[Contribution from the Institute of Organic Chemistry of the University of Budapest]

DIMERIC PROPENYL PHENOL ETHERS. XIII. ON METANETHOLE AND ITS TETRALIN ISOMERS

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Previous investigations (1, 2) have shown that metanethole has the structure of a 1-*p*-anisyl-2-methyl-3-ethyl-6-methoxyindan (I) since: (*a*) dehydrogenation failed to produce a naphthalene derivative; (*b*) the conversion of isoanethole (II) with stannic chloride, aluminium chloride, or titanium^{IV} chloride yields about 10% metanethole; (*c*) chromic acid oxidation of metanethole affords *p*-anisic acid, *o*-anisoylanisic acid, and a neutral colorless degradation-product $C_{18}H_{18}O_4$, the latter being found to undergo dehydration in the presence of alkali or of mineral acids to yield 1-*p*-anisyl-2-methyl-Δ^1-inden-3-one (III). However, van der Zanden and de Vries (3) expressed doubts as to the correctness of the structure assigned to metanethole on the above evidence. Their objections are the following: (*a*) Chromic acid oxidation of metanethole produces under certain conditions a neutral, orange-colored degradation-product ($C_{18}H_{14}O_4$) of m.p. 180.5° which—being a 1-*p*-anisyl-4-ethyl-3,4-naphthoquinone (IV)—would not be expected to arise from a structure I "unless one assumes an improbable course of the reaction with ring-opening and subsequent ring-closure"; (*b*) Both the Δ^1- and the Δ^2-isomer of 1-*p*-anisyl-2-methyl-3-ethyl-6-methoxyindene yield on catalytic hydrogenation the same indan I of m.p. 99° which, while its structure cannot be doubted, is definitely not identical with metanethole of m.p. 135°. On these reasons the authors consider the alternative of a 1-*p*-anisyl-4-ethyl-7-methoxytetralin (VI)[1] as being more consistent with the reactions and the presumable structure of metanethole.

However, the fact is the above arguments would not necessarily contradict the structure originally assigned to metanethole, while alternative VI remains difficult to reconcile with: (*a*) the expected mechanism of the acid-catalyzed dimerization of anethole; (*b*) the partial conversion of isoanethole to metanethole, and—particularly—(*c*) the behavior of metanethole on dehydrogenation.

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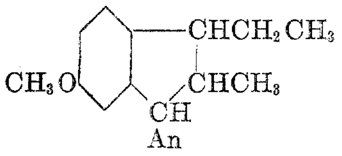
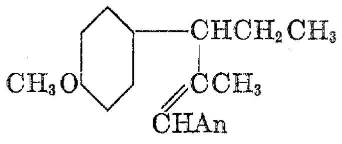
[1] Alternative VI represents an analog of the basic formula VII proposed some years ago by Staudinger and Dreher (4) for polyanethole on the evidence that the specific viscosity values of polyanethole samples were found to be actually about 30% higher than the values computed from the Staudinger viscosity formula on basis of the earlier suggested structure VIII (5). In preparative support of the suggestion that the anethole units of the polymer would be linked by C^{α}—$C^{\gamma'}$, rather than C^{α}—$C^{\beta'}$, bonds, it was stated that polyanetholes decompose on thermal cracking to anethole and to α,δ-di-*p*-anisyl-Δ^{α}-hexene that at 350° will be further decomposed to α,δ-di-*p*-anisylbutane, ethane, ethylene, and hydrogen. Preliminary experiments have shown, however, that chromic acid oxidation of cautiously sulfonated samples of polyanethole produces at least 0.6–0.7 mole of acetic acid per anethole unit. This seems to indicate the presence of mostly intact C-methyl groups in the polymer, unless eventual depolymerization during oxidation is to be made responsible for the formation of acetic acid.



I



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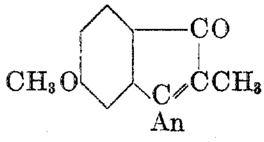
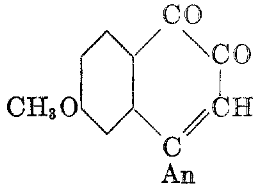
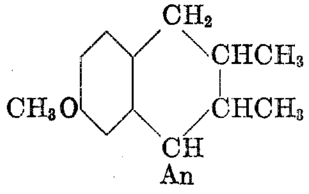


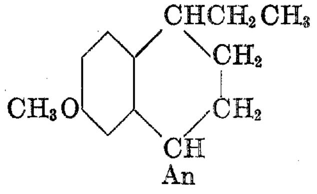
III



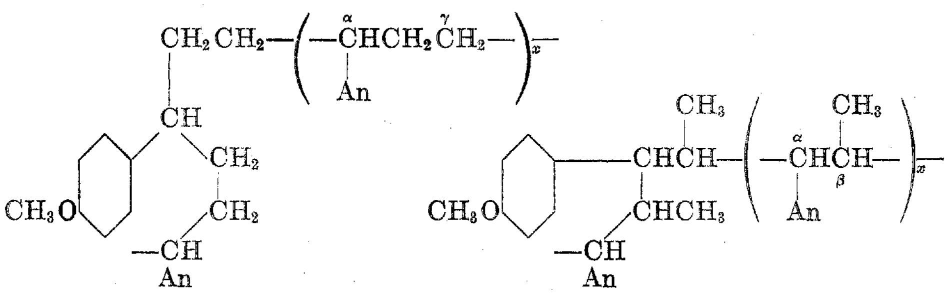
IV



V



VI



VII VIII

$An = C_6H_4(OCH_3)—4$

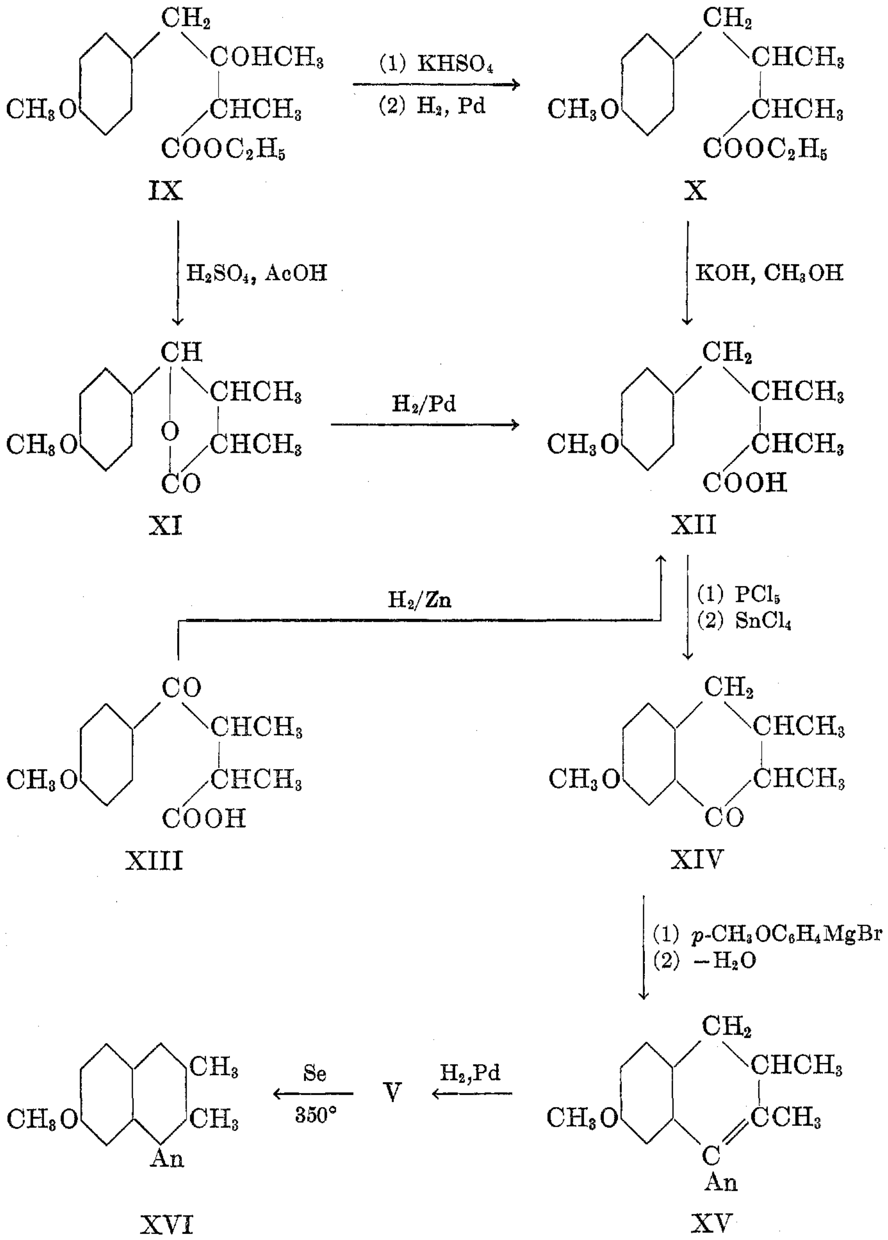
The fact that metanethole and diisohomogenol afford on dehydrogenation no naphthalene derivative is considered to constitute evidence—based on a fairly large amount of information on related compounds (6)—that these dimeric propenylphenol ethers cannot be tetralin derivatives. It was on this evidence that in the case of diisohomogenol Cartwright and Haworth (7) decided in favor of the indan structure, having found that 1-veratryl-6,7-dimethoxytetralin would readily undergo—quite in contrast to diisohomogenol—dehydrogenation to the corresponding naphthalene. The more direct comparison of diisohomogenol with 1-veratryl-2,3-dimethyl-6,7-dimethoxytetralin was made impossible by the fact that the tetralin remained unavailable by synthetic methods. However, the close analogy in the behavior of the two tetralins could not be doubted. Since it was unlikely that the presence of two methyl groups or of an ethyl group should materially effect the dehydrogenation of a 1-aryltetralin (*cf.* 8), the suggestion of van der Zanden and de Vries appears, for this reason, little justified. It must be admitted, however, that at present no direct evidence is available on the dehydrogenation of tetralins of the stated type of substitution and therefore the investigation of 1-*p*-anisyl-2,3-dimethyl-7-methoxytetralin (V) and of 1-*p*-anisyl-4-ethyl-7-methoxytetralin (VI) appeared desirable.

The synthesis of tetralin V requires α,β-dimethyl-γ-*p*-anisylbutyric acid (XII) as starting material. That acid was obtained by three different routes: (*a*) The condensation of anisole with α,β-dimethylsuccinic anhydride (m.p. 80–82°) by a Friedel-Crafts reaction gave somewhat unsatisfactory results (9), since the crystallization of α,β-dimethyl-γ-*p*-anisyl-γ-ketobutyric acid (XIII) was difficult, while the crude acid had a tendency to polymerize in the subsequent Clemmensen-Martin reduction; (*b*) Larger quantities of acid XII were prepared more conveniently from *p*-anisylacetone. This ketone was obtained either from anisole by a four-step route in about 10% over-all yield (*cf.* 10), or by oxidation of anethole with red lead in glacial acetic acid followed by hydrolysis of the resulting glycol diacetate mixture, the yield in this case being 52%. In a recently published paper Buzas and Dufour (11) report the similar oxidation of anethole, in more dilute solutions, 65% yield being obtained. *p*-Anisylacetone was condensed with ethyl α-bromopropionate, dehydratation of hydroxy ester IX with potassium hydrogen sulfate producing the corresponding $\Delta^{\beta,\gamma}$-crotonic ester presumably mixed with some of the $\Delta^{\alpha,\beta}$-siomer. The mixture was subsequently hydrogenated to X and then hydrolyzed to acid XII. (*c*) Hydroxy ester IX reacts with conc'd sulfuric acid to give crystalline α,β-dimethyl-γ-*p*-anisylbutyrolactone (XI). Catalytic hydrogenation of XI also gave, with fission of the lactone ring, acid XII.

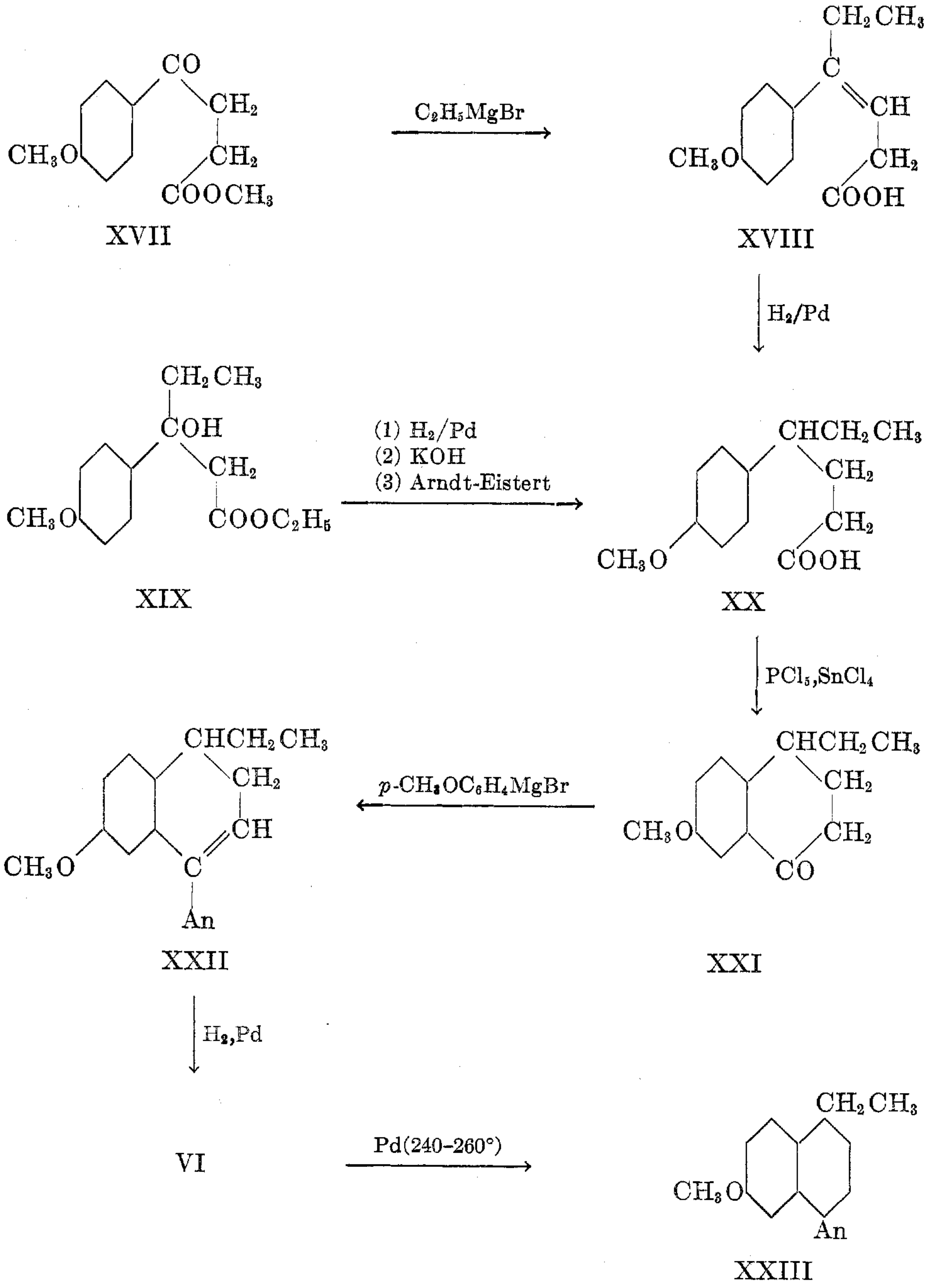
Cyclization of the acid by the phosphorus pentachloride-stannic chloride method (12) produced 2,3-dimethyl-7-methoxytetralone (XIV) in acceptable yield.

While α,β-dimethyl-γ-*p*-anisylbutyric acid was found to be insoluble in dilute alkali carbonate solutions, 2,3-dimethyl-7-methoxytetralone forms no oxime or semicarbazone under the usual conditions. For the low polarity of these compounds not only the methyl group adjacent to the carbonyl seems to be responsible but also the simultaneous methoxy substitution of the aromatic ring, since γ-*p*-anisylbutyric acid and β-methyl-γ-*p*-anisylbutyric acid are freely soluble in dilute sodium carbonate, and 7-methoxytetralone or 3-methyl-7-methoxytetralone—as also 2-methyl- and 2,4-dimethyl-tetralone (13, 14)—exhibit normal behavior toward carbonyl reactants. Accordingly, in the reaction of tetralone XIV with *p*-anisylmagnesium bromide, the dihydronaphthalene XV formed in but moderate yield. Tetralin V was prepared from the latter by catalytic hydrogenation.

The dehydrogenation of tetralin V proceeds similarly to that of 1-*p*-anisyl-7-methoxytetralin, both tetralins readily yielding the corresponding naphthalene in the presence of selenium at 350°.

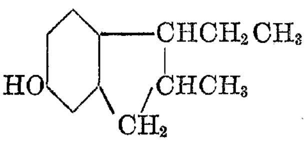


For the synthesis of tetralin VI, γ-*p*-anisylcapric acid (XX) had to be prepared. This was obtained: (*a*) from *p*-methoxypropiophenone condensed with ethyl bromoacetate, the resulting hydroxy ester (XIX) having been subjected, after undergoing hydrogenation and subsequent hydrolysis, to an Arndt-Eistert reaction; (*b*) from methyl γ-*p*-anisyl-γ-ketobutyrate (XVII) reacted with ethylmagnesium bromide, the resulting unsaturated acid (XVIII) being hydrogenated subsequently [*Cf.* (14)]. Cyclization of acid XX gave 4-ethyl-7-methoxytetralone (XXI) which was then converted to the tetralin VI in the usual way.



Dehydrogenation of tetralin VI with selenium at 350° gave a colored oil which could not be induced to crystallize or to form a picrate. The evolution of hydrogen selenide having been observed to begin even at 190–200°, in a second experiment the temperature was not allowed to exceed 260°, and in this case a crystalline naphthalene (XXIII) was obtained either with selenium or palladized charcoal.

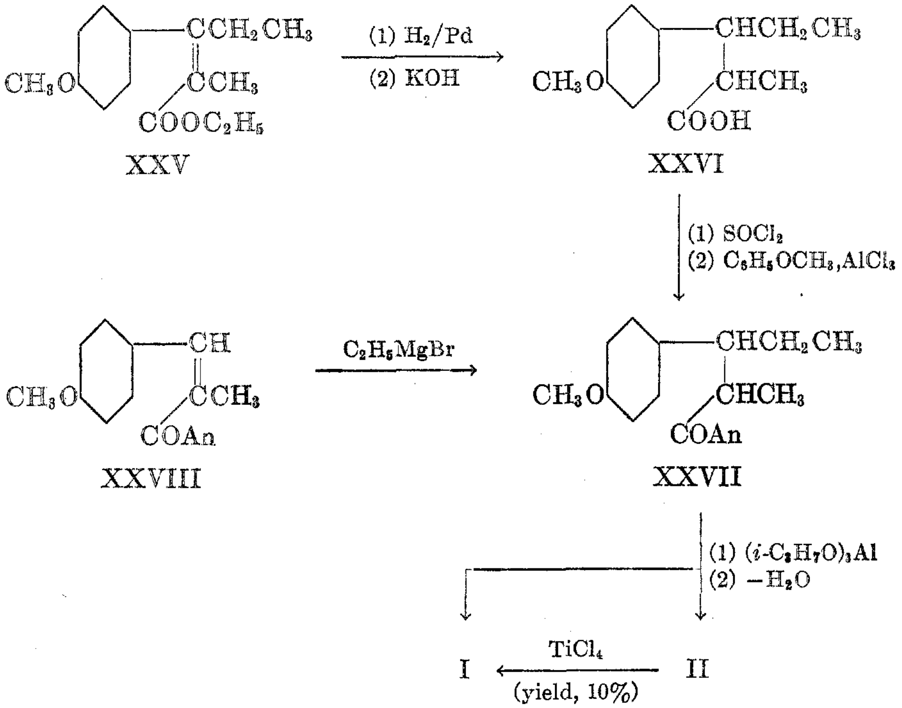
As the above results lead to a prediction that a tetralin of structure V or VI would undergo dehydrogenation, while a number of methods invariably failed to produce a naphthalene derivative from metanethole, a tetralin structure for the latter would appear to be highly improbable. At the same time, the indan I structure originally suggested for metanethole finds definitive confirmation in the observation, reported by Pailer, Müller, and Porschinski (15), that hydrogen iodide splits metanethole—in complete accordance with structure I—into 1-ethyl-2-methyl-5-hydroxyindan (XXIV) and phenol.



XXIV

The following formation of metanethole—by cyclization of an acyclic precursor—represents another conclusive proof of the indan structure of metanethole. The reaction of β-*p*-anisoylanethole (XXVIII) with ethylmagnesium bromide proceeds, as already stated by Stuart, Shukis, and Tallman (16), by 1,4-addition of the Grignard reagent (*cf.* 17). The authors describe the resulting β-anisoyl-γ-*p*-anisylpentane (XXVII) as a substance crystallizing from an equal volume of alcohol in two isomeric forms with melting points 52° and 72° respectively. In our case, the reaction failed to produce crystalline material. although the analysis and the further conversion of the substance obtained leaves little doubt as to its essential identity with the crystalline ketone described by Stuart, Shukis, and Tallman. The possibility that, for unforeseen reasons, our substance should be a structural isomer of XXVII resulting from an eventual 1,2-addition of the Grignard reagent appears to be excluded by the fact that, in analogy with the experience of Shukis and Ritter (18) in the alternative syntheses of γ-*p*-anisoyl-δ-*p*-anisylhexane, the product of the Friedel-Crafts reaction of α-methyl-β-*p*-anisylvaleryl chloride with anisole proved to be entirely identical with the oily ketone obtained from XXVIII. The ketone XXVII is stated to be rather unreactive forming no crystalline derivatives with carbonyl reactants. Also its reduction with aluminium isopropoxide was found to proceed rather slowly and, at least under the usual conditions of that procedure, incompletely. That fraction of the resulting product which is more volatile than the starting material proved to be isoanethole mixed with some metanethole. Synthetic isoanethole (II) produces with titanium^{IV} chloride—just like isoanethole obtained from anethole by dimerization [*cf.* (1)]—metanethole in the usual yield of 10%

[*cf.* 3], in further corroboration of the original suggestion of Baker and Enderby that metanethole would have, by analogy with that conversion (19), structure I.



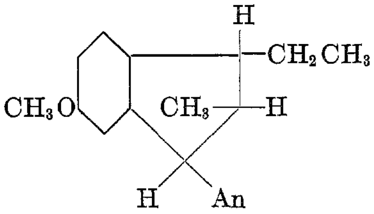
Under these circumstances, the observations of van der Zanden and de Vries would be expected to be reconciliable with the indan structure of metanethole. Indeed, this seems to be the case. The isolation of 1-*p*-anisyl-7-methoxy-3,4-naphthoquinone (IV) from oxidized metanethole remains entirely consistent with that structure, the questioned probability of a ring-opening and subsequent ring-closure in the oxidation process having been stated to occur in the closely related case of diisohomogenol. On evidence obtained by Doering and Berson (20), chromic acid appears to cleave the alicyclic ring of these indanes in the initial phase of oxidation. Indenone III, which is of synthetically established (3) structure, seems to be formed by ring-closure of a further oxidized (and so far not isolated) acyclic primary oxidation product, while in a still further phase the just formed alicyclic ring would be opened anew, the resulting acyclic α,β-diketone again undergoing ring-closure by way of an intramolecular aldol condensation.

Likewise, the stated non-identity of metanethole with synthetic indan I represents no contradiction to structure I of metanethole, the negative results experienced in the attempted interconversion remaining entirely consistent with the recently discussed (21) stereoisomeric interrelation of these substances. That relationship suggested that a distinction might be made between metanethole and synthetic indan I as the α- and the β-racemate, respectively, of the same 1-*p*-anisyl-2-methyl-3-ethyl-6-methoxyindan structure. An interconversion would fail for the reason that any stereoisomeric form of a structure like I remains fairly stable under not too drastic conditions, none of the asymmetric centers being readily accessible to inversion.

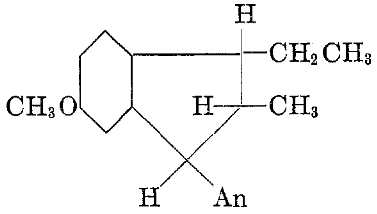
The respective mechanisms of the formation of these racemates appear to give already some indications concerning the actual configurations in question, the observation being made that (*a*) in the rearrangement of isoanethole, or in the dehydration of the reduction product of β-*p*-anisoyl-γ-*p*-anisylpentane, or in the dimerization of anethole, exclusively the α-racemate (metanethole) of m.p. 135° will be formed, while (*b*) in the hydrogenation of either of the two 1-*p*-anisyl-2-methyl-3-ethyl-6-methoxyindenes the β-racemate ("synthetic" indan I) of m.p. 100–101° would be the sole product.

The catalytic hydrogenation of a C—C double bond is known to occur mostly under preferential *cis* addition [*cf.* (8)]. This alone would constitute no safe configurational evidence in our case, since a host of examples demonstrates that, dependent on variable conditions, such as *e.g.* the presence of alkali in the reaction-mixture, *trans* addition may become considerable or even predominant (22), especially in the case of *trans*-substituted ethylenes (23). However, rigid alicyclic rings containing a double bond substituted with tertiary alkyl or aryl substituents represent ethylenes of fixed *cis* substitution. Such rings add hydrogen therefore—as known from a number of cases (24)—without exception and independently of eventual variations in the experimental conditions exclusively, or at least by far prevalently, in the *cis* position. For this reason, the conclusion that the doubly bonded carbons of the Δ^1-isomer of 1-*p*-anisyl-2-methyl-3-ethyl-6-methoxyindene acquire by hydrogenation of the double bond a C_1-C_2-*cis* configuration would be well within established experiences. By analogy, the C_2-C_3-*cis* configuration of the respective carbons in the hydrogenation product of the Δ^2-isomer of above indene appears to be secured with reasonable safety. The further experience that the respective hydrogenation-products of the two indene isomers are identical (3, 21) offers simultaneous evidence that (*a*) the β-racemate of I is to be considered as C_1-C_2-*cis*, C_2-C_3-*cis* configurated, (*b*) the hydrogenation of above indenes represents a cisoid *cis*-addition of hydrogen, *i.e.* both of the hydrogen atoms added will enter the indene in *cis* position relative to the hydrogen already present on the saturated carbon member of the alicyclic ring, since in case of a transoid *cis* addition the two isomeric indenes would form nonidentical hydrogenation products.

In the synthesis of the β-racemate, the final step of formation being addition of hydrogen which is subsequent to ring-closure, the carbons of the original double bond in the indene precursor would acquire of necessity a relative *cis* configuration. In the case of the α-racemate, however, ring-closure of an acyclic precursor being the final step of formation, a chance is offered to the substituents of the resulting saturated ring to take up a steric disposition that is not predetermined by the rigidity of an already fixed ring-system and which would differ from that present in the β-racemate on account of being more favorable in respect to energy content. Any racemate of structure I not identical with the *cis*,*cis* configurated β-racemate would differ from the latter only by one single alicyclic carbon inverted. Concerning the actual configuration of metanethole, *i.e.* the question as to which of the three alicyclic carbons would be the inverted one in the α-racemate, at present no definite answer seems to be available. However, the cyclization of isoanethole to metanethole appearing to represent a *trans* addition of the γ-*p*-anisyl group to the C_1-C_2 double bond, for metanethole either a C_1-C_2-*trans*, C_2-C_3-*cis* or a C_1-C_2-*trans*, C_2-C_3-*trans* configuration remains to be considered. From further investigations presently in progress we believe that the latter alternative is the more probable one.



metanethole, m.p. 135°
α-racemate (*trans, trans*?)



synthetic indan I, m.p. 100–101°
β-racemate (*cis, cis*)

EXPERIMENTAL

OXIDATION OF POLYANETHOLE

Polyanethole was prepared according to Staudinger and Dreher (4) by dropwise addition of 1 ml. of stannic chloride to a chilled solution of 5 g. of anethole in 5 ml. of anhydrous benzene. After being kept at room-temperature for five hours, the mixture was diluted with 20 ml. of benzene and shaken repeatedly with 10% hydrochloric acid. The benzene layer, washed consecutively with 5% sodium hydroxide solution and with water, left on evaporation an oil which solidified on subsequent trituration with pure methyl alcohol (from methyl oxalate) to a colorless powder. The product was refluxed with 30 ml. of *pure* methyl alcohol, then filtered while hot and washed with water. After drying over phosphorus pentoxide at 20 mm. and room temperature for several days, 2.7 g. of a colorless powder (Sample A) of the average mol. wt. 1220 (Rast) was obtained; liquefaction at 115–135°. When 1 ml. of titanium$^{\text{IV}}$ chloride was used in the above preparation in place of stannic chloride, the product (Sample B) (3.0 g.) had the average mol. wt. 1090 and was found to be liquefying at 95–100°. Neither of the samples absorbed hydrogen (in ethyl acetate solution) in the presence of a 5% palladium-charcoal catalyst at atmospheric pressure, while a parallel hydrogenation of isoanethole proceeded smoothly within 60 minutes.

For oxidation essentially the method of Kuhn and L'Orsa (25) was used. After dissolving 1.00 g. in 10 ml. of ice-cold conc'd sulfuric acid by shaking (12 hours), the slightly cherry-red solution was diluted with 25 ml. of water and then added to a mixture of 60 ml. of 5 *N* sodium dichromate, 25 ml. of conc'd sulfuric acid, and 50 ml. of water. After being refluxed for two hours, the excess of dichromate was destroyed by the dropwise addition of 10% hydrogen peroxide and the mixture was made alkaline with 30 g. of potassium hydroxide dissolved in 30 ml. of water. It was cooled in ice, and then acidified with 30 ml. of phosphoric acid (*d.* 1.7). The solution was next slowly distilled during which period 25 ml. of water was added gradually from a dropping-funnel. In the first 40 ml. of the distillate, which was found to contain no sulfate ions (by 5% $BaCl_2$), the acetic acid was determined by titration with 0.1 *N* sodium hydroxide, using phenolphthalein as indicator. Samples A and B gave 0.260, 0.279 and 0.277, 0.288 g. of acetic acid, respectively, corresponding to 0.645, 0.689, 0.676, and 0.712 mole of acetic acid calculated for $(C_{10}H_{12}O)_n$ per anethole unit.

Oxidation without previous sulfonation gave lower values, ranging from 0.43 to 0.54 mole of acetic acid, solution of the samples in the oxidation mixture then being incomplete. The residues of the evaporated titrated solutions were used to identify the acid in form of (a) the silver salt.

Anal. Calc'd for $C_2H_3AgO_2$: Ag, 64.6. Found: Ag, 64.2.

(b) Acetanilide, colorless plates from hot water, melting at 115° alone or mixed with an authentic specimen.

THE SYNTHESIS AND DEHYDROGENATION OF 1-*p*-ANISYL-7-METHOXYTETRALIN

7-Methoxytetralone (12) readily yields a *semicarbazone* under the usual conditions. Long colorless needles from alcohol, m.p. 224–226°, decomp.

Anal. Calc'd for $C_{12}H_{15}N_3O_2$: N, 18.0. Found: N, 17.6, 17.8.

1-p-Anisyl-7-methoxy-3,4-dihydronaphthalene. When 53.4 g. (0.3 mole) of 7-methoxytetralone in 200 ml. of ether was added to a solution, prepared from 8.7 g. (0.3 g.-atom + 10%) of magnesium turnings and 67 g. (0.3 mole + 20%) of *p*-bromoanisole in 200 ml. of ether, under vigorous stirring at room temperature, an oily complex instantly separated. Stirring was continued for another 15 minutes, then the mixture was poured into an ice-cold 5% ammonium chloride solution and 200 ml. of ethyl acetate. The organic layer, washed twice with water and dried over calcium chloride, left on evaporation at gradually reduced pressure an oily residue. This was distilled at 0.1 mm., giving as a first fraction a mobile colorless liquid, b.p. 135–145°. With increasing temperature the pressure varied between 0.1 and 0.8 mm., water being evolved from the mixture. At 190–200° a second fraction of a highly viscous pallid resin was obtained. Upon redistillation the first fraction gave 13 g. (24%) of 7-methoxytetralone, b.p. 140°/0.1 mm. and m.p. 61–62°, the higher-boiling part being added to the second fraction. This latter gave 51 g. of a pale yellow glass, b.p. 180–182°/0.1 mm., which rapidly crystallized from 120 ml. of alcohol, yielding 44 g. (70%) of colorless glistening plates, m.p. 65–66° [For the isomer with the methoxy group in the 6-position the b.p. 167°/0.15 mm. and m.p. 102° are recorded (26)]. In preparations using one-tenth of the above quantities the yield varied regularly between 10 and 25%.

A 5% solution of the product in glacial acetic acid (a) readily decolorized bromine and (b) gave a deep red coloration with conc'd sulfuric acid. For analysis the substance was twice recrystallized from alcohol containing 20% ethyl acetate without a change in melting point.

Anal. Calc'd for $C_{18}H_{18}O_2$: C, 81.2; H, 6.8.
Found: C, 81.2, 81.2; H, 7.1, 7.3.

1-p-Anisyl-7-methoxytetralin. A 10% solution of the foregoing dihydronaphthalene in 200 ml. of alcohol was hydrogenated at atmospheric pressure, in the presence of 1 g. of a 10% palladium-charcoal catalyst. In ten hours 1550 ml. of hydrogen were absorbed (calc'd 1680 ml.), the product slowly crystallizing from the solution. The mixture was warmed until boiling, then filtered and brought to crystallization by cooling in ice-water. After two recrystallizations from alcohol, 16.5 g. of stout colorless plates, m.p. 91°, were obtained. A 5% solution of the substance in glacial acetic acid gave but a feeble coloration with conc'd sulfuric acid, while an alcoholic solution under the same conditions gave a bright orange color.

Anal. Calc'd for $C_{18}H_{20}O_2$: C, 80.6; H, 7.5; OCH_3, 23.1.
Found: C, 80.8, 80.7; H, 7.6, 7.6; OCH_3, 22.9, 22.9.

1-p-Anisyl-7-methoxynaphthalene. (*a*) An intimate mixture of 2.7 g. (0.01 mole) of the above tetralin and 1.6 g. (0.02 g-atom) of red selenium was slowly heated (metal-bath) to 350° and kept there for six hours. On distillation at 2 mm. a pale yellow oil was obtained that crystallized readily from 4 ml. of alcohol. Recrystallization from alcohol-ethyl acetate (2:1) with the addition of charcoal, produced 1.7 g. of colorless plates, m.p. 85–86°. [For the 6-methoxy isomer m.p. 96–97° is recorded (26)]. (*b*) Replacing selenium in above experiment with 0.64 g. (0.02 g-atom) of finely powdered sulfur, the same product was obtained. The mixture was brought to 250° in about 90 minutes, this temperature being maintained for 15 minutes. The pale yellow distillate (0.5 g.) crystallized from ether-petroleum ether in small colorless needles, m.p. 85–86°. Recrystallization from alcohol-ethyl acetate afforded faintly yellow flat needles, m.p. 85–86°. A mixture of samples (a) and (b) showed no depression of the melting point. The solution in glacial acetic acid gave a deep yellow coloration on addition of conc'd sulfuric acid.

Anal. Calc'd for $C_{18}H_{16}O_2$: C, 81.8; H, 6.2.
Found (a): C, 81.6, 81.7; H, 6.2, 6.3.
(b): C, 81.7, 81.8; H, 6.3, 6.4.

After solution in alcoholic picric acid (saturated at room temperature), the deep orange solution deposited on slow evaporation large orange colored prisms, m.p. 82–83°, of a rather unstable *picrate*.

Anal. Calc'd for $C_{18}H_{16}O_2 \cdot C_6H_3N_3O_7$: N, 9.1. Found: N, 8.9, 8.8.

A *dinitro derivative* was obtained by adding 1 ml. of conc'd nitric acid to a solution of 0.4 g. of the naphthalene in 4 ml. of glacial acetic acid. The readily crystallizing product was several times recrystallized from glacial acetic acid, yielding 0.2 g. of intensely bright yellow needles, m.p. 217–218°.

Anal. Calc'd for $C_{18}H_{14}N_2O_6$: N, 7.9. Found: N, 7.6, 7.7.

THE SYNTHESIS AND DEHYDROGENATION OF 1-*p*-ANISYL-2,3-DIMETHYL-7-METHOXYTETRALIN

The preparation of p-anisylacetone from anisole. (a) *p-Methoxybenzyl chloride* (27) was prepared from 324 g. (3 moles) of anisole and 303 ml. of a 40% solution of formaldehyde (representing 4 moles of formaldehyde) by saturation of the mixture at −5° to −2° with dry hydrogen chloride within three hours. An initially formed colorless gelatinous suspension was dissolved again as saturation proceeded. The mixture was then poured onto ice and the oily layer was separated, dried over calcium chloride, and then fractionated at 16 mm. After a forerun (b.p. 60–110°) of about 40 ml., 220 g. (47%) of a colorless oil, b.p. 115–120°, was obtained, while 150 g. of higher-boiling material was left behind. (b) *p-Anisylacetonitrile* (28). A solution of 157 g. (1 mole) of *p*-methoxybenzyl chloride in 400 ml. of benzene was mixed with 105 g. of 70% pure sodium cyanide (representing 1.25 mole) in 400 ml. of water, and was stirred energetically for eight hours at 70°. After separation of the benzene layer, the aqueous solution was repeatedly extracted with ether. The extracts combined with the dark brown benzene solution, were washed with water and dried over sodium sulfate. After removal of the solvents at slightly reduced pressure, the remaining brown oil yielded on fractionation at 14 mm., 106 g. (70%) of a colorless liquid, b.p. 144–154°. A residue of higher-boiling tarry material was rejected. (c) *α-p-Anisyl-β-ketobutyronitrile.* A solution, prepared from 21 g. (0.72 g-atom + 20%) of metallic sodium and 260 ml. of absolute alcohol, was mixed with 106 g. (0.72 mole) of *p*-anisylacetonitrile in 95 ml. of dry ethyl acetate and refluxed on the water-bath for two hours, with occasional shaking. After 24 hours at room temperature, the mixture was poured into 400 ml. of water and was shaken with benzene or ether, in order to remove alkali-insoluble material. The alkaline layer was freed from dissolved organic solvents by being warmed to 30° at 20 mm. pressure, and then acidified with acetic acid. The precipitated oil quickly solidified into a mass of practically colorless needles, m.p. 80°, that crystallized readily from alcohol. Yield, 70 g. (62%). Goodall and Haworth (10) report for this substance, m.p. 80° and pale yellow color. (d) *p-Anisylacetone.* α-*p*-Anisyl-β-ketobutyronitrile (100 g.) was dissolved, with shaking and occasional warming on the water-bath, in a mixture of 150 ml. of conc'd sulfuric acid and 50 ml. of water. The resulting clear red-brown solution was placed upon the water-bath. After ten minutes, 900 ml. of water was added and the mixture was warmed for four hours. Extraction with ether followed, the extracts being washed subsequently with water and 5% sodium carbonate, then dried over sodium sulfate and freed from the solvent. Fractionation of the residue at 16 mm. gave 45–50 g. (47–52%) of a pale yellow liquid, b.p. 142–145°, which readily produced a semicarbazone (long colorless needles, m.p. 170–173°, from alcohol). Over-all yield, 9–11%.

The preparation of p-anisylacetone from anethole. To 592 g. (4 moles) of anethole in 200 ml. of glacial acetic acid, stirred constantly at 60°, 2500 g. (3.8 moles) of red lead were added in 50-g. lots, each portion being allowed to dissolve with decoloration before addition of a further quantity. Addition was completed in about six hours, while stirring was continued for an additional period of two hours at 70°. After dilution of the mixture with 6 liters of water, the supernatant oil was separated and the aqueous layer was repeatedly extracted with a total of 1800 ml. of benzene. The oil and the benzene extracts were combined and washed twice with water, once with 5% sodium carbonate and then again with water. The solution was freed from the solvent and dissolved water under slightly reduced pressure and then unchanged anethole (120 g.) was removed by distillation at 13 mm., until the boiling point rose above 152°. The residue was mixed with a four-fold volume of 25% sulfuric acid and kept boiling under reflux and vigorous stirring for six hours. After cooling, the oil was separated and the aqueous layer was extracted with benzene. The dark yellow oil was combined with the benzene extracts, washed with water, with 5% sodium carbonate, and again with water. The solution was dried with sodium sulfate and freed subsequently from the solvent on the water-bath. Distillation of the remaining yellow oil at 13 mm. gave, after a small forerun (30 g.), 273 g. of a pale yellow liquid of b.p. 142–146°, leaving behind 110 g. of higher boiling products. Yield, 52% (based on actually consumed anethole).

Separation of the fraction of b.p. 152–190°/13 mm. from the mixture, before treatment with sulfuric acid, gave a rather viscous bright yellow oil. Redistillation of this material afforded a practically pure mixture of the two α-methyl-β-*p*-anisylglycol diacetates, b.p. 177–196°/13 mm. (362 g., 45%). The conversion to *p*-anisylacetone proceeds nearly quantitatively in this case.

The ketone was obtained colorless only after repeated distillations from zinc foil. For the conversions here reported the crude product is sufficiently pure. The semicarbazone had m.p. 172–173°.

Buzas and Dufour (11) by working with more diluted solutions obtained a product, b.p. 145–147°/22 mm., in 65% yield.

Ethyl α,β-dimethyl-β-hydroxy-γ-p-anisylbutyrate (IX). A solution of 48 g. (0.3 mole) of *p*-anisylacetone and 60 g. (0.3 mole + 10%) of ethyl α-bromopropionate in 200 ml. of dry benzene was added to 22 g. (0.3 g-atom + 5%) of zinc foil (previously activated by heating with a few crystals of iodine). The mixture was heated until practically all metal dissolved (two to three hours). The somewhat viscous and opalescent red-brown solution was then cooled to room-temperature and poured into 10% sulfuric acid mixed with an equal weight of crushed ice. The benzene layer, after being washed twice with 200 ml. of 10% sulfuric acid or 5% hydrochloric acid and then with water, was dried over calcium chloride and evaporated at slightly reduced pressure. Distillation of the residue at 17 mm. gave between 110 and 175° a forerun of unreacted ethyl α-bromopropionate and *p*-anisylacetone, the reaction product distilling at 185–210° as a viscous yellow oil. Redistillation of the latter gave 54 g. (62%) of a pale yellow liquid, b.p. 203–206°/17 mm. or 193–196°/13 mm. A 5% solution in glacial acetic acid gave with conc'd sulfuric acid an initially faint, quickly deepening maroon coloration.

Anal. Calc'd for $C_{15}H_{22}O_4$: C, 67.6; H, 8.2.
Found: C, 67.7, 67.5; H, 8.4, 8.4.

α,β-Dimethyl-γ-p-anisylbutyrolactone (XI). A solution of 24 g. of hydroxy ester IX in 90 ml. of glacial acetic acid was mixed, without cooling, with 24 ml. of conc'd sulfuric acid and then warmed on the water-bath for 90 minutes. The deep brown solution was poured into ice-water, extracted with benzene, and the extract washed twice with water, twice with 5% sodium carbonate, and then again with water. Upon removal of the solvent at reduced pressure, a dark brown slowly crystallizing oil was obtained. Distillation of this product gave a pale yellow liquid, b.p. 152–154°/0.05 mm., about 5 g. of polymerized material being left behind. The distillate, partly solidifying in the receiver, readily crystallized from 20 ml. of alcohol, yielding 10–13 g. of stout colorless prisms, m.p. 85°. For analysis these were twice recrystallized from the solvent.

A 5% solution of the substance in glacial acetic acid (a) did not decolorize bromine, and (b) gave no coloration with conc'd sulfuric acid at room temperature (the warmed mixture turning gradually to dark orange with green fluorescence). The substance was insoluble in aqueous alkali and did not consume alkali in alcoholic solution at room temperature, while boiling hot alcoholic solutions could be titrated without difficulty. Aqueous alkaline solutions, obtained by gradually replacing the alcohol of an alcoholic alkaline solution on the water-bath with water, precipitated the lactone on addition of dilute hydrochloric acid.

Anal. Calc'd for $C_{13}H_{16}O_3$: C, 70.9; H, 7.3; Neut. equiv., 220.3.
Found: C, 71.0, 71.0, 70.8; H, 7.4, 7.3, 7.3; Neut. equiv., 224, 218.

α,β-Dimethyl-γ-p-anisyl-γ-ketobutyric acid (XIII). To 12.6 g. (0.088 mole + 10%) of aluminum chloride in 30 ml. of nitrobenzene, 6 g. (0.044 mole + 25%) of anisole and then 5.5 g. (0.044 mole) of α,β-dimethylsuccinic anhydride [m.p. 80–82°, (9)] were added in small portions at −5°. After 24 hours at room temperature the solution was poured upon crushed ice and conc'd hydrochloric acid and the mixture steam-distilled (three to four hours). The remaining dark brown semisolid was extracted with benzene and the extract washed with conc'd hydrochloric acid and water. Evaporation at reduced pressure left a partially crystallizing residue. This was mixed with about 5 ml. of alcohol, then kept for a few hours in the ice-box; in this way 3 g. of a somewhat colored crude acid, m.p. 106–108°, was obtained. The mother liquor was evaporated, the oily residue being subsequently dissolved in ether and extracted with 10% sodium carbonate. Acidification of the filtered extract with hydrochloric acid precipitated an oil that slowly solidified. After 48 hours the solid was air-dried and dissolved in a little benzene; 2 g. of nearly colorless needles, m.p. 125–127°, crystallized. The two crops of crystalline acid were separately recrystallized from water (charcoal) and were found to afford identical material: 4.2 g. (45%) of slender colorless prisms, m.p. 131–132°. For analysis the product was recrystallized from a little alcohol. A solution in glacial acetic acid acquired a bright orange color on addition of conc'd sulfuric acid.

Anal. Calc'd for $C_{13}H_{16}O_4$: C, 66.0; H, 6.8; Neut. equiv., 236.3.
Found: C, 66.2, 66.1; H, 7.1, 6.9; Neut. equiv., 237.

α,β-Dimethyl-γ-p-anisylbutyric acid (XII). (*a*) *From hydroxy ester* IX. An intimate mixture of 40 g. of IX and 30 g. of anhydrous potassium hydrogen sulfate was kept at 150–160° for two hours; then the temperature was raised to 170° and the pressure reduced to 0.1 mm. The distillate afforded on redistillation 34 g. of a pale greenish yellow oil, b.p. 175–190°/15 mm. The product, dissolved in glacial acetic acid, rapidly decolorized bromine and gave an instant deep maroon coloration with conc'd sulfuric acid. The oil, dissolved in 200 ml. of alcohol, was hydrogenated in the presence of a 10% palladium-charcoal catalyst at atmospheric pressure, absorbing in about ten hours 2700 ml. of hydrogen. On subsequent distillation 29 g. of an almost colorless oil (X), b.p. 132–135°, was obtained. This was refluxed with 200 ml. of 10% methyl alcoholic potassium hydroxide for two hours, the methyl alcohol being gradually replaced with water. The clear orange colored solution, diluted with 200 ml. of water and extracted repeatedly with ether, precipitated an oil on acidification with dilute hydrochloric acid. This was isolated with ether and distilled at 154–156°/0.06 mm., affording 20 g. of a viscous colorless liquid, n_{D}^{20} 1.5052 and neut. equiv. 224.9. (*b*) *From lactone* XI. A solution of α,β-dimethyl-γ-*p*-anisylbutyrolactone in 160 ml. of alcohol, hydrogenated at atmospheric pressure in the presence of a 10% palladium-charcoal catalyst, absorbed in about ten hours 1105 ml. of hydrogen. Evaporation of the filtered solution left an oil distilling at 152–153°/0.05 mm. as a viscous colorless liquid (10.3 g.), n_{D}^{20} 1.5049 and neut. equiv. 218.7. (*c*) *From acid* XIII. A mixture of 5 g. of α,β-dimethyl-γ-*p*-anisyl-γ-ketobutyric acid (m.p. 131°), 6.5 g. of amalgamated zinc foil, 15 ml. of toluene, and 10 ml. of conc'd hydrochloric acid was refluxed for 14 hours, 1 ml. of conc'd hydrochloric acid being added every hour. Then the toluene layer was separated, washed repeatedly with water, and evaporated at 14 mm. The residue distilled at 152–155°/0.05 mm. as an almost colorless viscous oil (3.9 g.), n_{D}^{20} 1.051 and neut. equiv. 226.4.

The acid was titrated in 20% alcohol at room temperature. The substance is freely soluble in aqueous 8% sodium hydroxide and is insoluble in 10% sodium carbonate. The solution in conc'd sulfuric acid is orange colored, while the solution in glacial acetic acid acquires, on addition of conc'd sulfuric acid, a bright yellow color.

Anal. Calc'd for $C_{13}H_{18}O_3$: C, 70.2; H, 8.2; Neut. equiv., 222.3.
Found: C, 70.3, 70.3, 70.0; H, 8.4, 8.5; 8.3.

The *sodium salt* separated from a solution of 1 g. of the acid in 15 ml. of aqueous 8% sodium hydroxide in flat colorless needles. These were recrystallized from a small quantity of water and then dried over silica gel at room temperature at 1 mm. On being heated, the substance melted at 88–92°, resolidified at about 115° and melted again at 195–200°, different preparations showing sometimes considerable deviations from these averages. The salt is readily soluble in alcohol.

Anal. Calc'd for $C_{13}H_{17}NaO_3 \cdot 0.5H_2O$: Na, 9.0. Found: Na, 8.9, 9.2.

2,3-Dimethyl-7-methoxytetralone (XIV). Employing mechanical stirring during the whole procedure, a chilled solution of 22 g. (0.1 mole) of acid XII in 200 ml. of anhydrous benzene was added to 22 g. (0.1 mole + 5%) of phosphorus pentachloride. In about 15 minutes almost complete dissolution took place, the solution being warmed subsequently to 50° for 15 minutes. Chilled again to 0°, a solution of 18 ml. (0.1 mole) of stannic chloride in 18 ml. of benzene was added from a dropping-funnel in about five minutes. The mixture assumed an orange coloration and an oily complex formed that quickly separated on the bottom of the flask. After about 15 minutes, 100 ml. of conc'd hydrochloric acid mixed with crushed ice was added, causing rapid decoloration and solution of the complex. Stirring was discontinued and the benzene layer was separated, while the aqueous layer was extracted several times with benzene. The combined benzene solutions were washed twice with 20% hydrochloric acid, twice with water, then twice with 10% sodium carbonate, and again with water. On removing the solvent at reduced pressure, a slightly colored quickly crystallizing residue was obtained that distilled at 134–136°/0.05 mm. as a pale yellow, quickly resolidifying oil. Recrystallization from a small quantity of alcohol, or from ether-petroleum ether, afforded 17 g. (85%) of colorless stout rhombic prisms, m.p. 63–65°. The solution in glacial acetic acid, on addition of conc'd sulfuric acid, acquired a bright yellow color that turned gradually to orange.

No oxime or semicarbazone was obtained.

Anal. Calc'd for $C_{13}H_{16}O_2$: C, 76.4; H, 7.9; OCH_3, 15.2.
Found: C, 76.6, 76.5; H, 7.9, 8.1; OCH_3, 15.0, 15.4.

1-p-Anisyl-2,3-dimethyl-7-methoxy-3,4-dihydronaphthalene (XV). To a solution prepared from 2.7 g. (0.1 g-atom + 10%) of magnesium turnings and 21.0 g. (0.1 mole + 10%) of *p*-bromoanisole in 80 ml. of ether, was added 15 g. (0.075 mole) of XIV in 150 ml. of benzene-ether (2:1) with vigorous stirring. After being refluxed for 60 minutes, the mixture was poured into ice-water containing 5% ammonium chloride and 2% hydrochloric acid. The supernatant layer was removed and washed repeatedly with 2% hydrochloric acid and with water. The solution was dried with calcium chloride, leaving on evaporation a pale yellow oil. Distillation of this material afforded (*a*) 65–75°/16 mm., 4.5 g. of *p*-bromoanisole; (*b*) 140–160°/0.1 mm., a yellow oil containing 9.5 g. of unchanged 2,3-dimethyl-7-methoxytetralone; (*c*) 180–200°/0.05–0.1 mm., 9.2 g. of a pale yellow viscous oil. The latter fraction was redistilled. At 185–190°/0.1 mm., 1.0 g. of a yellow liquid was obtained that partly crystallized from 1.0 ml. of alcohol, yielding 0.3 g. of *p,p'*-dianisyl (29), colorless glistening plates, m.p. 175–176°.

Anal. Calc'd for $C_{14}H_{14}O_2$: C, 78.4; H, 6.6.
Found: C, 78.7, 78.5; H, 6.7, 6.7.

At 190–210°/0.1 mm. a pale yellow highly viscous oil (7.5 g.) distilled, crystallizing from 8 ml. of alcohol in colorless clusters of needles. Recrystallization from 30 ml. of alcohol afforded 6 g. (28%) of stout colorless prisms, m.p. 84–86°. This gave a deep cherry red coloration with alcoholic sulfuric acid, and instant decoloration of bromine in chloroform or in glacial acetic acid.

Anal. Calc'd for $C_{20}H_{22}O_2$: C, 81.8; H, 7.5; OCH_3, 21.1.
Found: C, 81.8, 81.6; H, 7.9, 7.7; OCH_3, 20.5, 21.2.

The yield did not improve on replication of the synthesis with the threefold of above quantities.

1-p-Anisyl-2,3-dimethyl-7-methoxytetralin (V). A solution of 10 g. of XV in 200 ml. of alcohol, hydrogenated at atmospheric pressure in the presence of 1.0 g. of 10% palladium-charcoal, absorbed in eight hours 600 ml. of hydrogen (calc'd 750 ml.). The mixture, warmed until boiling and then filtered, was concentrated to 80 ml., depositing on cooling 6.5 g. of elongated stout needles, m.p. 121–123° (the mother liquor yielding on further concentration 1.7 g. of XV). Two consecutive recrystallizations from glacial acetic acid raised the melting point to 124–126°; a feeble orange coloration in glacial acetic acid on addition of conc'd nitric acid.

Anal. Calc'd for $C_{20}H_{24}O_2$: C, 81.0; H, 8.2; OCH_3, 20.9.
Found: C, 80.7, 80.8; H, 8.5, 8.4; OCH_3, 20.9, 20.9.

Upon seeding the warm saturated solution in glacial acetic acid, or the melt, with metanethole of m.p. 135°, and *vice versa,* no alteration of the respective melting points was observed. A 1:1 mixture of V with metanethole of m.p. 135° melts at 109–119°, the 1:2 mixture melting at 108–113°. To a mixture of 0.1 g. of V and 1.0 ml. of glacial acetic acid 0.8 ml. of conc'd nitric acid was added. In about five minutes an orange colored solution was obtained which remained perfectly clear on prolonged standing [Metanethole gave under strictly identical conditions yellow needles, m.p. 190–191°, of the dinitro derivative (1) within eight minutes].

The *dibromo derivative* was prepared by adding to 0.3 g. (0.001 mole) of V in 10 ml. of glacial acetic acid, 10 ml. of glacial acetic acid containing 0.45 g. (0.003 mole) of bromine. After short standing, very slender colorless needles, m.p. 153–154°, separated. A 1:1 mixture of the product and dibromometanethole of m.p. 137–138° was found to melt at 120–125°.

Anal. Calc'd for $C_{20}H_{22}Br_2O_2$: C, 52.9; H, 4.9.
Found: C, 52.6, 52.7; H, 5.0, 5.2.

1-p-Anisyl-2,3-dimethyl-7-methoxynaphthalene (XVI). A mixture of 3.0 g. (0.01 mole) of tetralin V and of 3.1 g. (0.02 g-atom + 100%) of finely powdered red selenium, slowly heated to 350° and kept at this temperature for eight hours (metal-bath), at 2 mm. gave a pale yellow oily distillate contaminated with some selenium. Crystallization from ethyl acetate-alcohol 1:1, followed by further purification through the picrate, afforded 0.9 g. of colorless bricks, m.p. 82–83°. The solution in glacial acetic acid acquired on addition of conc'd nitric acid a fairly intense orange coloration.

Anal. Calc'd for $C_{20}H_{20}O_2$: C, 82.1; H, 6.9.
Found: C, 82.1, 82.3; H, 7.1, 7.1.

The *picrate,* obtained by dissolving XVI in an alcoholic solution of the calculated amount of picric acid (saturated at room temperature), forms red needles, m.p. 127–128°.

Anal. Calc'd for $C_{20}H_{20}O_2 \cdot C_6H_3N_3O_7$: N, 8.1. Found: N, 8.3, 8.2.

A mixture of the monobromo and the dibromo derivative of XVI separated from a dilute solution in glacial acetic acid on addition of bromine as colorless needles, melting at 156–164° after recrystallization from alcohol.

On addition of 1 ml. of conc'd nitric acid to 0.4 g. of XVI in 10 ml. of glacial acetic acid, pale yellow needles separated within a few minutes from the dark orange solution. The product, recrystallized from butyl acetate, melted at 204–206°, after softening at 165°, changing its color when exposed to light from light yellow to beige, the surface of the crystals turning deep brown. Analysis indicated the composition of a dinitro derivative of XVI, the actual figures spreading over a considerable range.

THE PREPARATION OF 3-METHYL-7-METHOXYTETRALONE

Ethyl β-methyl-β-hydroxy-γ-p-anisylbutyrate. From a mixture of 20 g. of *p*-anisylacetone, 21 g. of ethyl bromoacetate and 8 g. of activated zinc foil in 90 ml. of anhydrous benzene, 25 g. of a pale yellow oil, b.p. 195–196°/15 mm., was obtained, employing the procedure described for IX.

Anal. Calc'd for $C_{14}H_{20}O_4$: C, 66.6; H, 7.9.
Found: C, 66.4, 66.5; H, 8.2, 8.1.

β-Methyl-γ-p-anisylbutyrolactone. A solution of 24 g. of the above hydroxy ester in 90 ml. of glacial acetic acid was mixed with 25 ml. of conc'd sulfuric acid, and kept on the water-bath for 90 minutes. Subsequent isolation and distillation of the reaction product gave 16 g. of a pale yellow liquid, b.p. 167–168°/0.05 mm. Dissolved in 18 ml. of alcohol, 5.3 g. of stout colorless prisms separated. After one recrystallization from the same solvent, the melting point was 93–94°. The product did not decolorize bromine. At room temperature the solution in glacial acetic acid gave no coloration with conc'd sulfuric acid. The substance was insoluble in 10% aqueous sodium carbonate, or in 8% aqueous sodium hydroxide. Acidification of the alkaline solutions, obtained by gradual dilution of the solution in warm alcoholic alkali with water and subsequent removal of the alcohol, precipitated a quickly solidifying oil, which was readily crystallized from dilute alcohol, forming colorless plates, m.p. 93–94°, and was found to be identical with the starting material.

Anal. Calc'd for $C_{12}H_{14}O_3$: C, 69.9; H, 6.8; Neut. equiv., 206.1.
Found: (a) C, 69.9, 69.9; H, 7.1, 7.1; Neut. equiv., 205, 210.
(b) C, 70.0; H, 7.0; Neut. equiv., 209.
a = original sample; b = sample recovered from alkaline solution

β-Methyl-γ-p-anisylbutyric acid. A solution of 2.06 g. (0.01 mole) of the above lactone in 50 ml. of alcohol absorbed, at atmospheric pressure in the presence of a 5% palladium-charcoal catalyst, 190 ml. of hydrogen in 14 hours. The filtered solution was evaporated and the oily residue was shaken with 150 ml. of 5% sodium carbonate and 100 ml. of ether. Acidification of the alkaline layer gave an oily precipitate that was isolated by extraction with ether as a not solidifying colorless viscous oil (1.6 g.). The product was readily soluble in cold 10% sodium carbonate or in 8% aqueous sodium hydroxide. It gave no coloration with alcoholic sulfuric acid.

Anal. Calc'd for $C_{12}H_{16}O_3$: Neut. equiv., 208.1. Found: Neut. equiv., 212, 210.

3-Methyl-7-methoxytetralone. The solution of 1.5 g. of the above acid in 20 ml. of benzene was added to 1.4 g. of phosphorus pentachloride, and to the resulting solution 1.4 ml. of stannic chloride in 5 ml. of benzene was added as in the preparation of XIV. Hydrolysis of the deep orange crystalline complex was accomplished by the addition of 10 g. of ice and 5 ml. of conc'd hydrochloric acid to the reaction mixture. Evaporation of the benzene layer left an oil which solidified, on being chilled, to a mass of colorless crystals. Recrystallization from petroleum ether afforded 0.7 g. of stout colorless needles, m.p. 36–37°. The solution in glacial acetic acid turned to bright orange on addition of conc'd sulfuric acid.

Anal. Calc'd for $C_{12}H_{14}O_2$: C, 75.8; H, 7.4.
Found: C, 75.4, 75.6; H, 7.6, 7.5.

The *semicarbazone* formed readily when 0.3 g. of the tetralone and 0.2 g. of semicarbazide acetate was refluxed in 80 ml. of 50% alcohol for one hour. On standing overnight, the solution deposited colorless rosettes, affording after one recrystallization from dilute alcohol, 0.3 g. of stout needles, m.p. 175–176°.

Anal. Calc'd for $C_{13}H_{17}N_3O_2$: N, 17.0. Found: N, 16.7, 16.9.

THE SYNTHESIS AND DEHYDROGENATION OF 1-*p*-ANISYL-4-ETHYL-7-METHOXYTETRALIN

β-Hydroxy-β-p-anisylvaleric acid (corresponding to XIX). A mixture of 54 g. (0.33 mole) of *p*-methoxypropiophenone, 56 g. (0.33 mole) of ethyl bromoacetate, and 22 g. (0.33 g-atom) of zinc foil in 100 ml. of anhydrous benzene was refluxed until the metal dissolved (two to three hours). Worked up as usual, 56 g. of a pale yellow oil (XIX), b.p. 178–180°/10 mm., was obtained. The product was sufficiently pure for the preparation of XX. In the present case the product was refluxed with 300 ml. of 10% methyl alcoholic sodium hydroxide for three hours and then water was added. After extraction of the turbid mixture with ether, acidification of the alkaline layer with 10% hydrochloric acid precipitated an oil that was isolated by extraction with ether. The extract, washed and dried as usual, gave on evaporation a crystalline residue. This was recrystallized from ether, yielding 51 g. (68%) of small colorless needles, m.p. 96–97° decomp.

Anal. Calc'd for $C_{12}H_{16}O_4 \cdot H_2O$: C, 59.5; H, 7.5; Neut. equiv., 242.2.
Found: C, 59.7, 59.6; H, 7.6, 7.7; Neut. equiv., 239

β-p-Anisylvaleric acid. The above acid (50 g.) was esterified upon solution in 250 ml. of alcohol saturated with dry hydrogen chloride at 0° for 18 hours. After 30 minutes' refluxing, the solution was evaporated. Subsequent distillation afforded 46 g. of XIX as a colorless oil of b.p. 170–172°/9 mm. (The undistilled ester XIX likewise is usually suited for the subsequent hydrogenation.) The ester was dissolved in 150 ml. of alcohol and hydrogenated at atmospheric pressure, in the presence of 0.8 g. of a 5% palladium-charcoal catalyst, absorbing 4.6 liters of hydrogen in eight hours. The solution was filtered and after addition of 15 g. of sodium hydroxide in 150 ml. of alcohol, it was refluxed for three hours. After removal of 200 ml. of the solvent, water was added and the mixture was extracted with benzene. Acidification of the alkaline layer precipitated an oil. This was isolated by extraction with benzene, evaporation of the solvent leaving a solid residue. Crystallization from benzene afforded 26 g. (43%) of colorless needles, m.p. 75–77°.

Anal. Calc'd for $C_{12}H_{16}O_3$: C, 69.2; H, 7.7; Neut. equiv., 208.2.
Found: C, 69.3, 69.4; H, 7.8, 8.0; Neut. equiv., 206.

The *chloride* was prepared from 15 g. of the acid refluxed with 30 ml. of thionyl chloride for two hours, the product, after removal of the excess reagent, distilling at 148–150°/11 mm. as a faintly colored oil (13.3 g.).

The *amide* separated on dissolving a sample of above chloride in aqueous 25% ammonia. Washed with water, it formed colorless needles, m.p. 97–98°.

Anal. Calc'd for $C_{12}H_{17}NO_2$: N, 6.7. Found: N, 6.5, 6.7.

Methyl γ-p-anisyl-γ-ketobutyrate (XVII). A mixture of 11 g. of γ-*p*-anisyl-γ-ketobutyric acid, 30 ml. of absolute methyl alcohol, and 2 ml. of conc'd sulfuric acid was refluxed for six hours, then poured upon ice and extracted with ether. The extract was washed with sodium carbonate solution, dried with calcium chloride, and freed from the solvent. The oily residue, b.p. 155–160°/0.05 mm., solidifies in the receiver to a colorless mass of needles, m.p. 50°.

Anal. Calc'd for $C_{12}H_{14}O_4$: C, 64.9; H, 6.3.
Found: C, 64.7; H, 6.4.

γ-p-Anisyl-Δ^{β}-pentenoic acid (XVIII). A solution, prepared from 3.6 g. (0.15 g-atom) of magnesium foil, 16.3 g. (0.15 mole) of ethyl bromide, and 65 ml. of ether, was slowly added by drops to a vigorously stirred and cooled to −10° solution of 21 g. (0.1 mole) of XVII in 120 ml. of ether and 30 ml. of benzene. The mixture was then warmed gradually to 40° and kept there, with continuous stirring, for three hours. After standing overnight, the pale yellow crystalline complex was decomposed by addition of ice and conc'd hydrochloric acid. The ethereal layer was repeatedly extracted with 10% sodium carbonate solution, the extract precipitating the acid as a yellow oil on acidification. This was isolated by extraction with ether. Upon removing the solvent, the oily residue (11.6 g., 51%) solidified on standing to a mass of flat needles. No solvent, or solvent mixture, having been found to be satisfactory for recrystallization, the product was distilled at 0.05 mm. The solidifying but somewhat waxy distillate was smeared upon a porous tile and in this way soft colorless small needles, m.p. 54–55°, were obtained. A solution in glacial acetic acid gave no appreciable coloration on the addition of conc'd nitric acid.

Anal. Calc'd for $C_{13}H_{16}O_3$: C, 70.9; H, 7.3; Neut. equiv., 220.3.
Found: C, 70.7, 70.8; H, 7.4, 7.5; Neut. equiv., 225.

γ-p-Anisylcapric acid (XX). (*a*) A solution of 13.2 g. of β-*p*-anisylvaleryl chloride in 40 ml. of absolute ether was mixed with 300 ml. of an ethereal solution of diazomethane prepared from 30 g. of nitrosomethylurea. After 12 hours at room temperature the solvent was removed and the remaining yellow oil was dissolved in 60 ml. of dioxane. The solution was then added dropwise, with vigorous stirring, to a mixture of silver oxide (prepared from 14 g. of silver nitrate) and 14 g. of sodium thiosulfate in 300 ml. of water warmed to 60–70°. After the addition was completed, the mixture was stirred for one additional hour at 70°, and then made alkaline with aqueous 8% sodium hydroxide. Following to filtration through a small column of alumina, the clear solution was acidified with 3% nitric acid and the precipitated oil was isolated by extraction with ether. Removal of the solvent left 9 g. of a yellow oil, b.p. 180°/1.5 mm., that solidified after some standing to a faintly colored waxy mass of crystals. This was smeared onto a porous tile and small colorless needles, m.p. 38–40°, were obtained. No solvent for recrystallization was found. (*b*) A solution of 11.5 g. of XVIII in 100 ml. of alcohol was hydrogenated in the presence of a 5% palladium-charcoal catalyst and a few drops of 10% palladous chloride solution; in eight hours 1100 ml. of hydrogen was absorbed. Evaporation of the filtrate left 11.0 g. of a colorless oil, b.p. 150°/0.05 mm., which readily crystallized on being seeded with a sample of the acid obtained by method (*a*). The waxy crystal mass was freed from a contaminating oil as above, when the product melted at 37–39°.

Anal. Calc'd for $C_{13}H_{18}O_3$: C, 70.2; H, 8.2; Neut. equiv., 222.3.

Found: C, 70.0, 70.2; H, 8.3, 8.3; Neut. equiv., 217, 212.

4-Ethyl-7-methoxytetralone (XXI). To 8 g. of phosphorus pentachloride, 8 g. of crude (waxy) XX in 80 ml. of dry benzene was added with ice-cooling. The mixture, after being warmed with stirring to 60° for 15 minutes and then chilled again, was mixed with 7.2 ml. of stannic chloride in 30 ml. of benzene. The instantly separating pale yellow solid dissolved upon the addition of a mixture of conc'd hydrochloric acid and crushed ice. The usual isolation produced 5.2 g. (71%) of a mobile pale yellow liquid, b.p. 126–130°/0.3 mm. It gave a rather faint brown yellow coloration with conc'd sulfuric acid in glacial acetic acid solution.

Anal. Calc'd for $C_{13}H_{16}O_2$: C, 76.4; H, 7.9.

Found: C, 76.3; H, 8.2.

A *semicarbazone* readily formed on refluxing 0.2 g. of XXI in 15 ml. of 60% alcohol with 0.2 g. of semicarbazide acetate (two hours); after one recrystallization from alcohol colorless needles, m.p. 169–171°, were obtained.

Anal. Calc'd for $C_{14}H_{19}N_3O_2$: N, 15.9. Found: N, 16.0, 15.9.

1-p-Anisyl-4-ethyl-7-methoxy-3,4-dihydronaphthalene (XXII). From a solution of 1.8 g. (0.0075 g-atom) of magnesium foil and 14 g. (0.0075 mole) of *p*-bromoanisole in 70 ml. of ether, and 10 g. (0.005 mole) of 4-ethyl-7-methoxytetralone (XXI) in 30 ml. of ether, the dihydronaphthalene was obtained by the usual procedure. Stout colorless prisms, m.p. 70–71°, after one recrystallization from alcohol, (6.8 g., 34%) were obtained. It gave a deep red brown coloration with conc'd sulfuric acid in glacial acetic acid solution and instant decoloration of bromine.

Anal. Calc'd for $C_{20}H_{22}O_2$: C, 81.8; H, 7.5.

Found: C, 81.7, 81.8; H, 7.7, 7.8.

1-p-Anisyl-4-ethyl-7-methoxytetralin (VI). A solution of 5.7 g. of XXII in 80 ml. of alcohol, hydrogenated in the presence of 0.5 g. of a 10% palladium-charcoal catalyst at atmospheric pressure, absorbed in 60 minutes 420 ml. of hydrogen. The mixture was warmed until boiling, then filtered and concentrated to 30 ml. to give long colorless slender needles (5.0 g.), melting after two recrystallizations from alcohol at 78–80°. The solution in glacial acetic acid gave on addition of conc'd sulfuric acid a pale orange coloration which however is more intensive than that of metanethole under identical conditions.

Anal. Calc'd for $C_{20}H_{24}O_2$: C, 81.0; H, 8.2.

Found: C, 80.9, 81.1; H, 8.1, 8.2.

Upon addition of 0.8 ml. of conc'd nitric acid to a suspension of 0.1 g. of the substance in 1.0 ml. of glacial acetic acid, a deep orange colored solution was obtained that remained perfectly clear on prolonged standing.

1-p-Anisyl-4-ethyl-7-methoxynaphthalene (XXIII). (*a*) A mixture of 2 g. of VI and 1.4 g. of red selenium, heated very gradually within four hours to 250–260° and kept at this temperature for six hours, gave on subsequent distillation at 0.1 mm. a pale yellow oil

(Higher temperature was found to be detrimental). The distillate, dissolved in 4.0 ml. of alcohol-ethyl acetate (9:1), crystallized after a few days in soft clusters composed of very slender, somewhat interlacing, colorless needles, m.p. 68–70° (0.4 g.). (*b*) Heating a mixture of 2.0 g. of VI and 1.0 g. of 10% palladium-charcoal as above, followed by distillation at 0.06 mm. afforded 0.9 g. of a colorless oil that readily crystallized from a little ether and was recrystallized from a small amount of alcohol. Interlacing very fine needles (0.5 g.), m.p. 69–70° alone or mixed with the product of the selenium method. It gave an intense yellow coloration in glacial acetic acid on addition of conc'd nitric acid. Upon analyzing the substance, it was found that it retains tenaciously traces of impurities that are difficult to remove by repeated recrystallizations from alcohol and which cause no negligible spreading of the figures obtained for carbon. The following is the analysis of a sample recovered from the picrate, then filtered in ethereal solution through a small column of aluminium oxide and recrystallized twice from alcohol, being finally dried over phosphorus pentoxide at 20°/3 mm.

Anal. Calc'd for $C_{20}H_{20}O_2$: C, 82.1; H, 6.9.
Found: C, 82.2, 81.7, 81.6; H, 7.1, 7.1, 6.9.

The *picrate* crystallized from an alcoholic solution of XXIII containing a slight excess of picric acid as red-brown bricks or stout needles, m.p. 78–82°. The product was dried for analysis over phosphorus pentoxide at 20°/3 mm.

Anal. Calc'd for $C_{20}H_{20}O_2 \cdot C_6H_3N_3O_7$: C, 59.9; H, 4.4; N, 8.1.
Found: C, 60.0; H, 4.7; N, 8.3, 8.3.

SYNTHETIC PREPARATION OF A MIXTURE OF ISOANETHOLE AND METANETHOLE

β-p-Anisoylanethole (*p,p'*-Dimethoxy-*α*-methylchalcone, XXVIII). A mixture of 16.4 g. (0.1 mole) of *p*-methoxypropiophenone and 13.6 g. (0.1 mole) of *p*-anisaldehyde was chilled in ice and saturated with a current of dry hydrogen chloride (two hours). The resulting viscous and turbid solution was kept in the ice-box for two days. On adding benzene to the resulting crystal cake a solution was obtained, which was washed subsequently with water, with 10% sodium carbonate, and again with water, then dried with sodium sulfate and evaporated. The unchanged reactants were removed by distillation at 1 mm., the product distilling at 196–202°/0.05 mm. as a slight yellow oil that readily crystallized from an equal volume of alcohol, yielding 20.6 g. (85%) of stout colorless needles, m.p. 60–62° [*cf.* (30)]. Addition of 15 ml. of glacial acetic acid to the original mixture before saturation with hydrogen chloride lowered the yield to 50%.

Anal. Calc'd for $C_{18}H_{18}O_3$: C, 76.6; H, 6.4.
Found: C, 76.8, 76.8; H, 6.7, 6.5.

α-Methyl-β-p-anisylvaleric acid (XXVI). A solution of 82 g. (0.5 mole) of *p*-methoxypropiophenone and 104 g. (0.5 mole) of ethyl *α*-bromopropionate in 250 ml. of benzene was refluxed with 36 g. (0.55 g-atom) of zinc foil until the metal dissolved (three hours). Proceeding in the usual manner, 90 g. of a pale yellow oil, b.p. 165–180°/20 mm., was obtained. This was mixed with 90 g. of anhydrous potassium hydrogen sulfate and heated in an oil-bath to 150° for two hours. The benzene extract, after being washed with water and with 10% sodium carbonate and dried with sodium sulfate, left on evaporation an oily residue from which 70 g. of an oily fraction of b.p. 155–175°/15 mm. were obtained. On subsequent hydrogenation in 200 ml. of alcohol in the presence of 3 g. of a 10% palladium-charcoal catalyst at atmospheric pressure, 7.0 liters of hydrogen were absorbed in 20 hours. The filtrate afforded, on evaporation and subsequent distillation, 58 g. of a colorless oil, b.p. 167–168°/12 mm. The product was subsequently hydrolysed by being warmed on the water-bath for four hours with 200 ml. of 10% aqueous sodium hydroxide and 60 ml. of alcohol. Extraction of the cooled mixture with ether and acidification of the alkaline layer precipitated an oil. This was extracted with benzene and obtained as a pale yellow viscous liquid of b.p. 192–198°/20 mm. and 161–163°/0.05 mm., respectively. The first crystals were obtained by dissolving the acid in 90 ml. of benzene and keeping the solution for weeks at room temperature. In later preparations the substance spontaneously crystallized in the receiver during distillation as large colorless rosettes of long silky needles, m.p. 106–107° (31–39 g.). For analysis the substance was recrystallized from ethyl acetate-petroleum ether, or also from methyl alcohol-water (1:5); in the latter case the resulting crystallizate was dried subsequently at 56°/1 mm. over phosphorus pentoxide. In either case the melting point was found to be raised to 107–108°.

Anal. Calc'd for $C_{13}H_{18}O_3$: C, 70.2; H, 8.3; Neut. equiv., 222.3.
Found: C, 70.2, 70.3; H, 8.3, 8.4; Neut. equiv., 224, 220.

In agreement with the experience of van der Zanden and de Vries (3), alkaline extraction of residual benzene mother-liquors of the substance, and hydrochloric acid precipitation gave an oily mixture of b.p. 192–196°/20 mm. and neut. equiv. 218, which solidified but partially. The over-all yield of crystalline *trans* acid varied between 28 and 35%, the total yield of acids being somewhat more than 50%. For the subsequent preparations the crystalline acid of m.p. 107–108° was used.

β-p-Anisoyl-γ-p-anisylpentane (XXVII). (*a*) To a vigorously stirred solution, prepared from 7.3 g. (0.3 g-atom) of magnesium turnings and 33 g. (0.3 mole) of ethyl bromide in 100 ml. of ether and cooled to −10°, 28 g. (0.1 mole) of XXVIII in 250 ml. of ether was added by drops (90 minutes). The mixture was stirred for an additional period of three hours, during which the temperature was allowed to rise slowly to that of the room. The colorless paste was then poured into an ice-cold 5% ammonium chloride solution and extracted as usual. The oily reaction product yielded on distillation 14 g. (45%) of a light yellow oil, b.p. 185–187°/0.05 mm. (*b*) After refluxing 11 g. (0.05 mole) of XXXVI with 30 ml. of thionyl chloride for one hour and then removing the excess reagent by distillation at 12 mm., the residue was dissolved in 100 ml. of anisole. To the solution, cooled to +5°, 27 g. (0.2 mole) of aluminum chloride was added in small portions. After being kept at 8° for one hour and at 15–20° for three hours, the mixture was poured into 80 ml. of 20% hydrochloric acid mixed with 200 g. of ice and then extracted with ether. The residue of the washed etheral extract afforded on subsequent distillation, after a forerun of anisole, 12 g. (78%) of a light yellow viscous oil, b.p. 180–185°/0.04 mm. For analysis the samples were redistilled, an almost colorless viscous oil of 187–189°/0.05 mm. being obtained which could not be induced to crystallize from alcohol or any other solvent. It gave no coloration with alcoholic ferric chloride solution and the solution in glacial acetic acid did not decolorize bromine and was found to give orange coloration with conc'd sulfuric acid. No oxime or semicarbazone was obtained.

Anal. Calc'd for $C_{20}H_{24}O_3$: C, 76.9; H, 7.7.
Found: (a) C, 76.6, 76.7; H, 7.8, 7.7.
(b) C, 76.9, 76.9; H, 7.8, 8.0.

Stuart, Shukis, and Tallman (16) claim to have obtained the substance by method (a) as crystals from an equal amount of alcohol, two isomers of m.p. 52° and 72°, respectively, being formed. We have subjected the oily samples *a* and *b* separately, in parallel experiments, to the subsequent reduction with practically identical results.

α,γ-Di-p-anisyl-β-methyl-Δ^{α}-pentene (Isoanethole, II). To a solution of 6.1 g. (0.02 mole) of XXVII, prepared either by method *a* or *b*, in 80 ml. of absolute isopropyl alcohol, 40 ml. of a 10% aluminum isopropoxide solution in isopropyl alcohol was added, the mixture being boiled under partial reflux until the acetone test of the distillate (with 3,5-dinitrophenylhydrazine) became negative (in 24–30 hours about 60 ml. of distillate being collected). The mixture, after being brought to room temperature, was decomposed by the addition of ice and 5% hydrochloric acid and then extracted with benzene. The extract was washed subsequently with 5% hydrochloric acid and with 5% sodium carbonate and dried with magnesium sulfate. After evaporation, the remaining oil gave, in the subsequent distillation at 0.01 mm., three fractions: at 160–162° a pale yellow somewhat viscous liquid (3.2 g.), at 180–185° a more viscous oil (0.9 g.), and at 190–220° a highly viscous oily distillate (1.0 g.). The first fraction soon solidified in the receiver during distillation. The second was for the most part readily soluble in alcohol, while the third fraction was but partly soluble in hot alcohol-glacial acetic acid (9:1), the dissolved part reappearing at room temperature in oily, almost semisolid, drops.

Upon triturating the first fraction with 10 ml. of alcohol-glacial acetic acid (9:1) at room-temperature, the undissolved solid was removed and the filtrate was evaporated. Subsequent distillation of the residue gave 2.0 g. of a faintly colored liquid of b.p. 160–162°/0.01 mm., n_D^{15} 1.587; instant decoloration of bromine in glacial acetic acid.

Anal. Calc'd for $C_{20}H_{24}O_2$: C, 81.0; H, 8.2; C=C, 1.
Found: C, 80.6, 80.9; H, 8.2, 8.3; C=C, 1.06 (hydrogenation).

Baker and Enderby (1) report for isoanethole, prepared by dimerization of anethole, b.p. 192–193°/0.1 mm. and n_D^{20} 1.5867. We find for isoanethole of similar origin b.p. 160–162°/0.01 mm. and a viscosity identical with that of the synthetic product.

1-p-Anisyl-2-methyl-3-ethyl-6-methoxyindan, α-racemate (Metanethole, I). (*a*) The solid separated from the first fraction in the above preparation forms small colorless needles of m.p. 128–129° (0.8 g.). Recrystallization from glacial acetic acid raised the melting point to 134–135° which remains undepressed on admixture of an authentic specimen of metanethole of m.p. 135°, long colorless needles (0.7 g.) being obtained. (*b*) Alternately, 2.1 g. of above obtained isoanethole was mixed with 1.0 ml. of titanium^{IV} chloride under cooling with ice-water and the mixture was kept at 0° for one hour, and then at room temperature for three hours. It was then extracted with a mixture of benzene and 10% hydrochloric acid. The benzene layer, washed repeatedly with 10% hydrochloric acid and then with water, left on evaporation a deeply colored highly viscous oil. This was dissolved in a 4:1 mixture of alcohol and glacial acetic acid and left standing overnight. A crystallizate of m.p. 114–118° (0.24 g.) was obtained which was subsequently recrystallized from alcohol and then from glacial acetic acid. Colorless rosettes of slender needles, m.p. 132–133° (0.18 g.) were formed. A 1:1 mixture with an authentic specimen of metanethole melted at 133–134° (In a parallel experiment with 10 g. of isoanethole prepared from anethole, 1.0 g. of metanethole, m.p. 134°, was obtained).

Anal. Calc'd for $C_{20}H_{24}O_2$: C, 81.0; H, 8.2.
Found: C, 81.2, 80.8; H, 8.4, 8.3.

The *dinitro derivative* crystallized from a mixture of 50 mg. of the substance, 0.5 ml. of glacial acetic acid, and 0.4 ml. of fuming nitric acid, after 30 minutes at room temperature. Recrystallized from alcohol, the substance forms pale yellow needles, m.p. 191° alone or mixed with an authentic (1) specimen.

Anal. Calc'd for $C_{20}H_{22}N_2O_6$: N, 7.3. Found: N, 7.5, 7.4.

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SUMMARY

The synthesis and dehydrogenation of 1-*p*-anisyl-7-methoxytetralin, 1-*p*-anisyl-2,3-dimethyl-7-methoxytetralin, and 1-*p*-anisyl-4-ethyl-7-methoxytetralin is described.

By partial conversion of β-*p*-anisoyl-γ-*p*-anisylpentane the 1-*p*-anisyl-2-methyl-3-ethyl-6-methoxyindan structure of metanethole is further confirmed. The probable racemic configuration of the latter is discussed.

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