fig. 2.—Absorption spectra in ethanol: ●, 6-methoxy-α-tetralone: $\lambda_{max.}$ = 276 mμ, log ε = 4.22; O, 6,6′-dimethoxy-1,2,3,3′,4,4′-hexahydro-1′,2′-oxido-1,2′-binaphthyl: $\lambda_{max.}$ = 283 mμ, log ε = 3.54.

The hydrogenation of 6-methoxy-α-tetralone to the corresponding alcohol (the immediate precursor of the dimer) is subject to variations,

(4a) Hillmer and Schorning, *Z. physik. Chem.*, **A167**, 407 (1933).

(5) Goodall and Haworth, *J. Chem. Soc.*, 2482 (1930).

(6) Hillmer and Schorning, *Z. physik. Chem.*, **A168**, 81 (1934).



XII

the exact cause of which has not been established. Frequently there were isolated, after the absorption of one mole of hydrogen, equimolar amounts of the deoxygenated 6-methoxytetralin, and unchanged ketone. In view of the frequent facilitation of such catalytic oxygen-cleavage reactions by acidic media, and since the alcohol used in the unsuccessful hydrogenations was in fact slightly acidic, we attempted, usually with success, to avoid this undesirable result by using as solvent ethanol which had been freshly distilled from sodium hydroxide. On the other hand, the reductions by this method proceeded more slowly and, in one case, the reaction would not start at all until a very small quantity of hydrochloric acid was added: it then proceeded rapidly and without untoward result (*i. e.*, no oxygen cleavage). In none of our hydrogenations did we observe concomitant formation of 6-methoxytetralin and 6-methoxy-α-tetralol; it seems unlikely, therefore, that the alcohol is an intermediate in the formation of the deoxygenated product.

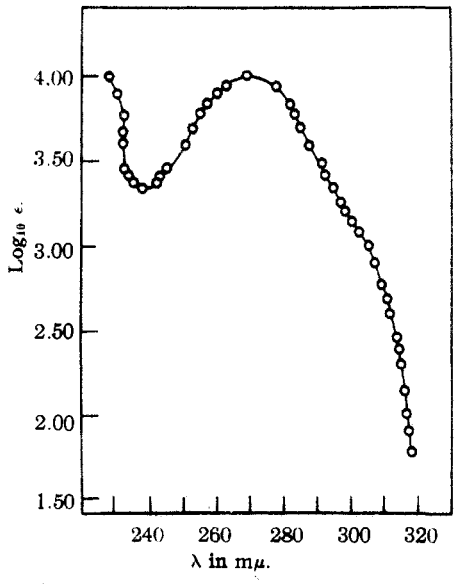
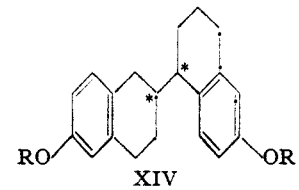


Fig. 3.—Absorption spectrum of 6-methoxy-3,4-dihydronaphthalene in ethanol.

Although 6-methoxy-α-tetralone is now a readily available intermediate[7] the somewhat unpredictable course of the hydrogenations described above led us to investigate a more reliable source of the dimer. Oxidation of 6-methoxytetralin with red lead in acetic acid at room temperature gave a good yield of 6-methoxy-α-tetralol acetate[8] which, like the corresponding alcohol, was smoothly transformed into the dimer (III) by the action of hydrobromic acid.

The alkaline hydrolysis of the above acetate did not proceed smoothly: the main product was a new liquid *substance*, which is formulated as 6-methoxy-3,4-dihydronaphthalene (II) on the basis of analyses, physical properties and, in particular, the absorption spectrum (Fig. 3). In accordance with this view, the compound is transformed by aqueous hydrobromic acid into the dimer (III). The substance also was obtained occasionally during the distillation of 6-methoxy-α-tetralol (prepared by hydrogenation of the corresponding ketone), in consequence of conditions which we have not attempted to define precisely.

Certain structural similarities between the dimer and compounds of the stilbestrol and hexestrol types led us to carry out a number of demethylation experiments, with the object of obtaining phenols of possible high oestrogenic activity. Anomalous results were obtained in the demethylation of the dimer itself; the *yellow* product was strongly acidic, and formed with soda a bright *scarlet* crystalline sodium salt. We have not pursued this line of investigation further.[9] On the other hand, by boiling with hydriodic acid in acetic acid, we effected successfully the demethylation of the *dihydro-dimer* (XIV, R = CH_3) to the phenol (XIV, R = H), m. p. 187–190°, and of the completely aromatized compound (V, R = CH_3) to the phenol (V, R = H), m. p. 187–188.5°.



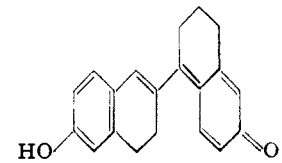
XIV

We should like to express our appreciation to Parke Davis and Co. for a grant to Harvard University for a Fellowship, which was held by the junior author while carrying out this investigation.

(7) One of us, with R. B. Loftfield, will describe in a subsequent communication, an excellent method for the preparation of the ketone from β-naphthol in 50% yield.

(8) Prior preliminary notice of the successful execution of this reaction has been given, without details, by Johnson and Anderson, *cf.* ref. 2.

(9) These observations suggest that oxidation has taken place at some stage in the reaction with formation of XIII. We may point



XIII

out in support of this suggestion that the self-condensation of 6-methoxy-α-tetralone by *aqueous* sodium hydroxide (presumably with hydrolysis of the O-methyl groups [*cf.* Peak, Robinson and Walker, *J. Chem. Soc.*, 753 (1936)]) gives a similar product. The most reasonable formulation of the latter is a desmotrope of XIII with an additional hydroxyl at position 1.

Experimental

6-Methoxytetralin, b. p. 129–131° (11 mm.) and **6-methoxy-α-tetralone,** m. p. 77–78°, were prepared from *ar*-(2)-tetralol by methylation and oxidation, following procedures developed in this Laboratory by other workers.[7]

6-Methoxy-1-acetoxy-1,2,3,4-tetrahydronaphthalene.—To 34.2 cc. of 6-methoxytetralin dissolved in 200 cc. of glacial acetic acid and 100 cc. of acetic anhydride, 138 g. of red lead was added in portions with stirring during eight hours. The resultant clear yellow solution was poured into an equal volume of chopped ice, and stirred vigorously to facilitate the separation of a large yellow crystalline precipitate, which was removed at once, washed with a small amount of ice water, and dissolved in ether. After washing, drying and removal of solvent, the residual red oil was distilled *in vacuo*; after *ca.* 5 g. of lower boiling material, 22 g. of the tetralol acetate, b. p. 144–149° (3 mm.), was obtained.

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.89; H, 7.33. Found: C, 71.54; H, 6.94.

6-Methoxy-α-tetralol.—This substance was prepared by catalytic hydrogenation of 6-methoxy-α-tetralone. We have carried out this reaction a great many times; in our experience, the results are apt to vary, apparently adventitiously. Often the reduction proceeds directly to 6-methoxytetralin (*cf.* theoretical section). A typical cleavage experiment is reported.

The ketone (20 g.) in 400 cc. of 95% ethanol absorbed one mole of hydrogen in twenty-four hours on shaking over 0.3 g. of platinum oxide catalyst in the presence of 1 cc. of 1 *M* ferrous sulfate. After removal of catalyst and solvent, fractionation *in vacuo* gave 10 g. of 6-methoxytetralin, b. p. 135° (17 mm.), and 9.5 g. of unchanged 6-methoxy-α-tetralone, b. p. 180° (17 mm.), m. p. 76–78°, mixed with an authentic sample, m. p. 76–78°.

The following procedure illustrates the most consistently successful method: The ketone (10 g.) in 200 cc. of 95% ethanol (freshly distilled from sodium hydroxide) absorbed 1.2 moles of hydrogen in seventeen hours on shaking over 0.2 g. of platinum oxide. After removal of catalyst and solvent, 9.1 g. of 6-methoxy-α-tetralol, b. p. 175° (16 mm.), was obtained on fractionation *in vacuo* as a colorless, very viscous oil.

The Dimer (III): (a) From the Alcohol.—6-Methoxytetralol-1 (3.25 g.) was shaken with 32 cc. of 46% (by titration[10]) hydrobromic acid for twelve hours. The resultant solid pinkish-white ball, after recrystallization from ethanol, weighed 1.9 g. and had m. p. 74–75°.

Anal. Calcd. for $(C_{11}H_{12}O)_n$: C, 82.46; H, 7.55. Found: C, 83.33; H, 7.75.[11]

In view of the unsatisfactory analytical figures, the material was chromatographed on Brockmann alumina; the substance was put on with benzene, and eluted first with low-boiling petroleum ether, and then with benzene–petroleum ether (20/80). Fourteen (approximately weight equivalent) fractions were taken. All but three fractions, on evaporation and trituration with methanol, gave white crystalline material, m. p. 75–77°. The eleven fractions together constituted more than 90% of the original material, and were recrystallized from methanol, m. p. 75.5–77°.

Anal. Calcd. for $(C_{11}H_{12}O)_n$: C, 82.46; H, 7.55. Found: C, 82.59; H, 7.62. The other three fractions had melting points 69–74, 71–76, and 65–110°, and were not further investigated. As will be evident from (b, below), the tedious chromatographic separation may be obviated by distillation *in vacuo* of the crude dimer.

(b) From **6-Methoxy-α-tetralol Acetate.**—The acetate (*vide supra*) (12.2 g.) was shaken for forty-eight hours with 150 cc. of 46% hydrobromic acid. The resultant viscous red material was taken up in ether, washed with soda, then water, dried, and distilled *in vacuo* after removal of solvent. The very viscous yellow oil (6.0 g., b. p. 233–238° (3 mm.)) obtained, on crystallization from methanol–ethyl acetate, separated in beautiful long needles, m. p. 75.5–76.5° (3.6 g.); recrystallized from ethanol, m. p. 76–77°.

Anal. Calcd. for $(C_{11}H_{12}O)_n$: C, 82.46; H, 7.55. Found: C, 82.65; H, 7.58. The absorption spectrum was taken in absolute ethanol (*vide* Fig. 1). Determination of the molecular weight (Rast). Calcd. for $C_{22}H_{24}O_2$: 320.4. Found: 290 (Tiedcke); 333 (R. H. E.).

Perbenzoic Acid Oxidation of the Dimer.—The purified dimer (2.53 g., 0.0079 mole) dissolved in 200 cc. of chloroform was treated with 1.19 g. of perbenzoic acid in 50 cc. of chloroform. The reaction, which was carried out below 5°, was followed iodimetrically:

Time, hr.	0.0645 *N* $Na_2S_2O_3$/cc. (aliquot), cc.
0	1.07
2	0.27
19	.11
25	.10
26	.10

These figures indicate one double bond for a molecular weight of 320. The reaction mixture, which still possessed oxidizing power, was washed with dilute bisulfite solution, soda, and water; removal of solvent and trituration with methanol–petroleum ether gave 0.8 g. of material, m. p. 124–126°; recrystallized from ethanol, faintly yellow needles, m. p. 127–128.5°.

Anal. Calcd. for $C_{22}H_{24}O_3$: C, 78.54; H, 7.19. Found: C, 78.45; H, 7.69. The absorption spectrum was taken in absolute ethanol (*vide* Fig. 2). Determination of the molecular weight (Rast). Calcd. for $C_{22}H_{24}O_3$: 336.4. Found: 322, 326 (Tiedcke).

Hydrogenation of the Dimer.—The dimer (1.30 g.) in 10 cc. of glacial acetic acid took up 116 cc. of hydrogen (t = 25.5°, p = 680 mm.) and stopped, on shaking 254 minutes over reduced platinum oxide. Calcd. for $C_{22}H_{24}O_2$: mol. wt., 320.4. Found (by hydrogenation): mol. wt. 307. On removal of catalyst and solvent, a viscous oil was obtained which resisted attempts at crystallization.

Demethylation of the Dihydro-dimer.—The oil from the above experiment was dissolved in 5 cc. of glacial acetic acid, heated to boiling, and 5 cc. of 57% hydriodic acid was added drop by drop during twenty minutes. After boiling until a test portion was completely soluble in caustic soda, the reaction mixture was poured into 50 cc. of 1% sodium bisulfite; the resulting flocculent yellow precipitate (1.1 g.) was recrystallized from dilute acetic acid, m. p. 170–176° (0.5 g.). Successive recrystallizations from glacial acetic acid: first, m. p. 174–184°; second, m. p. 177–184°; third [after sublimation at 190° (2 mm.), glass obtained] 177–186°. A fourth recrystallization from *n*-butyl ether, m. p. 181–187°, and, finally, from aqueous alcohol, gave white microcrystalline needles, m. p. 187–190° (0.2 g.).

Anal. Calcd. for $C_{20}H_{22}O_2$: C, 81.59; H, 7.53. Found: C, 81.01; H, 8.08.

Sharp-melting samples of this material were extremely difficult to obtain; the crude material is undoubtedly a mixture of stereoisomers of the formula XIV (R = H), which has two asymmetric carbon atoms (starred). The similar situation in the case of the hydrogenated dimer XIV (R = CH_3) was doubtless responsible for the failure of this material to crystallize.

Oxidation of the Dimer: (a) By Potassium Permanganate.—The dimer (2.3 g.) in 55 cc. of acetone with 2.3 g. of sodium bicarbonate was oxidized with 2.64 g. of potassium permanganate during nine hours at 0°. After standing overnight the precipitated manganese dioxide was removed. The residual red oil after evaporation of the acetone was taken up in acetic acid and precipitated with water. The crystalline material which separated (0.78 g., m. p. 79–81°) was recrystallized (m. p. 83.5–85°) and gave analytical figures indicating partial oxidation (C, 81.55; H, 7.01); the material was then oxidized in 50 cc. of acetic

(10) The use of 46% acid (Long and Burger[1] used 48% material) actually results in a much smoother reaction; a solid product is obtained directly.

(11) Long and Burger[1] found: C, 83.13; H, 7.86.

acid with 0.5 g. of permanganate at room temperature during three hours. The residue after filtration and evaporation *in vacuo* was taken up in ether, washed with soda, water, dried, and decolorized. From the extract, 0.6 g. of a viscous red oil was obtained which on solution in methanol, decolorization, precipitation with water, and two recrystallizations from methanol gave VII, 0.02 g., clusters of white needles, m. p. 107.5–108.5°. The material was identical in all respects with that obtained by chromic acid oxidation of the dimer (*vide infra*). Mixtures of VII with the dimer had melting points intermediate between those of the pure substances (*cf.*, *e. g.*, the partially oxidized material described above).

The manganese dioxide from the first oxidation (above) was leached with 350 cc. of boiling water. After concentration to half-volume, acidification gave 0.5 g. of a dark gum, which was taken up in soda, decolorized, extracted with ether to remove neutral impurities, and reacidified. The resultant granular yellow solid was crystallized from acetic acid to give pure IV: first, m. p. 201–203°; second, m. p. 201.5–203° (0.10 g. of colorless needles). Neut. equiv. Calcd. for $C_{11}H_{12}O_5$: 112.2. Found: 112.6.

(b) **By Chromic Acid.**—To the dimer (0.90 g.) in 75 cc. of glacial acetic acid, a solution of 0.56 g. of chromium trioxide in 15 cc. of glacial acetic acid and 10 cc. of water was added dropwise with stirring during one hour. After removal of most of the acetic acid *in vacuo*, water was added. The reaction mixture was extracted with ether, which was then washed with soda, water, and dried. The neutral residue after removal of solvent, crystallized from ethanol (0.15 g.), m. p. 107–108.5°. This material (VII), twice recrystallized from ethanol, formed long white needles, m. p. 108–109°.

Anal. Calcd. for $C_{22}H_{22}O_2$: C, 82.95; H, 7.00. Found: C, 83.56; H, 7.14.

Mixed with the material of like melting point from the permanganate oxidation (*vide supra*), m. p. 107.5–109°. The synthesis of this substance is described below.

Dehydrogenation of the Dimer: (a) With Sulfur.—The dimer (1.20 g., 0.0038 mole) mixed intimately with 0.60 g. of sulfur was heated on a metal bath; the hydrogen sulfide evolved was collected in a nitrometer over dilute sulfuric acid previously saturated with the gas. Evolution of gas began at 200°, and heating to 300° during two hours drove off 221 cc. (0.0092 mole) of hydrogen sulfide. The black mass was extracted with hot dilute acetic acid, the extract was evaporated *in vacuo*, the residue was extracted with methanol, from which a gummy solid separated on cooling. On recrystallization from methanol–ethyl acetate, 0.3 g. of V ($R = CH_3$) was obtained as white needles, m. p. 88–90°. This material was identical with that prepared more smoothly and in better yield by catalytic dehydrogenation (see (b), below).

In a similar experiment, extraction of the initial fusion product with ether left a light yellow residue, which on crystallization from toluene separated in straw-colored needles, m. p. 210–212° (10 mg.). Qualitative tests indicated the presence of sulfur in the material, and it was not further investigated.[12]

(b) **By Catalytic Dehydrogenation.**—The dimer (4.2 g., 0.013 mole) was mixed with 2.6 g. of 10% palladium-charcoal catalyst, and heated in a stream of carbon dioxide at 300° during four hours; the evolved gases (866 cc., 91% of the theoretical quantity for three moles of hydrogen per mole of compound) were collected over 20% sodium hydroxide solution in the usual way. The product was taken up in ether. The residual oil after evaporation of the filtered ethereal solution was distilled *in vacuo*, b. p. 255–260° (3 mm.). Crystallization of the viscous yellow distillate from the minimum quantity of acetic acid gave V ($R = CH_3$) as beautiful white needles, m. p. 89–90° (1.95 g.). Recrystallized from glacial acetic acid, m. p. 91–92°.

Anal. Calcd. for $C_{22}H_{18}O_2$: C, 84.03; H, 5.77. Found: C, 84.29; H, 5.93.

(12) *Cf.* Hudson and Robinson, *J. Chem. Soc.*, 718 (1941), for a similar result in the sulfur dehydrogenation of a tetralin derivative.

Mixed with the material of like melting point from the sulfur dehydrogenation ((a), above), the m. p. was 88–90°. The synthesis of this compound is described below.

6,6′-Dihydroxy-1,2′-binaphthyl (V, R = H).—To 6,6′-dimethoxy-1,2′-binaphthyl (0.8 g.) in 5 cc. of boiling glacial acetic acid, 5 cc. of 57% hydriodic acid was added dropwise during twenty minutes. The reaction mixture was boiled until a test portion was completely soluble in 5% aqueous sodium hydroxide. On pouring into 50 cc. of 1% sodium bisulfite solution, 0.6 g. of gummy material separated, which was crystallized from the minimum quantity of acetic acid as a purplish microcrystalline powder, m. p. 184–185° (0.4 g.). On recrystallization from acetic acid in the presence of a trace of zinc dust, the substance (V, R = H) separated in small light-yellow needles, m. p. 187–188.5°.

Anal. Calcd. for $C_{20}H_{14}O_2$: C, 83.90; H, 4.93. Found: C, 83.53; H, 5.43.

6-Bromo-β-naphthol was prepared by the elegant method of Franzen and Staubel[3]; from it, however, **6-methoxy-2-bromonaphthalene** was prepared more smoothly and in better yield by catalytic etherification, with methanol and sulfuric acid, than by the dimethyl sulfate–alkali method of those authors. The phenol (46 g.) in 50 cc. of methanol and 10 cc. of concentrated sulfuric acid was heated under reflux overnight. The solid mass of crystalline material was removed, washed in turn with methanol, water, caustic soda, and water, and crystallized from ethanol, white needles (43 g.), m. p. 102–103°. After distillation *in vacuo* (b. p. 160–164° (3 mm.)), m. p. 105–106°.

Condensation of 6-Methoxy-2-naphthylmagnesium Bromide with 6-Methoxy-α-tetralone.—In order to carry out successfully the preparation of the Grignard reagent, it was essential to use freshly distilled bromo compound.

6-Methoxy-2-bromonaphthalene (7.11 g.) in 250 cc. of dry ether was added during eight hours to 0.85 g. of magnesium turnings suspended in a small volume of ether under a current of dry nitrogen at the reflux temperature [ethyl bromide (0.8 cc.) and a crystal of iodine were added to start the reaction]. The solution was concentrated to 100 cc., 75 cc. of dry benzene was added, and the reaction-mixture was boiled for forty-eight hours with stirring. After addition of 6-methoxy-α-tetralone (4.3 g.) in 50 cc. of dry benzene, the solution was heated further for twenty-four hours. Then, with vigorous stirring, 100 cc. of 20% ammonium chloride solution was added; the organic layer was separated, washed, dried (sodium sulfate) and concentrated, finally *in vacuo*. Trituration of the residue with ether and methanol gave 3 g. of a yellowish-white solid, which crystallized from benzene–methanol in white needles, m. p. 127–128°. Twice recrystallized from benzene–methanol, the 6,6′-dimethoxy-3,4-dihydro-1,2′-binaphthyl (VI) separated in needles, m. p. 126°.

Anal. Calcd. for $C_{22}H_{20}O_2$: C, 83.50; H, 6.38. Found: C, 83.26; H, 6.04.

6,6′-Dimethoxy-1,2′-binaphthyl (V, $R = CH_3$) (by synthesis).—Dehydrogenation over 10% palladium charcoal catalyst (1 g.) of 1.5 g. of the synthetic compound (VI) at 300° gave 90 cc. of hydrogen (80%) at 25° and 760 mm., and, after solution of the organic product in ether, removal of catalyst, and evaporation of solvent, 1.4 g. of crystalline material, m. p. 87–92°. On recrystallization from glacial acetic acid, 6,6′-dimethoxy-1,2′-binaphthyl (V, $R = CH_3$) separated in white needles, m. p. 91–92°, identical in appearance with the substance obtained by the dehydrogenation of the dimer (*vide supra*), and mixed with that material, m. p. 91–92°.

Synthesis of 6,6′-Dimethoxy-1,2,3,4-tetrahydro-1,2′-binaphthyl (VII).—On hydrogenation of 107 mg. of the Grignard product (VI) (above), in glacial acetic acid over 50 mg. of reduced platinum oxide, 9.8 cc. (110% of the theoretical) of hydrogen was taken up during forty minutes (*p*, 760 mm.; *t*, 25°). After removal of catalyst, the product was precipitated as lustrous white plates (80 mg.), which were crystallized from alcohol, m. p. 106–107°. After two recrystallizations from ligroin, m. p. 107.5–

108.5°, mixed with the chromic acid (*or* permanganate) oxidation product of the dimer (*vide supra*), m. p. 107–108°.

6-Methoxy-3,4-dihydronaphthalene.—In the course of the above work, this material was obtained occasionally during distillation of 6-methoxy-α-tetralol, from hydrogenation of 6-methoxy-α-tetralone. The observation that the material in the pot was deep green when the decomposition occurred suggests that the irregularity was caused by the presence of a small amount of chromium salts in the ketone.

6-Methoxy-α-tetralone (9.0 g.) was hydrogenated in the usual way (*vide supra*). During distillation, decomposition occurred, and water appeared in the condenser: Fraction 1; 5.8 g., b. p. 110–118° (3 mm.); Fraction 2: 2.6 g. crystalline solid, m. p. 77–78°, b. p. 130–135° (3 mm.), mixed with 6-methoxy-α-tetralone, m. p. 77–78°. The low-boiling material was redistilled, 3.0 g., b. p. 107–111° (2.5 mm.); d^{30} 1.068; $n^{21}D$ 1.5825; M_R, 50.5. Calcd. for $C_{11}H_{12}O$, 4|", 48.3, ΔM_R = 2.2.

Anal. Calcd. for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 81.82; H, 7.53.

The physical constants may be compared with those of 6-methoxy-1,2,3,4-tetrahydronaphthalene [b. p. 105–106° (4 mm.), d^{19} 1.039, $n^{26.5}D$ 1.5441]. The absorption spectrum of the dihydro compound was measured in ethanol (Fig. 3), $\lambda_{max.}$ = 269 mμ, log ε = 4.00.

After shaking 2.8 g. of the material with 46% hydrobromic acid for twelve hours, a crystalline solid was obtained, which on crystallization from alcohol separated in lustrous white needles (1.72 g.), m. p. 70–72°. Recrystallized from alcohol, the m. p. was 75°; mixed with the dimer, m. p. 75°.

The dihydro compound also was obtained by the hydrolysis of 6-methoxy-1-acetoxytetralin with alcoholic sodium hydroxide.

Summary

The acid-catalyzed dehydration of 6-methoxy-1,2,3,4-tetrahydro-1-naphthol gives 6,6′-dimethoxy-1,2,3,3′,4,4′-hexahydro-1,2′-binaphthyl.

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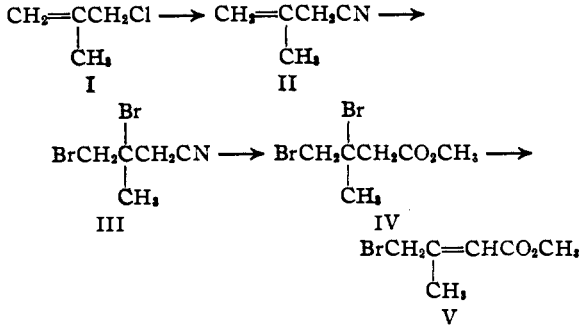
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Reformatsky Condensations Involving Vinylogs of Haloacetic Esters. II.[1] Methyl γ-Bromosenecioate

BY REYNOLD C. FUSON AND PHILIP L. SOUTHWICK[2]

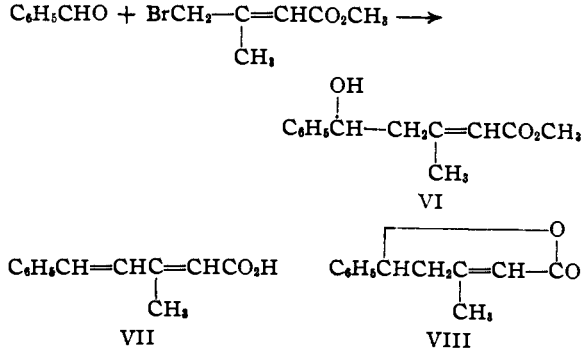
By the use of γ-halocrotonates in the Reformatsky reaction a synthetic route was found to polyene acids.[1] This method has now been extended to a β-methyl-γ-halocrotonate, methyl γ-bromosenecioate (V). The use of this new ester makes possible the extension of a carbon chain by an isoprene unit and thus opens the way for the synthesis of truly carotenoid chains.

After this work had been completed it was discovered that very similar results had been obtained by Ziegler, Schumann and Winkelmann.[3] One of the chief differences between our work and that of the German writers lies in the method of synthesis of the bromoester (V). The direct bromination of the senecioic ester[4] appears to be more convenient than our method which involved the conversion of methallyl chloride into methyl γ-bromosenecioate by the following scheme.



It was found that attempts to purify the ester obtained by this method were attended by very serious losses. For this reason the ester was used in a somewhat impure condition.

To determine whether the methyl γ-bromosenecioate could be condensed with carbonyl compounds by the Reformatsky method, a test run was made with benzaldehyde. The results were similar to those of Ziegler, Schumann and Winkelmann. The isolation and purification of the products presented difficulties. During the distillation and hydrolysis of the expected hydroxy ester (VI), decomposition occurred giving rise to a mixture of compounds. Chief of these were two isomeric unsaturated acids, evidently *cis–trans* forms of β-styrylcrotonic acid (VII). It is not clear which of these isomers corresponds to the product (m. p. 157°) described by Ziegler, Schumann and Winkelmann.



A third product isomeric with the two acids appeared to be the corresponding lactone (VIII).

(1) For the preceding paper see Fuson, Arnold and Cooke, THIS JOURNAL, 60, 2272 (1938).

(2) Abbott Fellow, 1942–1943.

(3) Ziegler, Schumann and Winkelmann, *Ann.*, 551, 120 (1942).

(4) Ziegler, Späth, Schaaf, Schumann and Winkelmann, *ibid.*, 551, 80 (1942).