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ROTAMERISM DURING DEMETHYLATION OF THE 2,5-DIMETHOXY-2,5-DIMETHYL-3,4-DIPHENYLHEXANES¹

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ABSTRACT

The fission of methanol from the diastereomeric 2,5-dimethoxy-2,5-dimethyl-3,4-diphenylhexanes leads to products which are best explained in terms of restriction about the central carbon-carbon bond. As would be expected from its stable conformation the dd,ll diastereomer easily forms the 2,2,5,5-tetramethyl-3,4-diphenyltetrahydrofuran, but the *meso* diastereomer forms a tetrahydrofuran with difficulty. On the other hand the *meso* diastereomer readily undergoes Friedel-Crafts types of condensation leading in different media to either 3,3-dimethyl-1-isopropenyl-2-phenylindane, 3,3-dimethyl-1-isopropyl-2phenylindene or 5,5,10,10-tetramethyl-4b,5,9b,10-tetrahydroindeno[2,1-a]-indene. These indenes are the expected products from a consideration of the conformation of the *meso*-dimethoxydimethyldiphenylhexane which is most free from steric restriction.

The two possible diastereomers of 2,5-dimethoxy-2,5-dimethyl-3,4-diphenylhexane have been reported (1). One is a liquid (IV), very viscous, which has resisted attempts to cause it to crystallize during three years. Treatment with a variety of acidic demethylating agents forms only one product, 2,2,5,5tetramethyl-3,4-diphenyltetrahydrofuran (III). This cyclic ether has been prepared by methylation of the corresponding diol II which was synthesized from dimethyl dd,ll-diphenylsuccinate (I) and methyl iodide Grignard reagent, and the oil (IV) therefore must have the same dd,ll configuration (3). The ease



with which this dd, ll-2,5-dimethoxy-2,5-dimethyl-3,4-diphenylhexane (IV) may be converted to the tetrahydrofuran might have been predicted by consideration of the hindrance which would be imposed by the bulky sub-

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stituents. Thus of the three possible rotamers*, IVa, b, c, that one (IVa) which might be expected to be in preponderance because of symmetrical disposition and minimum in crowding of the substituent group is also the rotamer in which pivotal rotation to form dd,ll-III would separate the phenyl groups (compare IVa with dd,ll-III).



*The term "rotamer" (7) seems to us so much more appropriate than "restriction isomer" (11) that we have abandoned the latter term in favor of the former. However the concept of electrostriction is implicit in any discussion of these isomers.

The solid 2,5-dimethoxy-2,5-dimethyl-3,4-diphenylhexane (V) must necessarily be the dl,ld (meso) diastereomer. If one examines the structures corresponding to rotamers it is evident that the most symmetrical form (Vb, which probably represents all of this diastereomer in the solid form) will have the conformation least favorable for cyclization to the diastereomeric 2,2,5,5tetramethyl-3,4-diphenyltetrahydrofuran (meso-III). Furthermore conversion of either of the enantiomeric forms (Va or Vc) to meso-III would be hindered to the extent that pivotal rotation would bring the phenyl groups closer together. In consequence it might be expected that this cyclization does occur with difficulty; this is found to be the fact. However the cyclization does occur under the unique influence of hydriodic acid in boiling dioxane. The product is evidently meso-III since it contains neither hydroxyl groups nor aliphatic unsaturation and its ultraviolet absorption spectrum is almost identical with that of dd,ll-III.

This method for preparation of *meso*-III is better than mixtures of hydrobromic and acetic acids which were used by Berman *et al.* (1) to obtain the same compound to which they did not assign a structure. But it should be noted that one of these two methods is required for the formation of *meso*-2,5-dimethyl-3,4-diphenyltetrahydrofuran (III), in contrast to formation of the dd,ll diastereomer which occurs in diverse reaction media.

In further contrast the formation of the *meso* (but not the dd,ll) diastereomer III is accompanied by at least one by-product. The isolable contaminant is 2,5-dimethyl-3,4-diphenylhexadiene-1,5 (VI), the preparation of which has previously been described (1) as the treatment of *meso*-2,5-dimethoxy-2,5dimethyl-3,4-diphenylhexane (V) with sodium chloride, acetic anhydride, and sulphuric acid.

We have reinvestigated the diene VI and have improved its mode of preparation by use only of potassium bisulphate and acetic anhydride. We have also confirmed the structure of VI by ozonolysis and by catalytic reduction (with difficulty) to *meso-2,5*-dimethyl-3,4-diphenylhexane (VII) (8). This additional proof has been welcome. One might normally expect that the elimination of two molecules of methanol from V would lead to 2,5-dimethyl-3,4-diphenylhexadiene-2,4 (XII) instead of the nonconjugated 1,5-diene (VI) which actually is obtained. But such an expectation does not take into account the steric aspects of the diene XII.

However our oxidation of the isolated diene VI may explain why the conjugated diene was not obtained by demethanolation. With chromium trioxide in acetic acid four products have been isolated besides unchanged VI. In addition to benzoic acid, two diastereomeric acids have been isolated as their esters, which conform in analysis with that expected for dimethyl *ddld*,*lldl*-and *ddll*,*lldd*-2,5-dimethyl-3,4-diphenyladipates. Finally a ketone has been isolated in small amount as its dinitrophenylhydrazone; according to analysis this is 5-methyl-3,4-diphenylhexen-5-one-2 (VIII). One might expect this partial oxidation product of an ordinary nonconjugated diene. The dimethyl-diphenyladipic acids (IX) are unexpected except as one considers the unusual oxidations of hindered alkenes such as 1,1-dineopentylethene (X) (4, 10). This

732



compound yields dineopentyl acetic acid (XI) which, like IX, contains the same number of carbon atoms as does the alkene. In view of similar evidence of hindrance in our derivatives of diphenylethane it may not be surprising that



no method of methanol removal from the 2,5-dimethoxy-2,5-dimethyl-3,4diphenylhexanes (IV and V) has yet produced the conjugated diene XII.

The practical preparation of 2,5-dimethyl-3,4-diphenylhexadiene-1,5 (VI) by potassium bisulphate and acetic anhydride does produce, in trace yield, another hydrocarbon of the same empirical formula, but it is not XII. Instead we believe it to be 1,1-dimethyl-3-isopropenyl-2-phenylindane (XIII) which may be prepared more satisfactorily by a two-step reaction. When *meso*-dimethoxydimethyldiphenylhexane (V) is treated with the Lucas reagent (equimolar mixture of zinc chloride and concentrated hydrochloric acid) two moles of methanol are eliminated and one mole of hydrogen chloride is added. We believe the product to be 2-chloro-2-[3,3-dimethyl-2-phenylindanyl]-propane, XIV. Treatment of XIV with alcoholic sodium hydroxide or alumina leads to the dimethylisopropenylphenylindane (XIII).

The empirical formula of XIII is established as $C_{20}H_{22}$ by elemental analysis and molecular weight determinations. The presence of the terminal double bond has been established by ozonolysis, from which a 35% yield of the dimedone derivative of formaldehyde may be isolated. This yield, under the conditions of the entire ozonolysis procedure, indicates one double bond per $C_{20}H_{22}$ unit (9). Moreover indirect proof establishing the presence of the phenylindane nucleus is afforded by examination of a second product obtained during preparation of the tertiary chloride, XIV.

Actually this second product is the major one (40 versus 17%) and like XIII, has the empirical formula $C_{20}H_{22}$. This product, 3,3-dimethyl-2-phenyl-1-isopropylindene (XV) may also be formed from *meso*-dimethoxydimethyl-diphenylhexane (V) by reflux with 50% hydriodic acid (76%) or by boron fluoride etherate in boiling petroleum ether (60%) or by 90% sulphuric acid at room temperature (50% yield). This compound has been assigned structure XV for several reasons. Firstly it resists hydrogenation at 20-50° with either platinum or nickel up to 1500 lb. gauge pressure and bromine will not add to it, although substitution seems to occur. Secondly the compound behaves as

a highly-conjugated aromatic system: it imparts a deep red color to tetranitromethane, and its ultraviolet absorption resembles that of stilbene. In conformity with this similarity it reacts with sodium to form a highly-colored adduct in 1,2-dimethoxyethane (3).

The substance believed to be 3,3-dimethyl-1-isopropyl-2-phenylindene (XV) does undergo ozonization, but none of formaldehyde, acetaldehyde, or acetone can be detected among the products. However a diketone, $C_{20}H_{22}O_2$, has been isolated as its mono 2,4-dinitrophenylhydrazone. Since no carbon atoms are lost the keto linkages are evidently the result of oxidative fission of the indene double bond. In addition to this diketone the ozonization yields an acid believed to be *o*-carboxyphenylisopropiophenone (XVI) on the basis of analysis and neutralization equivalent. The keto group in this acid is nonreactive, and this property might be expected if XVI existed in ketol form. If this acid is considered to be an oxidative degradation product of the diketone then the latter may be formulated as *o*-isobutyrylphenylisopropiophenone (XVII).

We believe that this evidence justifies the formulation of 3,3-dimethyl-1isopropyl-2-phenylindene (XV). Since this structure is isomeric with that of 3,3-dimethyl-1-isopropenyl-2-phenylindane (XIII) the characterization of XV would tend to support that of XIII. Thus the formation of XV and (via XIV) of XIII may be presumed to proceed through an intermediate portrayed for convenience as the electropositive particle XVIII. The reaction resembles that by which 1,1-dimethyl-3-phenyl-1-propanol is converted to 1,1-dimethylindane (2) by means of 85% sulphuric acid.

According to this postulation the Friedel-Crafts type of cyclization which produces XIII and XV ought to continue further through the intermediate cation XVIII (under conditions wherein it was sufficiently stable) to form 5,5,10,10-tetramethyl-4b,5,9b,10-tetrahydroindeno[2,1-a]indene (XIX). Actually a compound conforming with this analysis and molecular weight may be formed by treatment of either XIII or XV or even V with concentrated sulphuric acid. However the tetracyclic XIX can best be prepared by treatment of *meso*-2,5-dimethoxy-2,5-dimethyl-3,4-diphenylhexane (V) with anhydrous hydrofluoric acid. We believe the tetracyclic structure XIX to be authentic because no reaction occurs with ozone, because the ultraviolet absorption spectrum closely resembles that of XIII and of indane itself, and finally because chromic acid oxidation gives the known α,α -dimethylhomophthalic acid, XX.

Earlier in this report it has been suggested that bulky substituents on the central carbon atoms in diphenylethane tend to cause restriction about the pivotal linkage. According to this postulation the most stable (symmetrical) form of *meso*-2,5-dimethoxy-2,5-dimethyl-3,4-diphenylhexane, Vb, would form the cyclic ether, *meso*-2,5-dimethyl-3,4-diphenyltetrahydrofuran (*meso*-III), with difficulty in contrast to the easy conversion of IV to dd,ll-III. On the other hand inspection of structure Vb shows that this spatial conformation is favorable to removal of methanol by a Friedel-Crafts mechanism via intermediates which (for purposes of illustration) may be represented by the dication XXI. Loss of two protons may thus lead with conformational con-



venience to the indane, XIIIa, or the indene, XVIa (the latter being convertible by proton exchange to the former), while the same convenience may lead directly by proton loss from XXI to the indeno-indene (XIXa), also by proton exchange from XIIIa. These Friedel-Crafts processes do not preclude



direct proton loss from XXI to the nonconjugated diene VIa, but it may be seen that steric hindrance prevents the coplanarity expected for conjugation in the formation of XIIa. The series of products arising from methanol fission from *meso-2*,5-dimethoxy-2,5-dimethyl-3,4-diphenylhexane (*meso-III*) thus are expected ones from the aspect of steric restriction. However the specificity in respect of which the several products are formed in different reaction media shows that free-cationic structures such as XXI are probably fallacious and are certainly inadequate from the aspect of prediction. Such prediction may become possible when more is known about the co-ordination complexes of which free-ionic structures such as XXI represent a simplification.

EXPERIMENTAL*

meso-2,2,5,5-Tetramethyl-3,4-diphenyltetrahydrofuran (meso-III)

A solution of 0.5 gm. (0.00153 mole) of *meso*-2,5-dimethoxy-2,5-dimethyl-3,4-diphenylhexane, m.p. 137–138° C., and 0.30 ml. (0.0017 mole) of hydriodic acid (density 1.57) in 7.5 ml. of dioxane was boiled under reflux for eight hours, then poured into ice and the solid, m.p. 70–78° C. (0.37 gm., 86%), was filtered off. This crude product was extracted with 0.5 ml. of 95% ethanol leaving 2 mgm., m.p. 159–163° C., of 2,5-dimethyl-3,4-diphenylhexadiene-1,5 (VI). Evaporation of the extract left a residue, m.p. 84–87° C., which was heated at 80° C. (10 mm.) for two days. The residue, after this sublimation of impurities, weighed 0.23 gm. (53%), m.p. 92–93° C. This compound showed neither addition nor active hydrogen in the Grignard machine and it contained no methoxyl function. The ultraviolet absorption spectrum comprised a single peak at 260 m μ with $E_{molar} = 350$. The spectrum resembled closely that of the dd,ll diastereomer ($E_{molar} = 325$), except that absorption was slightly greater throughout the curve.

2,5-Dimethyl-3,4-diphenylhexadiene-1,5 (VI)

A solution of 5.0 gm. (0.0153 mole) of meso-2,5-dimethoxy-2,5-dimethyl-3,4-diphenylhexane (meso-III) and 2.1 gm. (0.0154 mole) of anhydrous po-



FIG. 2. -----5,5,10,10-Tetramethyl-4b,5,9b,10-tetrahydroindeno[2,1-a]indene (XIX) -------1,1-Dimethyl-3-isopropenyl-2-phenylindane (XIII)

*Melling points have been corrected against reliable standards. X-ray diffraction patterns are recorded as relative intensities $[I/I_1]$ at d spacings in A using CuK_α radiation (Ni filtered). Only the strongest lines were recorded.

tassium bisulphate in 50 ml. of acetic anhydride was boiled under reflux for four hours, then diluted with ice. The crude precipitate was water-washed, 3.15 gm., m.p. 90–143° C. It was dissolved in 30 ml. of hot absolute ethanol, filtered, and cooled, yielding 1.24 gm. (31%) of VI, m.p. 161–163° C. A mixture melting point with the substance reported previously (1) was not lowered. The ultraviolet absorption spectrum is shown in Fig. 1 for an ethanolic solution (4.21×10^{-5} moles per liter).

The ethanolic mother liquors were evaporated and the residue, m.p. 67–93° C., was sublimed at 65° C. (8 mm.), yielding 91 mgm., m.p. 71–74° C. (2%), of impure 1,1-dimethyl-3-isopropenyl-2-phenylindane (XIII).

Oxidation of meso-2,5-Dimethyl-3,4-diphenylhexadiene-1,5 (VI)

A mixture of VI (1.25 gm., 0.0048 mole) and 1.87 gm. (0.0187 mole) of dichromium trioxide, 50 ml. of acetic acid and 1.5 ml. (0.0833 mole) of water was heated at $90-100^{\circ}$ C. with stirring for one hour, then diluted with 50 ml. of water. The insoluble phase was filtered and dissolved in 10 ml. of diethyl ether plus 10 ml. of 5% aqueous sodium hydroxide. The etherous phase, washed with water, then dried and evaporated, left 97 mgm., m.p. 137-152° C. Crystallization from 1 ml. of absolute ethanol left 53 mgm. (4%) of unchanged VI, m.p. 159-162°C. The alkaline phase was acidified with concentrated hydrochloric acid. The precipitate, 0.207 gm. (13%), m.p. 305-308° C., was crystallized from acetic acid (120 ml. per gm.), m.p. 325-326° C. Strongest lines of the X-ray powder diagram are: [10] 4.21, 4.00; [7] 5.71, 4.69, 4.48, 3.83. Neut. equiv. calc. for C₂₀H₂₂O₄, 163; found, 155. This diastereomer of 2,5dimethyl-3,4-diphenyladipic acid (IX) was converted by etherous diazomethane into the methyl ester, crystallized from methanol, 100 ml. per gm., m.p. 108-109° C. Calc. for C₂₂H₂₆O₄: C, 74.5; H, 7.39. Found: C, 74.8; H. 7.41.

The original drowned reaction system from which VI and one diastereomer of IX had been removed by filtration was twice-extracted with 25-ml. portions of ether. This ether was water-washed and then thrice-extracted with 5-ml. portions of 5% aqueous alkali. The etherous phase was then evaporated leaving 0.372 gm. of an oil, 50 mgm. of which was treated with 1 ml. of a methanolic solution of 2,4-dinitrophenylhydrazine containing hydrogen chloride. The dinitrophenylhydrazone of 5-methyl-3,4-diphenylhexen-5-one-2 (VIII) (30 mgm., m.p. 211–214° C.) was twice-crystallized from 1: 1 ethanol – ethyl acetate (0.16 ml. per mgm.), m.p. 230–230.5° C. Calc. for C₂₅H₂₄N₄O₄: C, 67.6; H, 5.44; N, 12.6. Found: C, 68.2; H, 5.36; N, 12.4.

The combined alkaline extract of the etherous solution of VIII was acidified with concentrated hydrochloric acid. The gummy precipitate (0.475 gm.) was removed. The remaining aqueous phase, by ether extraction and sublimation after evaporation of the ether, yielded 11 mgm. (2%) of benzoic acid. The gummy precipitate was boiled under reflux with 2 ml. of methanol containing 10 mgm. of 96% sulphuric acid for three hours, then cooled to 0° C. This crude second diastereomer of dimethyl 2,5-dimethyl-3,4-diphenyladipate (ester of IX), 25 mgm., m.p. 130–140° C., was four times crystallized from 0.5 ml. of methanol, m.p. 163–164.5° C. Calc. for $C_{22}H_{26}O_4$: C, 74.5; H, 7.39. Found: C, 74.1; H, 7.45.

meso-2,5-Dimethyl-3,4-diphenylhexane (VII)

A solution of 80 mgm. (0.000306 mole) of 2,5-dimethyl-3,4-diphenylhexadiene-1,5 in 10 ml. of absolute ethanol containing 1 gm. of Raney nickel catalyst (W-1) was shaken 19 hr. with hydrogen at 1500 lb. pressure. The system was filtered and evaporated, leaving 63 mgm. (79%) of *meso*-dimethyldiphenylhexane, m.p. 149-150.5°. A mixture melting point with authentic material (7) was not depressed.

dl,ld-2-Chloro-2-[3,3-dimethyl-2-phenylindanyl]-propane (XIV)

A system comprising 1.00 gm. (0.00306 mole) of *meso*-2,5-dimethoxy-2,5dimethyl-3,4-diphenylhexane (*meso*-III) and 4.1 gm. (0.03 mole) of zinc chloride in 2.5 ml. (0.03 mole) of concentrated hydrochloric acid was stirred for 12 hr. The oily solid was taken up in 15 ml. of petroleum ether (b.p. 40- 60° C.); the solution was washed thoroughly with water, then dried, and evaporated. The crude 3,3-dimethyl-1-isopropyl-2-phenylindene (XV, 0.861 gm.) was crystallized from 5 ml. of hot methanol, 0.322 gm. (40%), m.p. 67- 68° C. A mixture melting point with the compound described later in this report was not depressed.

The methanolic filtrate was diluted to a volume of 10 ml., chilled to -80° C., and filtered to separate 0.16 gm. (18%) of the crude chloro compound XIV, m.p. 78-83° C. After two recrystallizations it melted at 89-90.5° C. and still gave a positive halide test with alcoholic silver nitrate. Calc. for C₂₀H₂₃Cl: C, 80.4; H, 7.76. Found: C, 79.7; H, 7.85.

3,3-Dimethyl-1-isopropenyl-2-phenylindane (XIII)

A. From XIV with Alcoholic Alkali

A solution of 0.23 gm. (0.01 atom) of metallic sodium in 3 ml. of absolute ethanol was combined with 0.076 gm. (0.000255 mole) of XIV in 1 ml. of the same solvent and boiled for two hours under reflux, then cooled, and diluted with 50 ml. of water. After slow separation the crude dimethylisopropenyl-phenylindane (XIII), 66 mgm. (99%), m.p. 67–73° C., was crystallized from hot methanol (1 ml. per gm.), m.p. 76–77° C. Mol. wt. (Rast) was calculated as 262; found 258. The X-ray powder pattern was: [10] 5.40, 5.18; [5] 3.80; [4] 6.32, 4.46, 4.07, 3.66. Calc. for $C_{20}H_{22}$: C, 91.5; H, 8.45. Found: C, 91.7; H, 8.61.

B. From XIV with Alumina

The crude reaction product from the preparation of XIV described above (0.837 gm.) was dissolved in 5 ml. of petroleum ether (b.p. 40–60° C.). This solution, on a 1.5×45 cm. column of alumina, was eluted with the same solvent yielding 0.486 gm. (61%) (75 ml. eluent) of 3,3-dimethyl-1-isopropyl-2-phenylindene (XV, m.p. 67–69° C.), 0.080 gm. (25 ml. eluent) of intermediate fraction, m.p. 50–65° C., and 0.242 gm. (30%) (100 ml. eluent) of 3,3-dimethyl-1-isopropenyl-2-phenylindane (XIII, m.p. 73–75° C.). The ultraviolet absorption spectrum of XIII is shown in Fig. 2.

Ozonization of 3,3-Dimethyl-1-isopropenyl-2-phenylindane (XIII)

A solution of 0.102 gm. $(3.88 \times 10^{-4} \text{ mole})$ of XIII in 6 ml. of pre-ozonized and purified carbon tetrachloride was treated with 1.8 liters of 6% ozonized oxygen at 0° during 100 min. The solid ozonide was hydrolyzed with 20% acetic acid and 150 mgm. of zinc dust in the carbon tetrachloride medium at 40-50° C. with a stream of nitrogen bubbling through. No acetone could be detected in the effluent gas by acid-methanolic 2,4-dinitrophenylhydrazine. The nonaqueous layer was removed.

The aqueous layer was distilled almost completely and the distillate adjusted to pH 4.0-4.5 with acetic acid and sodium hydroxide; then 0.1 gm. of dimedone in 30 ml. of water was added. The precipitate, methylene-*bis*dimethyldihydroresorcinol, weighed 0.386 gm., m.p. 188-189° C., mixture melting point with authentic material not lowered. Yield of formaldehyde is thus 34.6% based on one methylene group per mole of XIII.

3,3-Dimethyl-1-isopropyl-2-phenylindene (XV)

A system comprising 5.0 gm. (0.0153 mole) of *meso*-2,5-dimethoxy-2,5-dimethyl-3,4-diphenylhexane (*meso*-III) and 70 ml. of hydriodic acid (density 1.54) was boiled under reflux for 12 hr., then poured into ice. The crude product, 4.12 gm., m.p. 55-62° C., was dissolved in 10 ml. of hot methanol and the solution was cooled to 0° C. The crystals, 3.06 gm. (76%), m.p. 68.5-69.5° C., were recrystallized from hot methanol (2 ml. per gm.), m.p. 69-70° C. Calc. for $C_{20}H_{22}$: C, 91.5; H, 8.45. Found: C, 91.3; H, 8.65.

The X-ray powder pattern of XV is: [10] 4.19; [9] 4.72; [8] 7.49, 6.96, 6.15, 5.71. The ultraviolet absorption spectrum in absolute ethanol $(4.32 \times 10^{-5} \text{ moles per liter})$ is shown in Fig. 1. *meso*-III may also be converted to XV in 50% yield by 90% sulphuric acid at 25° C. or in 60% yield by boron fluoride etherate in boiling petroleum ether (b.p. 40–60° C.).

Disodium Adduct of XV

A solution of 0.26 gm. (0.001 mole) of dimethylisopropylphenylindene (XV) in 7 ml. of 1,2-dimethoxyethane was shaken with 0.10 gm. (0.0041 atom) of sodium under nitrogen. A deep red color appeared at once. After three days the system was treated with gaseous carbon dioxide; then the dimethoxyethane was vacuum-evaporated and replaced with 10 ml. each of diethyl ether and water. The etherous phase, water-washed, dried, and evaporated left 0.13 gm. (50%) of an oily solid which, crystallized from 2 ml. of methanol, gave 50 mgm. (19%) of unchanged XV.

The alkaline phase was acidified with concentrated hydrochloric acid to precipitate 0.13 gm., m.p. 156–175° C. From this mixture was isolated a few milligrams of pure compound by crystallization from 85: 15 petroleum ether (b.p. 60–70° C.) – benzene (30 ml. per gm.), m.p. 203–204° C. Calc. for $C_{21}H_{24}O_2$: C, 81.7; H, 7.85. Found: C, 81.8; H, 8.04. According to this analysis the compound is 3,3-dimethyl-1-isopropyl-2-phenyl-1 or 2-indanecarboxylic acid. However if the hydrogen value were slightly in error the compound could be 3,3,3',3'-tetramethyl-1,1'-diisopropyl-2,2'-diphenylbiindanyldicarboxylic acid.

Ozonization of XV

A solution of 1.04 gm. (0.004 mole) of XV in 25 ml. of preozonized and purified carbon tetrachloride was treated with 4.1 liters of 5% ozonized oxygen during three hours. The solvent was vacuum-evaporated and the residual oily ozonide was hydrolyzed by heating it under reflux with 15 ml. of water, 300 mgm. of zinc dust, and 1 mgm. each of hydroquinone and silver nitrate. The mixture was filtered, the zinc was washed with 15 ml. of benzene, and the phases were separated. The aqueous phase was warmed to $40-50^{\circ}$ and a stream of nitrogen was bubbled through it. No acetone in the effluent could be detected by dinitrophenylhydrazine reagent. The aqueous layer was then distilled, but dimedone showed the absence of any formaldehyde in the distillate.

The benzene phase was extracted once with 10 ml. of 10% aqueous sodium hydroxide and twice with 5-ml. portions of water. The combined extracts were acidified with concentrated hydrochloric acid, precipitating 0.130 gm., m.p. 173–190° C. This crude *o*-carboxyphenylisopropiophenone (XVI) was crystallized from 2 ml. of benzene, 0.115 gm. (11%), m.p. 208.5–209.5° C. Potentiometric titration showed $K_{\rm A} = 4.5 \times 10^{-7}$. Calc. for C₁₇H₁₆O₃: C, 76.1; H, 6.01; neut. equiv., 268. Found: C, 75.8; H, 6.04; neut. equiv., 256. The mother liquor from the crystallization yielded 1% of benzoic acid.

The benzene phase from which XVI was alkali-extracted was dried and then evaporated. When the oily residue (0.956 gm.) was treated with excess acidmethanolic 2,4-dinitrophenylhydrazine a derivative (0.446 gm.) was obtained, m.p. 201–203° C. This dinitrophenylhydrazone of *o*-isobutyrophenylisopropiophenone (XVII) was crystallized from acetic acid (20 ml. per gm.), m.p. 206– 207° C. Calc. for $C_{26}H_{26}N_4O_5$: C, 65.8; H, 5.52; N, 11.8. Found: C, 65.3; H, 5.51; N, 11.9.

When the ozonide of XV was heated in water alone (oxidative hydrolysis) a 28% yield of benzoic acid and a 13% yield of XVI was isolated, but none of the carbonyl-containing XVII was found. If, instead of ozonization, XV was oxidized with sodium dichromate – sulphuric acid in acetic acid the only isolable product was XVI.

5,5,10,10-Tetramethyl-4b,5,9b,10-tetrahydroindeno[2,1-a]indene (XIX)

A. From meso-III and Concentrated Sulphuric Acid

The meso-2,5-dimethoxy-2,5-dimethyl-3,4-diphenylhexane (meso-III, 0.50 gm., 0.00153 mole) was added to 5.0 ml. of concentrated sulphuric acid at 25° C. A bright red color appeared and an oil separated which crystallized after seven hours. The system was drowned with ice and the crude solid (88 mgm., 22%, m.p. 78-79° C.) was crystallized from 0.5 ml. of hot methanol, 51 mgm. of XIX, m.p. 82-83° C. Variation in time, temperature, or amount of sulphuric acid did not alter the yield. Calc. for $C_{20}H_{22}$: C, 91.5; H, 8.45; Mol. wt. (Rast), 262. Found: C, 91.5; H, 8.62; mol. wt. (Rast), 270.

B. From meso-III and Hydrogen Fluoride

The meso-III (2.50 gm., 0.077 mole) was added to 160 gm. of liquid hydrogen fluoride at -80° C. in a polythene bottle. A bright orange color developed.

740

The mixture was stirred for three to five hours at 0° C. and then was poured into ice. The aqueous mixture was extracted with 100 ml. of diethyl ether. This extract was washed with 10% aqueous alkali, then with water, and dried. The residue left by ether evaporation (1.93 gm., m.p. 70–77° C.) was crystallized from 7 ml. of hot methanol, 1.47 gm. (73%), m.p. 82–83° C. No reduction was apparent when the product was boiled for three hours with an excess of sodium in ethanol. XIX was also recovered after treatment with ozone. The ultraviolet absorption spectrum of XIX, Fig. 2, resembles that of indane when determined in absolute ethanol (5.30 $\times 10^{-5}$ moles per liter).

C. From Dimethylisopropenylphenylindane (XIII) and Sulphuric Acid

When 31.1 mgm. $(1.19 \times 10^{-5} \text{ mole})$ of XIII was added to 3.0 ml. of 96% sulphuric acid at 0° C. it liquefied and a yellow color appeared. After six hours the oil solidified. The solid obtained after drowning with ice weighed 10.6 mgm. (34%), m.p. 81–82° C., mixture melting point with material from A and B not lowered.

D. From Dimethylisopropylphenylindene (XV) and Sulphuric Acid

The hydrocarbon (XV, 10 mgm., 3.9×10^{-3} mole) was added to 0.10 ml. of 96% sulphuric acid at 20° C. A yellow color appeared but the solid did not liquefy rapidly. After five hours ice was added and the solid filtered, 2 mgm., m.p. 79-80° C. A mixture melting point with material prepared according to A, B, or C was not lowered. The product was recovered: 99% after one day at 15 lb. hydrogen pressure with Adams' platinum catalyst, 75% after shaking with Raney nickel catalyst (W-2) at 1500 lb. hydrogen pressure either at 25° C., or 80° C.

Bromination of Tetramethyltetrahydroindenoindene (XIX)

A solution of 0.52 gm. (0.002 mole) of XIX in 20 ml. of carbon tetrachloride with 0.64 gm. (0.008 mole) of bromine became colorless after eight hours and 0.64 gm. (0.0051 mole) of hydrogen bromide was evolved. Evaporation of the system left 0.801 gm. which was crystallized from benzene (20 ml. per gm.) finally to melt at 313–314° C. Elemental analysis showed the compound to contain bromine although it would not react with alcoholic silver nitrate. The X-ray diffraction powder diagram was: [10] 5.68, 5.52; [9] 3.33; [6] 6.25, 6.00, 3.85, 3.75. Calc. for $C_{20}H_{18}Br_2$: C, 57.4; H, 4.34. Found: C, 58.0; H, 4.46.

The first mother liquor from the benzene crystallization was evaporated and treated to get a steam distillate, 0.22 gm., m.p. 75–105° C. Repeated crystallization from petroleum ether (b.p. 60–70° C., 15 ml. per gm.) and from absolute ethanol (15 ml. per gm.) left 10 mgm., m.p. 206–207° C. Calc. for $C_{20}H_{19}Br: C, 70.8$; H, 5.64. Found: C, 70.7; H, 5.78.

Oxidation of Tetramethyltetrahydroindenoindene (XIX)

Either hot aqueous nitric acid or potassium permanganate seems to be inadequate as an oxidizing agent for XIX, but chromic acid is effective. A mixture of 12.0 gm. (0.04 mole) of sodium dichromate dihydrate in 43 ml. of 50 volume per cent aqueous sulphuric acid and 30 ml. of acetic acid was stirred for 20 hr. with 2.08 gm. (0.008 mole) of XIX. The system was then diluted with 50 ml. of water and extracted with 70 and then 20 ml. of diethyl ether. The etherous phase was washed with water, then extracted with alkali followed by water. The etherous phase was then dried and evaporated, leaving 1.05 gm. of gum which was crystallized from 5 ml. of hot absolute ethanol, 0.32 gm. (13%), m.p. $203-205^{\circ}$ C. (after recrystallization, $205-205.5^{\circ}$ C.). Calc. for $C_{20}H_{20}O_3$: C, 77.9; H, 6.53. Found: C, 78.3; H, 6.65. This product of unknown structure was recovered unchanged after long heating with hot 15% alkali in which it was insoluble. It reacted neither with hot hydrogen bromide in acetic acid nor with hydrogen in presence of Adams' platinum catalyst. It was also inert toward chromic acid and permanganate (in acetone) oxidation.

Evaporation of the mother liquor from the ethanolic crystallization of the 1.05 gm. of gum left a residue, m.p. $60-70^{\circ}$ C., which was extracted with 10 ml. of hot petroleum ether (b.p. $40-60^{\circ}$ C.). When cool the insoluble portion (0.288 gm.) melted at 180-206° C. while the solution, evaporated, left 0.508 gm., m.p. $65-75^{\circ}$ C. The latter was crystallized from 2 ml. of hot methanol, 0.354 gm. (17%) of unchanged XIX, m.p. $82-83.5^{\circ}$ C., mixture melting point not depressed. The 0.288 gm. portion was crystallized from 2 ml. of benzene, 0.035 gm., m.p. 236-240° C. For analysis this was crystallized from 1 ml. of methanol, m.p. 237-238.5° C. Calc. for $C_{20}H_{22}O_3$: C, 77.4; H, 7.14. Found: C, 77.4; H, 7.26.

The alkaline extract of the original ether solution was acidified with concentrated hydrochloric acid and then extracted with diethyl ether. This extract, dried, was evaporated, leaving 0.16 gm. which was sublimed at 100° C. (8 mm.) for 40 hr. The sublimate, 0.0983 gm., m.p. 65-72° C., was fractionally resublimed at 80° C. (10 mm.) to obtain an intermediate fraction, 52 mgm. (3%), m.p. 75-78° C. Crystallization of this crude dimethylhomophthalic anhydride from petroleum ether (b.p. 40-60° C., 10 ml. per gm.) raised the melting point to 80-81° C. Calc. for C₁₁H₁₀O₃: C, 69.5; H, 5.30. Found: C, 69.5; H, 5.30. This anhydride (5 mgm.) was dissolved in 0.5 ml. of 3% aqueous sodium hydroxide, then acidified with 0.05 ml. of concentrated hydrochloric acid, yielding the dimethylhomophthalic acid (XX, m.p. 126-127.5° C.). Vacuum resublimation converted XX to the anhydride. The alkaline solution of the anhydride was potentiometrically titrated with hydrochloric acid, equivalent weight, 94.6 (calc., 95.1), approximately $K_{A_1} = 2.5 \times 10^{-4}$, $K_{A_2} = 5.6 \times 10^{-6}$. When the anhydride (5 mgm.) was dissolved in 1 ml. of 10% aqua ammonia and the solution was evaporated to dryness, either the acid-amide or the diamide must have been formed (m.p. 165-173° C.); it was sublimed at 200° C. (8 mm.), m.p. 105-109° C. This crude homophthalimide, after two crystallizations from 0.25 ml. of water, melted at 118-119° C. The melting point reported previously (5, 6) is 119-120° C.

When the ratio of XIX to oxidizing agent was decreased the amount of $C_{20}H_{20}O_3$ was increased to 14% while none of the dimethylhomophthalic anhydride could be isolated. In contrast, increase of the ratio increased the yield of the anhydride to 7%.

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