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DIMERIC PROPENYL PHENOL ETHERS. XVII.[1] THE HYDROCARBON ANALOG OF THE CYCLIC DIMERS

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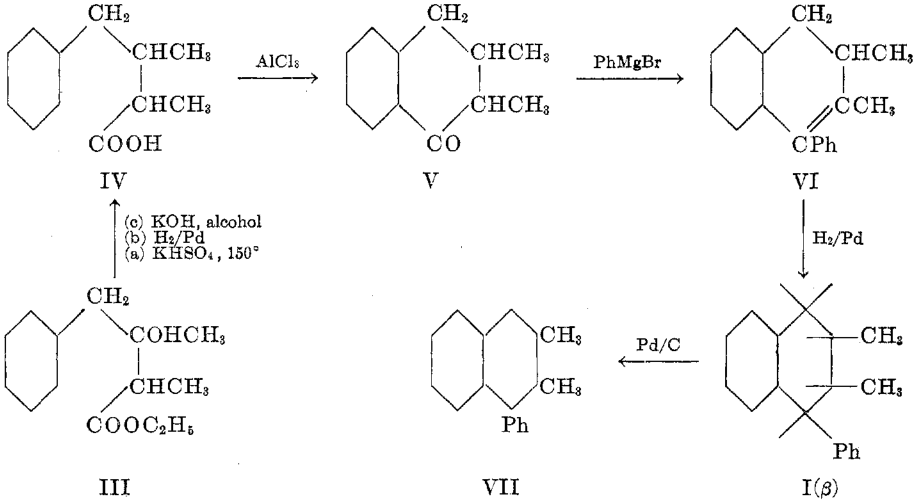
Propenylbenzene dimerizes in the presence of dilute mineral acids—in contrast to its alkoxylated derivatives—but reluctantly. Erdmann (1), making use of the observation that cinnamic acid smoothly produces a mixture of isomeric distyrenes on being refluxed with 40% sulfuric acid (2), prepared dimeric propenylbenzene by applying the method to α-methylcinnamic acid. From the product a cyclic dimer was isolated that gave *o*-benzoylbenzoic acid and traces of anthraquinone on being oxidized with chromic acid. On this evidence Erdmann assigned to the hydrocarbon, which he named methronole, the structure of a 1-phenyl-2,3-dimethyltetralin (I). Baker and Enderby (3) finding later that metanethole, the cyclic dimer of *p*-methoxypropenylbenzene, is a dimethoxy 1-phenyl-2-methyl-3-ethylindan, expressed the opinion that from analogy methronole is more likely to be a 1-phenyl-2-methyl-3-ethylindan (II). The present paper, comparing the two alternative structures, establishes the expected correctness of this opinion.

1-Phenyl-2,3-dimethyltetralin was synthesized from α,β-dimethyl-β-phenylbutyric acid (IV) (4). The conversion of the acid to 2,3-dimethyltetralone (V) (4), followed by reaction with phenylmagnesium bromide and consecutive hydrogenation, gave a tetralin I racemate which is probably C^1/C^2-*cis*, C^2/C^3-*cis* configurated (Iβ), (*cf.* 5). On being heated to 250–260° with palladized charcoal, this product readily undergoes dehydrogenation to 1-phenyl-2,3-dimethylnaphthalene, while under same conditions methronole remains practically unchanged.



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[1] Preceding paper: Part XVI, Müller, *J. Org. Chem.*, **17**, 1077 (1952).

1-Phenyl-2-methyl-3-ethylindan was prepared as follows: The reaction of 1-phenyl-2-methyl-Δ^1-indenone (VIII) (6) with ethylmagnesium bromide, which was followed by hydrogenation and consecutive dehydration of the resulting product to 1-phenyl-2-methyl-3-ethyl-Δ^2-inden (IX), gave on final hydrogenation the *cis,cis* racemate of indan II (*cf.* 5), which proved to be distinctly different from methronole.

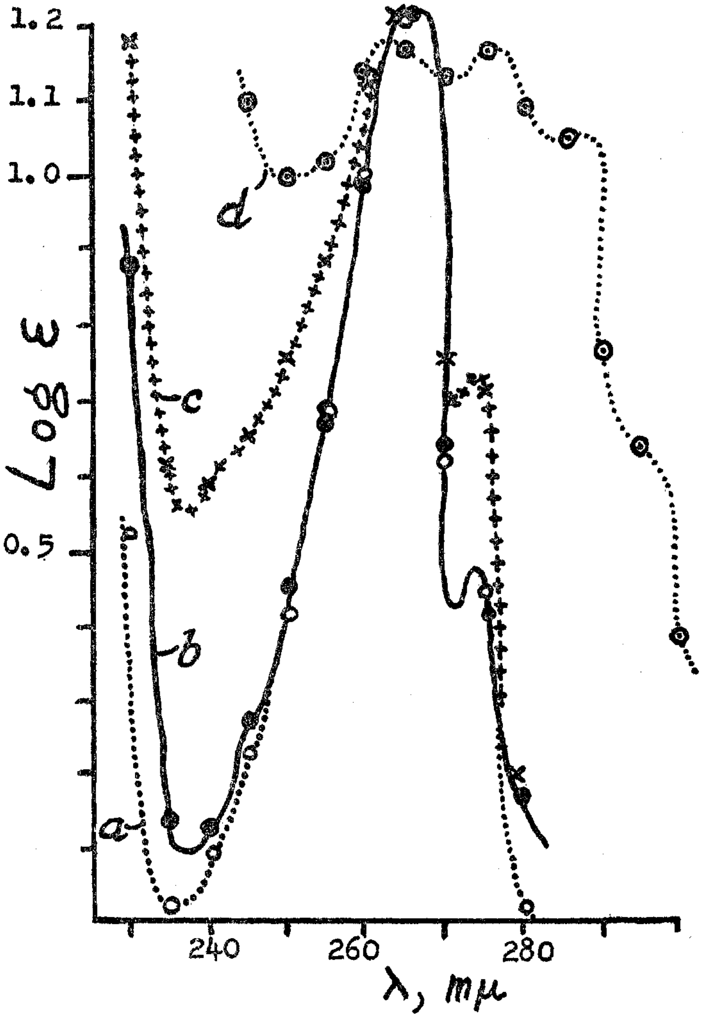
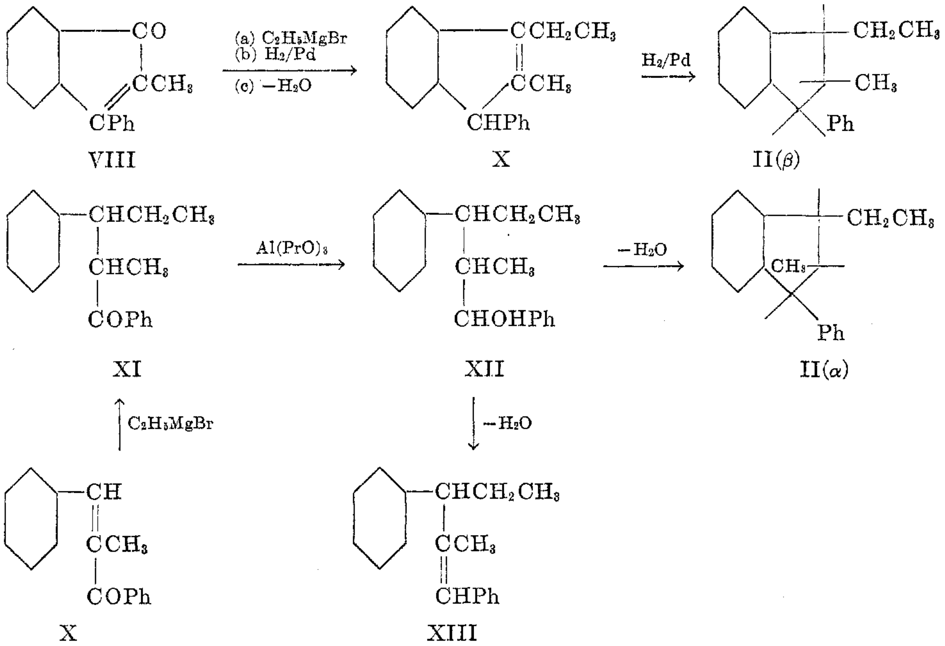


FIG. 1. ULTRAVIOLET ABSORPTION SPECTRA. (a) Methronole (Erdmann), n_D^{18} 1.5720; (b) Indan IIα racemate, n_D^{18} 1.5714; (c) Indan IIβ racemate, n_D^{18} 1.5777; (d) Tetralin Iβ racemate, n_D^{18} 1.6016. (Each substance as a 0.001 *molar* solution in isopropyl alcohol)

The alternative preparation of II from α-methylchalcone, by reaction of the latter with ethylmagnesium bromide, followed by reduction of the resulting ketone XI to XII and consecutive dehydration, gave after removal of eventually present unsaturated components, such as *e.g.* XIII, the indan II racemate which is expected to be *trans,trans* configurated. This was found to be identical with Erdmann's methronole (See Fig. 1).

Methronole is then in every respect analogous to the cyclic dimers which are formed from propenylphenol ethers on acid-catalyzed dimerization.



In connection with this work, lower homologs of indan II also have been prepared. Whereas the synthesis of the *cis,cis* racemate of 1-phenyl-2,3-dimethylindan was not connected with any special problem, the analogous synthesis of a 1-phenyl-3-methylindan was intended to afford a diastereoisomer of cyclic distyrene.[2] The reaction of 1-phenyl-3-indanone with methylmagnesium iodide, followed by hydrogenation, consecutive dehydration and repeated hydrogenation, gave a product in which the 1-phenyl and 3-methyl are possibly (*cf.* 5) collateral, whereas in cyclic distyrene these groups would be expected to occupy

[2] Under normal circumstances the acid-catalyzed dimerization of styrene gives mainly 1,3-diphenyl-Δ^1-butene (7). The presence of a cyclic isomer in the crude dimerizate was first observed by Risi and Gauvin (8), the olefin slowly rearranging under the conditions of the dimerization to 1-phenyl-3-methylindan (9). Spoerri and Rosen (9) identified the latter with that distyrene isomer which Stoermer and Kootz (10) described as 1,3-diphenyl-Δ^2-butene, and which Marion (11) found to be formed also from 1,3-diphenyl-Δ^3-butene on standing, if the latter isomer had been prepared by the sulfuric acid dehydration of 2,4-diphenylbutanol. The confusing reports (10, 11) that the distyrene isomer (whose cyclic structure has now been established) gave acetophenone, phenylacetaldehyde, and benzoic acid on ozonization must be attributed to the obvious presence of olefinic by-products in the samples ozonized.

rather the opposite sides of the alicyclic ring. The actual difference between the two substances is very slight, but still distinct (See Fig. 2).

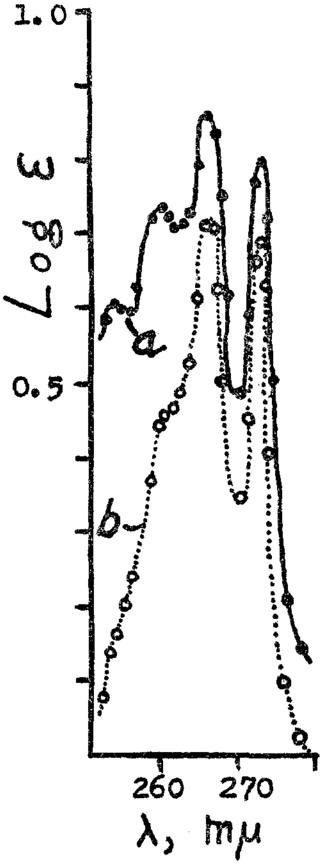


FIG. 2. ULTRAVIOLET ABSORPTION SPECTRA. (a) Synthetic 1-phenyl-3-methylindan, n_D^{18} 1.5795; (b) Cyclic dimerizate of styrene, n_D^{18} 1.5790. (Each substance as a 0.001 *molar* solution in methyl alcohol)

EXPERIMENTAL

Methronole (IIα). (*a*) In the preparation of propenylbenzene by dehydration of 89 g. of α-phenylpropanol (*cf.* 12), the resulting crude afforded on fractionation 30 g. of propenylbenzene, b.p. 75–78°/18 mm., n_D^{18} 1.5484, 11 g. of methronol b.p. 322–323°, n_D^{18} 1.5713, and 39 g. of higher polymerized material. (*b*) A vigorously stirred suspension of 100 g. of α-methylcinnamic acid in 1 liter of 40% sulfuric acid was refluxed until the oily layer no longer crystallized on standing overnight at room-temperature (about 30 hours). The oil was separated, then dissolved in ether, washed free of acid with *N* sodium hydroxide solution (the n_D^{18} being then 1.5655) and steam-distilled. After the greater part of the material had passed to the receiver (leaving behind highly viscous drops of oil), the distillate was extracted with ether. Removing the solvent, the residue was three times rectified at atmospheric pressure to give a mobile, nearly colorless liquid (25 g.) of b.p. 322–323°, n_D^{18} 1.5705. The substance was redissolved in 200 ml. of benzene and shaken with 100 ml. of conc'd sulfuric acid. After repeating this procedure four times, the solution was washed with water and then with 6% sodium carbonate solution. Subsequent evaporation and consecutive distillation afforded a perfectly colorless liquid, b.p. 182–183°/18 mm., and n_D^{18} 1.5720, with a slight violet fluorescence (traces of 9,10-diethyl-9,10-dihydroanthracene?) not shown by synthetic IIα. Yield, 15 g.

On heating 1 g. of this substance with 0.2 g. of 5% palladium-charcoal to 250–260° for four hours, subsequent distillation recovered 0.8 g. of practically unchanged material, n_D^{18} 1.5722.

1-Phenyl-2-methyl-3-ethyl-Δ^1*-inden-3-ol.* To a solution, prepared from 7 g. of magnesium foil and 45.5 g. of ethyl bromide in 150 ml. of dry ether, under cooling and stirring, a solution of 40 g. of 1-phenyl-2-methyl-Δ^1-indenone (VIII) (6) in 300 ml. of ether was added. After the first vigorous reaction, the mixture was refluxed on the steam-bath for one hour, then poured onto ice mixed with ammonium chloride solution. The ether layer was separated, subsequently washed with ammonium chloride solution and with water, dried with calcium chloride, and evaporated. The residue crystallized on addition of alcohol, forming on one recrystallization from the same solvent 31.5 g. of large colorless prisms, m.p. 119° which gave an instant decoloration of bromine in glacial acetic acid. The solution in conc'd sulfuric acid is dark red.

Anal. Calc'd for $C_{18}H_{18}O$: C, 86.4; H, 7.3.
Found: C, 86.3; H, 7.4.

1-Phenyl-2-methyl-3-ethylindanol. A solution of 25 g. of above indenol in 150 ml. of alcohol consumed, on being hydrogenated at atmospheric pressure in the presence of 0.8 g. of a 5% palladium-charcoal catalyst, 2445 ml. of hydrogen (calc'd 2240 ml.) in five hours. On evaporation of the filtrate, 22 g. of an almost colorless oil, b.p. 197–198°/8 mm., was obtained, that solidified at room temperature to form a brittle resin.

Anal. Calc'd for $C_{18}H_{20}O$: C, 85.7; H, 8.0.
Found: C, 85.8; H, 8.1.

1-Phenyl-2-methyl-3-ethyl-Δ^2*-inden* (IX). A solution of 20 g. of the above indanol in 40 ml. of acetic anhydride was refluxed for two hours, then it was poured into water and, after standing overnight, was extracted with ether. The extract, washed with sodium carbonate solution and dried with calcium chloride, left a bright yellow, at room temperature highly viscous oil, b.p. 165–166°/6 mm. (15 g.), which adds bromine with difficulty.

Anal. Calc'd for $C_{18}H_{18}$: C, 92.3; H, 7.7.
Found: C, 92.0; H, 7.9.

1-Phenyl-2-methyl-3-ethylindan, cis,cis-racemate (IIβ). A solution of 13.5 g. of IX in 100 ml. of alcohol was hydrogenated as usual, 1330 ml. of hydrogen having been absorbed in 90 minutes. The filtrate was evaporated, and the residue was distilled at atmospheric pressure to give a slightly yellow oil, b.p. 322–323°/758 mm. and 179/180°/13 mm., n_D^{18} 1.5777. Heating the substance with the one-fifth its weight of a 5% palladium-charcoal to 250–260° for four hours, followed by subsequent distillation at 18 mm. gave unchanged material of n_D^{18} 1.5785.

Anal. Calc'd for $C_{18}H_{20}$: C, 91.3; H, 8.6.
Found: C, 91.2; H, 8.7.

β-Benzoyl-γ-phenylpentane (XI). To a solution, prepared from 3.9 g. of magnesium foil and 18 g. of ethyl bromide in 100 ml. of ether, and cooled in an ice-salt mixture, 33 g. of benzalpropiophenone (α-methylchalcone, X) in 50 ml. of ether was added by drops, under vigorous stirring (*cf.* 5). Upon working up the mixture as usual, 24 g. of a pale yellow oil, b.p. 187–188°/16 mm. and n_D^{18} 1.5853, was obtained.

Anal. Calc'd for $C_{18}H_{20}O$: C, 85.7; H, 7.9.
Found: C, 86.1; H, 8.0.

1-Phenyl-2-methyl-3-ethylindan, trans, trans-racemate (IIα). To 20 g. of XI in 80 ml. of ether, 7.3 g. of lithium aluminium hydride in 200 ml. of ether was added. After gentle refluxing for two hours, the excess reagent was decomposed by addition of moist ether. The mixture was added to 2% hydrochloric acid, the ethereal layer being subsequently washed with water, dried with sodium sulfate, and then freed from the solvent. The remaining pale yellow viscous oil, n_D^{18} 1.5757, (19 g.), was refluxed with 200 ml. of 20% sulfuric acid for four hours, under vigorous stirring. Extraction with benzene followed. The extract, washed with sodium carbonate solution and then freed from the solvent, gave 17 g. of a viscous yellow oil, b.p. 195–198°/16 mm. and n_D^{21} 1.5725. Subsequent steam-distillation reduced the viscosity considerably. The benzene extract was washed subsequently several times with conc'd sulfuric acid, until the latter no longer acquired a color. After washings with sodium carbonate solution and with water, the solvent was removed; however, subsequent distillation gave only 4.7 g. of an almost entirely colorless oil, b.p. 186–188°/12 mm.; 322°/763 mm., showing after one redistillation n_D^{18} 1.5714. When warmed with one-fifth its weight of 5% palladium-charcoal, the recovered substance had n_D^{18} 1.5718.

Anal. Calc'd for $C_{18}H_{20}$: C, 91.3; H, 8.6.

Found: C, 91.2, 91.5; H, 8.6, 8.5.

α,β-Dimethyl-γ-butyric acid (IV). A solution of 100 g. of phenylacetone and 142 g. of ethyl α-bromopropionate in 500 ml. of dry benzene was refluxed with 51.2 g. of amalgamated zinc foil. The reaction started somewhat hesitatingly, requiring initiation with a few crystals of iodine or with some copper bronze. In about five hours the metal dissolved. The mixture was then poured upon ice mixed with 5% sulfuric acid, the benzene layer being washed subsequently with 5% sulfuric acid and with water. After drying with calcium chloride and removal of the solvent, the residue was distilled, affording 97–109 g. of a colorless liquid, b.p. 178° and n_D^{18} 1.4982. An intimate mixture of this hydroxy ester III with 60 g. of finely powdered potassium hydrogen sulfate was kept at 150° for two hours (oil-bath). The mixture was cooled, and then extracted with benzene. The extract, washed with water and dried with sodium sulfate, was freed from the solvent and then distilled. A yellow oil of b.p. 142–145°/13 mm. was obtained (71 g.), about 20 g. of a higher-boiling material remaining behind. On hydrogenating 14.8 g. of the unsaturated ester in 100 ml. of alcohol in the presence of 0.8 g. of a 10% palladium-charcoal catalyst, 1190 ml. of hydrogen were absorbed (Calc'd, 1325 ml.) in two hours. Evaporation of the filtrate gave 9.0 g. of a colorless mobile liquid, b.p. 144–148°/13 mm. and n_D^{18} 1.4983. This product was hydrolyzed by refluxing with 30 ml. of methanol containing 4 g. of potassium hydroxide (two hours). The solution was diluted with 200 ml. of water, then extracted with ether, acidified subsequently with conc'd hydrochloric acid, and again extracted with benzene. Evaporation of the benzene extract, and subsequent distillation of the residue, gave 7.0 g. of a colorless mobile liquid possessing a slight blue fluorescence, b.p. 167–168°/14 mm. and n_D^{18} 1.5126, (*cf.* 4).

Anal. Calc'd for $C_{12}H_{16}O_2$: C, 75.0; H, 8.4; Neut. equiv., 192.3.

Found: C, 75.1, 74.9; H, 8.4, 8.6; Neut. equiv., 188, 193.

2,3-Dimethyl-1-tetralone (V) was prepared from IV by following the description given by Schroeter, Lichtenstadt, and Irineu (4). Distillation of the crude product gave an almost colorless oil, b.p. 144–146°/12 mm. or 160–162°/16 mm., n_D^{18} 1.5438. In an ice-salt mixture the substance solidified to a colorless mass of crystals, m.p. +7°[reported (4), m.p. −1°].

Anal. Calc'd for $C_{12}H_{14}O$: C, 82.7; H, 8.1.

Found: C, 82.9; H, 8.4.

1-Phenyl-2,3-dimethyl-3,4-dihydronaphthalene (VI). A solution of 2.7 g. of magnesium and of 18 g. of bromobenzene in 50 ml. of ether was mixed at room temperature with 10 g. of V in 50 ml. of ether. No separation of a complex was observed. The mixture was refluxed on the steam-bath for 30 minutes, then decomposed by being added to ice mixed with an ammonium chloride solution. Isolation of the product in the usual manner gave 13.4 g. of an oil, which was subsequently distilled at 16 mm. Of the three fractions of the b.p. 126–128°, 154–156° and 176–178°, the last fraction contained 3.2 g. of a viscous oil. This was redistilled, a colorless oil of b.p. 175–177° being thereby obtained, having n_D^{18} 1.6016 and dissolving in conc'd sulfuric acid with an intense bright yellow color.

Anal. Calc'd for $C_{18}H_{18}$: C, 92.2; H, 7.7.

Found: C, 91.8; H, 7.9.

1-Phenyl-2,3-dimethyltetralin, trans, trans(?)-racemate (Iβ). On hydrogenation at atmospheric pressure in the presence of a 10% palladium-charcoal catalyst, 2.5 g. of VI in 70 ml.

of alcohol absorbed 185 ml. of hydrogen (Calc'd 224, ml.) in two hours. The filtrate was evaporated, the residue affording on subsequent distillation a viscous slightly yellow oil of b.p. 170–175°/18 mm. and n_D^{18} 1.5918. The product was redissolved in benzene, the solution being washed subsequently with conc'd sulfuric acid, until the latter no longer acquired a color. Isolation and consecutive distillation gave a colorless oil, n_D^{18} 1.6016, which dissolved in conc'd sulfuric acid with a faint yellow color.

Anal. Calc'd for $C_{18}H_{20}$: C, 91.3; H, 8.6.
Found: C, 91.6, 91.2; H, 8.6, 8.5.

1-Phenyl-2,3-dimethylnaphthalene (VII). Mixing 0.8 g. of VI with 0.2 g. of a 10% palladium-charcoal catalyst, and warming the mixture gradually in two hours to 260°, maintaining the temperature for another two hours, followed by distillation at 12 mm., gave an oil which crystallized readily from alcohol in large flat colorless needles (0.47 g.), m.p. 85–86°. Recrystallization from the same solvent did not affect the melting point. The substance dissolved in conc'd sulfuric acid without coloration. On analysis the values for carbon were found to be somewhat high, in spite of repeated purifications, in analogy to earlier experiences with similarly constituted naphthalenes (*cf.* 5, p. 1021).

Anal. Calc'd for $C_{18}H_{16}$: C, 93.1; H, 7.3.
Found: C, 93.5, 93.6; H, 7.6, 7.5.

The *picrate*, orange yellow needles, m.p. 112°, readily crystallized from a saturated alcoholic solution of picric acid.

Anal. Calc'd for $C_{18}H_{16} \cdot C_6H_3N_3O_7$: N, 9.1. Found: N, 9.7, 9.5.

1-Phenyl-2,3-dimethyl-Δ^1-indenol was prepared by adding 25 g. of 1-phenyl-2-methyl-Δ^1-indenone (VIII) in 300 ml. of ether to a solution of 5 g. of magnesium foil and 30 g. of methyl iodide in 100 ml. of ether. The mixture was refluxed, after the initial reaction, on the steam-bath for one hour, then poured upon ice mixed with an ammonium chloride solution. The ether layer was washed and then evaporated, leaving a residue which readily crystallized from alcohol in large colorless prisms, m.p. 112° (25.2 g.). The color reactions are identical with those of the 3-ethyl homolog.

Anal. Calc'd for $C_{17}H_{16}O$: C, 86.4; H, 6.8.
Found: C, 86.2; H, 7.0.

1-Phenyl-2,3-dimethylindan-3-ol. Upon hydrogenating 23 g. of the preceding indenol in alcoholic solution, in five hours 2290 ml. of hydrogen was absorbed (Calc'd, 2230 ml.). The filtrate was evaporated, the residue distilling as a highly viscous faintly yellow oil of b.p. 184–185°/8 mm. (21 g.). On standing this product crystallized, and was several times recrystallized from alcohol; m.p. 63°.

Anal. Calc'd for $C_{17}H_{18}O$: C, 85.7; H, 7.6.
Found: C, 85.5; H, 7.6.

1-Phenyl-2,3-dimethyl-Δ^2-inden. After refluxing 20 g. of above indanol with 40 ml. of acetic anhydride for two hours, the solution was poured into water and made alkaline with sodium hydroxide. On standing, the undissolved oil solidified. The product was collected, washed with water, and recrystallized from alcohol to give colorless glistening needles, m.p. 71° (17 g.). These gave an instant decoloration of bromine in glacial acetic acid. On being stored, the substance slowly decomposed to a ruby red resin.

Anal. Calc'd for $C_{17}H_{16}$: C, 92.6; H, 7.4.
Found: C, 92.4; H, 7.4.

1-Phenyl-2,3-dimethylindan, cis,cis-racemate. An alcoholic solution of 15 g. of the above inden absorbed 1615 ml. of hydrogen (Calc'd, 1528 ml.) in 90 minutes. The filtrate was evaporated, and a colorless, rather mobile liquid, b.p. 158–159°/5 mm., n_D^{18} 1.5760, was obtained. Yield, 13.5 g.

Anal. Calc'd for $C_{17}H_{18}$: C, 91.8; H, 8.2.
Found: C, 91.7; H, 8.2.

1-Phenylindanone, prepared from β,β-diphenylpropionic acid (13), forms big colorless prisms of m.p. 78°, crystallizing from alcohol.

The phenylhydrazone formed pale yellow needles, m.p. 133° (from alcohol).

Anal. Calc'd for $C_{21}H_{18}N_2$: N, 9.4. Found: N, 9.7, 9.6.

The 3,5-dinitrophenylhydrazone formed fiery red needles, m.p. 212° (from alcohol).

Anal. Calc'd for $C_{21}H_{16}N_4O_4$: N, 14.5. Found: N, 14.7, 14.7.

1-Phenyl-3-methylindan-3-ol. Upon dissolving 45 g. of still warm, molten 1-phenylindanone in 300 ml. of ether, and quickly adding it through a dropping-funnel to the solution prepared from 10 g. of magnesium foil and 60 g. of methyl iodide in 200 ml. of ether, the reaction was rather vigorous and had to be controlled by cooling. Then the mixture was refluxed for one hour on the steam bath, poured onto ice mixed with an ammonium chloride solution, and the ether layer separated. After washing as usual, and removing the solvent, the residue readily crystallized from alcohol, forming 25 g. of large colorless clusters, m.p. 85–86°.

Anal. Calc'd for $C_{16}H_{16}O$: C, 85.7; H, 7.2.
Found: C, 85.9, 86.0; H, 7.2, 7.3.

1-Phenyl-3-methyl-Δ^2-inden. Dehydration of 22 g. of above indanol, by refluxing the substance in 60 ml. of acetic anhydride for two hours, and subsequent decomposition of the excess reagent with dilute alkali, gave a quickly solidifying precipitate. Recrystallization from alcohol afforded 20 g. of colorless needles, m.p. 65°, dissolving with cherry red color in conc'd sulfuric acid.

Anal. Calc'd for $C_{16}H_{14}$: C, 93.1; H, 6.8.
Found: C, 93.5, 93.3; H, 6.9, 6.8.

1-Phenyl-3-methylindan. A solution of 17 g. of above inden in 100 ml. of glacial acetic acid absorbed on hydrogenation 1730 ml. of hydrogen (Calc'd, 1836 ml.) in two hours. The filtrate was freed from the solvent, and the residue was distilled. The resulting slightly yellow oil, b.p. 299–300°, (12 g.), was redissolved in benzene, and washed repeatedly with conc'd sulfuric acid. The benzene solution then was washed with sodium carbonate solution and with water and freed from the solvent. Distillation of the residue gave an entirely colorless liquid of b.p. 175–177°/14 mm., and n_D^{18} 1.5795.

Anal. Calc'd for $C_{16}H_{16}$: C, 92.2; H, 7.7.
Found: C, 92.1, 92.4; H, 7.9, 7.9.

Cyclic distyrene, prepared according to Risi and Gauvin (8) from crude distyrene, b.p. 118–120°/2 mm., by gentle oxidation with chromic acid, and then purified by shaking the benzene solution with conc'd sulfuric acid, had b.p. 299–301°/757 mm. and 175–177°/14 mm., and n_D^{18} 1.5790. Spoerri and Rosen (9) report n_D^{20} 1.5797, and for a sample further purified through the dibromide n_D^{20} 1.5805.

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SUMMARY

Methronole, a cyclic dimer of propenylbenzene prepared from α-methylcinnamic acid, is a 1-phenyl-2-methyl-3-ethylindan, presumably of *trans,trans* configuration. The cyclic dimers obtained by the acid-catalyzed dimerization of propenylphenol ethers are, therefore, the alkoxy analogs of this hydrocarbon.

A 1-phenyl-3-methylindan was prepared which is closely similar, although not entirely identical, with cyclic distyrene.

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