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DIMERIZATION OF STYRENE IN THE PRESENCE AND ABSENCE OF SOLVENT

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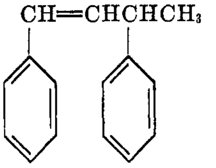
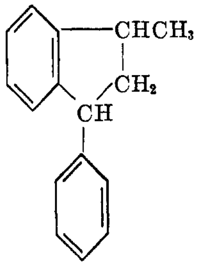
Styrene dimer was at first believed (1–5) to be 1,3-diphenyl-1-butene (I), but in 1936 Risi and Gauvin (6) showed that it was a mixture of this unsaturated dimer and a saturated dimer which they assumed to be 1-methyl-3-phenylindan (II). Risi and Gauvin offered no experimental evidence for the assumed structure of the saturated dimer. It was postulated by analogy with the established structures of the saturated dimers of 1,1-diphenylethylene (7) and α-methylstyrene (8).

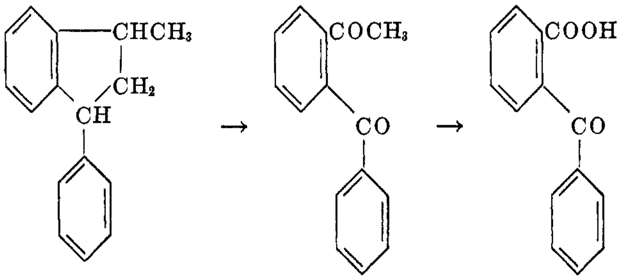


I



II

Spoerri and Rosen (9) recently published experimental evidence in support of the proposed indan structure of the saturated dimer. Their work disclosed that its ultraviolet spectrum was similar to that of indan and they obtained *o*-benzoylbenzoic acid (IV) by oxidation.



II III IV

The present paper confirms the findings of Spoerri and Rosen, and in addition presents (a) evidence for the existence of 1-methyl-3-phenylindan (II) in two isomeric forms (*cis*- and *trans*-racemic) and (b) information concerning the influence of solvent and catalyst upon the course of the dimerization reaction.

When styrene was dimerized in the absence of solvent or in the presence of inert (nonalkylatable) solvent, the saturated dimer content of the total

TABLE I

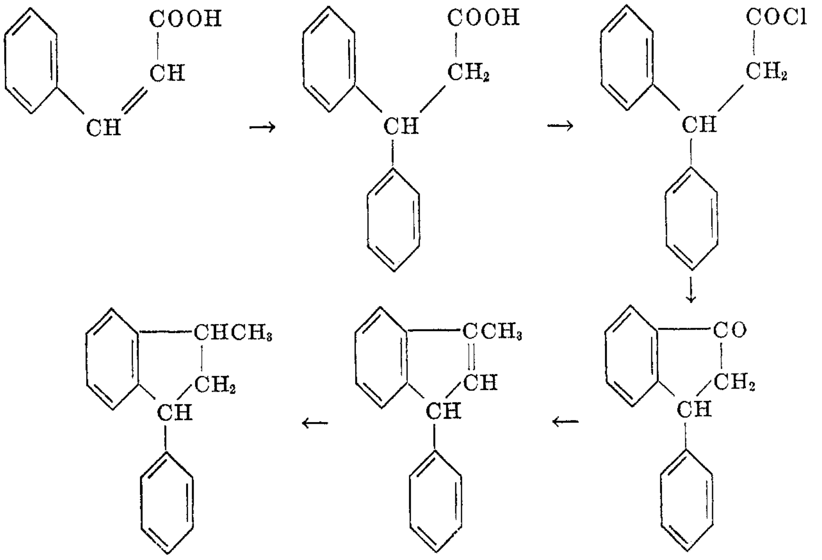
DIMERIZATION OF STYRENE UNDER DIFFERENT CONDITIONS

SOLVENT	SOLVENT / STYRENE (wt.)	CATALYST	SATURATED COMPONENT, %	COMPOSITION OF SAT'D COMPONENT, %		
				1-Methyl-3-phenylindan		Styrene-Ethylbenzene Alkylate[a]
				25.5° Isomer	9.5° Isomer	
None	0	SiO_2	30	56	44	0
None	0	H_2SO_4	87	46	54	0
n-Heptane	1.5	H_2SO_4	75	45	55	0
Benzene	1.5	H_2SO_4	50	39	41	20[b]
Ethylbenzene	1.5	H_2SO_4	75	20	22	58
Ethylbenzene	10	H_2SO_4	85	8	20	72
Ethylbenzene	1	H_3PO_4	90	30	47	23

[a] 1-(*p*-Ethylphenyl)-1-phenylethane. [b] 1,1-Diphenylethane.

dimerizate ranged from 30–90%, depending upon the reaction conditions (Table I). Separation of the saturated and unsaturated dimers was accomplished by distillation. The saturated dimer was found to be a mixture of two isomeric forms of 1-methyl-3-phenylindan, one melting at 25.5°, the other at 9.5°. Both isomers were oxidized in high yield (about 90%) to a mixture of *o*-acetylbenzophenone (III) and *o*-benzoylbenzoic acid (IV), the relative amounts of diketone and ketoacid depending upon the conditions of oxidation.

The 25.5° isomer was separated in 10% yield and 95% purity from the saturated dimer distillate by low-temperature crystallization. Pure 9.5° isomer was not separated from the mixture of saturated dimers, but was synthesized by the following reaction sequence, in which the final step involved the addition of hydrogen to 1-methyl-3-phenylindene.



[II, 9.5° Isomer]

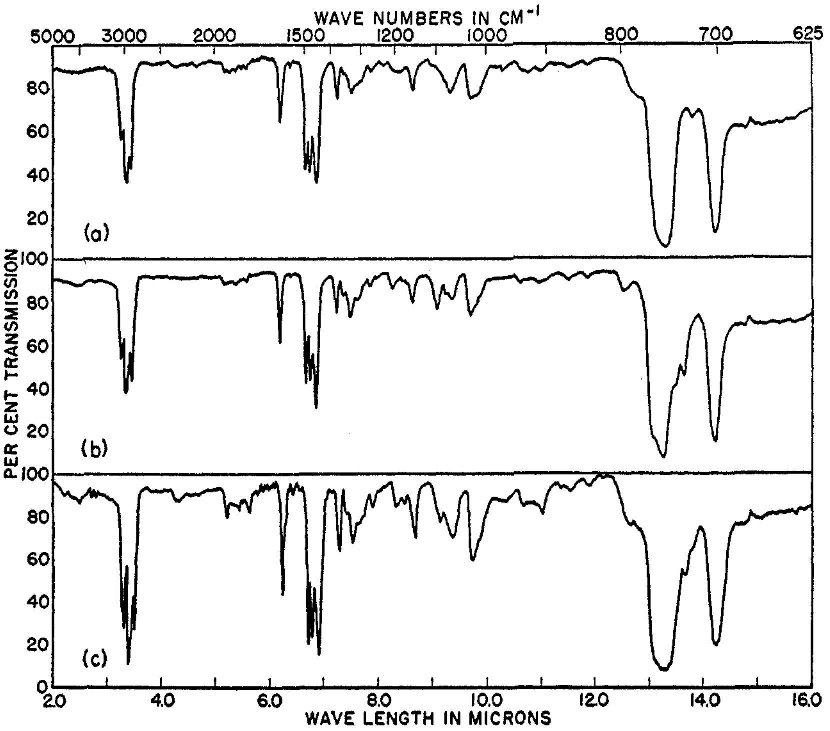


FIG. 1. INFRARED SPECTRA OF (a) 25.5° isomer of 1-methyl-3-phenylindan, (b) 9.5° isomer of 1-methyl-3-phenylindan, (c) saturated dimer of styrene containing 46% of the 25.5° isomer and 54% of the 9.5° isomer.

Treatment of the 9.5° isomer with aluminum chloride converted it to a mixture of the 9.5° and 25.5° isomers, from which the latter was isolated by low-temperature crystallization. Although it was not unexpected[1] to find 1-methyl-3-phenylindan existing in two stereoisomeric forms, the partial interconversion of the 9.5° isomer to the 25.5° isomer was somewhat novel. Müller, *et al.*, (10) have recently shown in a number of cases that indans obtained by the dimerization of styrene derivatives differ in physical properties from the isomeric indans resulting from the addition of hydrogen to the corresponding indenes. However, these investigators did not accomplish interconversion of the isomeric indans.

The two saturated styrene dimers were characterized by their infrared spectra, and their analytical determination in the saturated dimer mixtures was based on their absorption at 13.64 microns (Fig. 1).

The product obtained by dimerizing styrene in ethylbenzene solution in the presence of phosphoric acid as catalyst has been reported to be a mixture of 75% of 1,4-diphenyl-2-butene and 25% of 1-methyl-3-phenylindan (11, 12).

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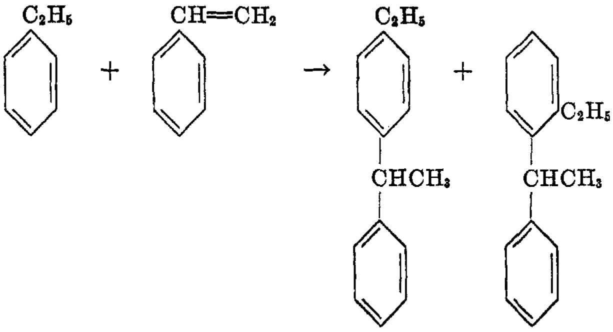
[1] Baker and Enderby [*J. Chem. Soc.*, 1094 (1940)], in the cyclization of isoanethole to metanethole [1-(p-anisyl)-2-methyl-3-ethyl-6-methoxyindan] observed the formation of a liquid coproduct which they suggested might contain some of the other three possible stereoisomeric 1,2,3-trisubstituted indans.

This alleged composition is incorrect. We have resolved this product into 10% of an unsaturated component [presumably 1,3-diphenyl-1-butene (I)] and 90% of a close-boiling three-component mixture of the two isomeric 1-methyl-3-phenylindans and 1-(*p*-ethylphenyl)-1-phenylethane (V). Component V is a styrene-ethylbenzene alkylate. Its presence was demonstrated spectrometrically and also by oxidation (to *p*-acetylbenzophenone and *p*-benzoylbenzoic acid). Obviously, ethylbenzene was a reactant and not an inert solvent as assumed. The presence of 1-(*o*-ethylphenyl)-1-phenylethane (VI), an isomeric styrene-ethylbenzene alkylate, was suspected but was not proved.



V VI

The dimerization of styrene in benzene solution results in a four-component mixture — unsaturated dimer, two saturated dimers, and 1,1-diphenylethane, the last named being separable by distillation.

The styrene-ethylbenzene alkylates (V and VI) required as spectrometric standards (Fig. 2) were prepared from the corresponding tertiary carbinols by dehydration followed by hydrogenation.

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EXPERIMENTAL

The melting points are corrected. The boiling points are not corrected. All dimerizations were made at atmospheric pressure. The distillation equipment was a 27-plate (theoretical) glass column packed with 3/32-inch glass helices.

DIMERIZATION OF STYRENE

With silica gel; no solvent. Styrene was pumped through a Vycor tube packed with silica gel catalyst at 0.1 liquid hourly space velocity in the presence of 5 moles of steam per mole of styrene. The catalyst temperature was 200°. The catalyzate contained 50% of dimer, 25% of trimer, and 25% of higher-boiling products. Two distillations of the dimer gave 30% of saturated component (b.p. 171–175°/20 mm., n_D^{20} 1.5822, d_4^{20} 1.0234) and 70% of unsaturated component (b.p. 183°/20 mm., n_D^{20} 1.5932, d_4^{20} 0.9996).

With sulfuric acid; no solvent. The procedure of Risi and Gauvin (6) was followed. Styrene (500 g.) was refluxed and stirred for 8 hours with 125 g. of 56% sulfuric acid. The hydrocarbon was extracted with ether, and the extract was washed with aqueous carbonate and dried. Distillation gave 352 g. of saturated dimer (b.p. 170–172°/20 mm., n_D^{20} 1.5790, d_4^{20} 1.0178), 53 g. of unsaturated dimer (b.p. 181–182°/20 mm., n_D^{20} 1.5932, d_4^{20} 0.9986), and 89 g.

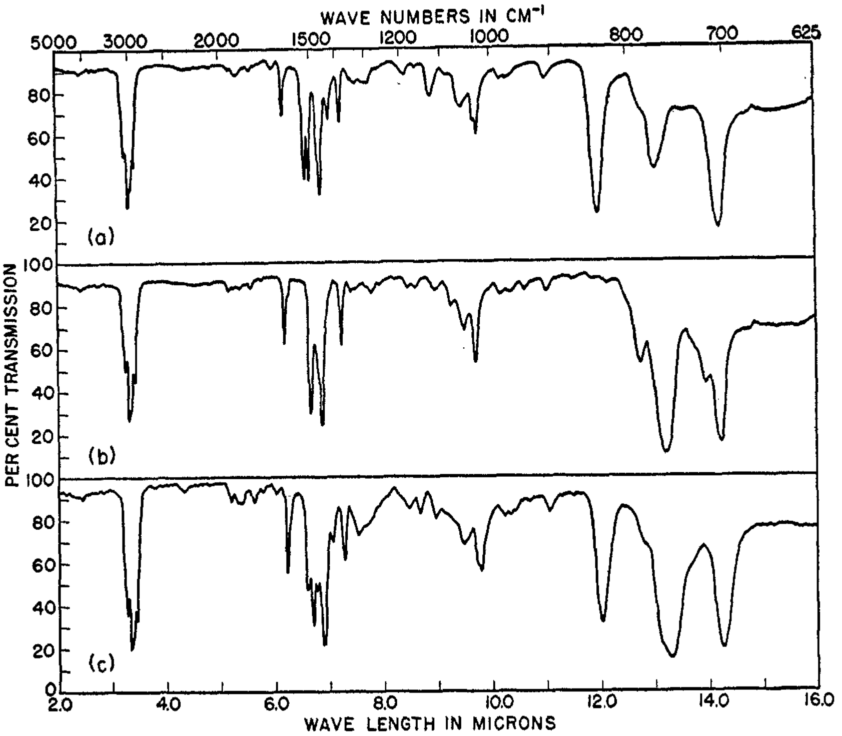

FIG. 2. INFRARED SPECTRA OF (a) 1-(*p*-ethylphenyl)-1-phenylethane, (b) 1-(*o*-ethylphenyl)-1-phenylethane, (c) saturated styrene dimer made in ethylbenzene and containing 8% of the 25.5° isomer, 20% of the 9.5° isomer, and 72% of 1-(*p*-ethylphenyl)-1-phenylethane.

of higher-boiling product. The carbon-hydrogen values of the saturated dimer corresponded to the composition $C_{16}H_{16}$.

Anal. Calc'd for $C_{16}H_{16}$: C, 92.3; H, 7.74.

Found: C, 92.4; H, 7.55.

The above experiment was repeated, and the hydrocarbon product was separated and subsequently refluxed and stirred for 40 hours with 4900 cc. of 65% sulfuric acid. The hydrocarbon layer was extracted with ether, and the extract was washed with aqueous carbonate and dried. Distillation gave 306 g. of saturated dimer (b.p. 171–172°/20 mm., n_D^{20} 1.5808, d_4^{20} 1.0245) and 111 g. of higher-boiling material. The melting point of the saturated dimer (extrapolated from its melting curve) was 14.8°. The melting range was at least 12°.

With sulfuric acid; n-heptane as solvent. A solution of 1000 g. of styrene in 1500 g. of *n*-heptane was added during 14 hours to 500 cc. of stirred 71% sulfuric acid at 100°. The hydrocarbon layer was separated, washed with aqueous sodium carbonate, dried, and distilled to give 702 g. of dimer fraction (b.p. 144–160°/5 mm.) and 208 g. of residue. Redistillation of the dimer fraction yielded 527 g. of saturated component (b.p. 170–172°/20 mm., n_D^{20} 1.5803, d_4^{20} 1.0237) and 175 g. of unsaturated component (b.p. 182°/20 mm., n_D^{20} 1.5931, d_4^{20} 0.9985).

With sulfuric acid; benzene as solvent. Styrene (1000 g.) in 1500 g. of benzene was dimerized in the presence of 250 cc. of 71% sulfuric acid as described above to give 530 g. of dimer fraction (b.p. 90–170°/4 mm.) and 436 g. of residue. Redistillation of the dimer fraction gave 53 g. of 1, 1-diphenylethane (b.p. 146°/20 mm., n_D^{20} 1.5725, d_4^{20} 0.9993), 212 g. of saturated dimer (b.p. 170–173°/20 mm., n_D^{20} 1.5819, d_4^{0} 1.0223), and 265 g. of unsaturated dimer (b.p.

182°/20 mm., n_D^{20} 1.5925, d_4^{20} 0.9999). The identity of 1,1-diphenylethane was established by comparing its infrared spectrum and other physical constants with those of an authentic sample.

With sulfuric acid; ethylbenzene as solvent. A solution of 1000 g. of styrene in 1500 g. of ethylbenzene was treated with 250 cc. of 71% sulfuric acid as described above. Preliminary distillation of the hydrocarbon catalyzate yielded 1248 g. of ethylbenzene [17% (252 g.) loss], 992 g. of "styrene dimer" (b.p. 136–153°/5 mm.), and 220 g. of residue. Redistillation resolved the "styrene dimer" into 744 g. of saturated material (b.p. 170–172°/20 mm., n_D^{20} 1.5690, d_4^{20} 0.9978) and 248 g. of unsaturated material (b.p. 181–182°/20 mm., n_D^{20} 1.5936, d_4^{20} 0.9991). The combined weight of the "styrene dimer" plus residue was 21% (212 g.) greater than that of the styrene charged. This increase was due to the aralkylation of ethylbenzene by styrene.

In another experiment in which a higher ethylbenzene/styrene ratio was used (208 g. of styrene, 2120 g. of ethylbenzene, and 250 cc. of 71% sulfuric acid), the preliminary distillation afforded 1980 g. of ethylbenzene [6.6% (140 g.) loss], 255 g. of "styrene dimer" (b.p. 136–150°/20 mm.), and 29 g. of residue. Redistillation resolved the "styrene dimer" into 217 g. of saturated hydrocarbon (b.p. 170–172°/20 mm., n_D^{20} 1.5659, d_4^{20} 0.9887), and 38 g. of unsaturated hydrocarbon (b.p. 181–182°/20 mm., n_D^{20} 1.5895, d_4^{20} 0.9995). The combined weight of the "styrene dimer" plus residue was 37% (76 g.) greater than that of the styrene charged.

With phosphoric acid; ethylbenzene as solvent. A solution of 1036 g. of styrene in 1036 g. of ethylbenzene was pumped over phosphoric acid-charcoal catalyst (11) at 140° and 0.9 liquid hourly space velocity. The catalyst, which contained 28.5% of phosphoric acid, was prepared by impregnating 6–8 mesh Columbia activated carbon (SKA) with 60% phosphoric acid, followed by drying for 24 hours at 120°. Preliminary distillation of the catalyzate gave 916 g. of ethylbenzene [11.6% (120 g.) loss], 754 g. of "styrene dimer" (b.p. 130–150°/4 mm.), and 291 g. of residue. Redistillation resolved the "styrene dimer" into 679 g. of saturated hydrocarbon (b.p. 170–172°/20 mm., n_D^{20} 1.5761, d_4^{20} 1.0119) and 75 g. of unsaturated hydrocarbon (b.p. 183°/20 mm., n_D^{20} 1.5925, d_4^{20} 0.9992). The combined weight of the "styrene dimer" plus residue was 1% (9 g.) greater than that of the styrene charged.

PREPARATION OF SPECTROMETRIC STANDARDS

1-Methyl-3-phenylindan (25.5° isomer). The saturated component of styrene dimer obtained by dimerizing styrene with sulfuric acid in the absence of solvent (melting range 12°) was recrystallized five times from petroleum ether by slow cooling in Dry Ice. Ten percent of the starting material was obtained as white crystals which melted at 25.5° with a 3.2° melting range. Its purity, estimated from its melting curve, was at least 95%. The n_D^{20} and d_4^{20} values for the (a) initial saturated dimer mixture, (b) 1-methyl-3-phenylindan (25.5° isomer), and (c) saturated dimer mixture recovered from the first mother liquor were: (a) 1.5808 and 1.0245, (b) 1.5810 and 1.0257, (c) 1.5805 and 1.0236.

1-Methyl-3-phenylindan (9.5° isomer). The reaction of cinnamic acid with benzene (13) in the presence of aluminum chloride gave an 87% yield of β,β-diphenylpropionic acid (m.p. 153.5–154.5°) which was subsequently converted to its acid chloride (14) by refluxing with thionyl chloride. The acid chloride, without isolation, was cyclized (14, 15) by the action of aluminum chloride to give a 74% yield of 3-phenyl-1-indanone (m.p. 76.5–77.5°; yellow crystals from methanol). Reaction of this indanone with methylmagnesium iodide, followed by dehydration of the resultant carbinol, produced an 80% yield of 1-methyl-3-phenylindene (m.p. 63–64°, white crystals from Methyl Cellosolve[2]).

Anal. Calc'd for $C_{16}H_{14}$: C, 93.2; H, 6.84; Mol. wt., 206.

Found: C, 93.5; H, 6.76; Mol. wt., 210.

The indene reacted with bromine at 15° in carbon tetrachloride solution to give a white monobromo derivative (m.p. 94–95°, crystallized from methanol).

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[2] Trade name for 2-methoxyethanol.

Anal. Calc'd for $C_{16}H_{13}Br$: C, 67.4; H, 4.59; Br. 28.0.
Found: C, 67.5; H, 4.67; Br. 27.7.

The indene was hydrogenated at 55° under 100 atmospheres of hydrogen in the presence of a nickel catalyst. The filtered catalyzate was washed with cold concentrated sulfuric acid, followed by water, and distilled to give a 90% yield of 1-methyl-3-phenylindan (m.p. 9.5°; b.p. 157°/12 mm., 172.5°/20 mm.; n_D^{20} 1.5809; d_4^{20} 1.0230).

Anal. Calc'd for $C_{16}H_{16}$: C, 92.3; H, 7.74; Mol. wt., 208.
Found: C, 92.5; H, 7.69; Mol. wt., 213.

Its purity, estimated from its melting curve, was 95%.

The above 9.5° isomer was isomerized to a mixture of the 9.5° and 25.5° isomers with aluminum chloride. A mixture of 25 g. of the 9.5° isomer and 2.5 g. of aluminum chloride was shaken for 71 hours at room temperature. The reaction mixture was poured into 75 cc. of water and the hydrocarbon was extracted with petroleum ether. Distillation gave 13 g. of distillate (b.p. 170–173°/20 mm., n_D^{20} 1.5804, d_4^{20} 1.0236) which was a mixture of 19% of the 25.5° isomer and 81% of the 9.5° isomer (according to infrared absorption). The presence of the 25.5° isomer was confirmed by twice crystallizing the isomerizate from petroleum ether, whereby a concentrate was obtained which contained 77% of the 25.5° isomer.

1-(p-Ethylphenyl)-1-phenylethane (V). *p*-Ethylacetophenone (370 g.) reacted with phenylmagnesium bromide (393 g. of bromobenzene plus 61 g. of magnesium) to give 1-(*p*-ethylphenyl)-1-phenylethanol, which without isolation was dehydrated by heating in ethanol-hydrochloric acid (16) to give 372 g. (72% yield) of 1-(*p*-ethylphenyl)-1-phenylethylene (b.p. 177°/20 mm., n_D^{20} 1.5921, d_4^{20} 0.9955). The substituted ethylene (247 g.) was hydrogenated in cyclohexane solution at 55° (100 atms. of hydrogen, nickel catalyst), to give 231 g. (93% yield) of 1-(*p*-ethylphenyl)-1-phenylethane (17); b.p. 170°/20 mm., n_D^{20} 1.5605, d_4^{20} 0.9746. The over-all yield was 67%.

Anal. Calc'd for $C_{16}H_{18}$: C, 91.4; H, 8.63.
Found: C, 91.2; H, 8.58.

1-(o-Ethylphenyl)-1-phenylethane (VI). Acetophenone (120 g.) reacted with *o*-ethylphenylmagnesium iodide (194 g. of *o*-iodoethylbenzene plus 24 g. of magnesium) to give 1-(*o*-ethylphenyl)-1-phenylethanol, which without isolation was dehydrated as above to produce 50 g. (24% yield) of 1-(*o*-ethylphenyl)-1-phenylethylene (b.p. 162.5°/20 mm., n_D^{20} 1.5861, d_4^{20} 0.9977). The ethylene compound (38 g.) was hydrogenated as above to give 27 g. (54% yield) of 1-(*o*-ethylphenyl)-1-phenylethane (b.p. 165°/20 mm., n_D^{20} 1.5650, d_4^{20} 0.9856). The over-all yield was 13%.

Anal. Calc'd for $C_{16}H_{18}$: C, 91.4; H, 8.63; Mol. wt., 210.
Found: C, 91.6; H, 8.64; Mol. wt., 211.

1,1-Diphenylethane (17, 18). The starting materials for the synthesis of this spectrometric standard were acetophenone and phenylmagnesium bromide. The intermediates were 1,1-diphenylethanol and 1,1-diphenylethylene. The over-all yield of 1,1-diphenylethane was 70%; b.p. 146°/20 mm., n_D^{20} 1.5725; d_4^{20} 0.9993.

PROOF OF STRUCTURE OF SATURATED DIMER

Oxidation of 1-methyl-3-phenylindan (25.5° isomer). A mixture of 3.0 g. of the 25.5° isomer, 9 cc. of acetic acid, 15 cc. of concentrated sulfuric acid, 90 cc. of water, and 21 g. of chromic acid was refluxed and stirred for 1 hour. The reaction mixture was diluted with water to 1300 cc., extracted with ether, and the ether extract was washed with aqueous carbonate. The ether was evaporated and the residue deposited 1.0 g. (31% yield) of *o*-acetylbenzophenone. After crystallization from *n*-hexane, this diketone melted at 99–100° (19) and its melting point was not depressed by admixture with authentic diketone. The carbonate extract was acidified, extracted with ether, and the ether was evaporated. The result was 2.2 g. (34% yield) of viscous, amber-colored oil which slowly solidified, and from which *o*-benzoylbenzoic acid (m.p. and mixture m.p. 129–130°) was isolated by crystallization from benzene-cyclohexane.

Oxidation of 1-methyl-3-phenylindan (9.5° isomer). Synthetic 1-methyl-3-phenylindan

(3.0 g., m.p. 9.5°) was oxidized as above except that the reflux period was 6 hours. The reaction mixture, diluted to 1300 cc. with water, was stored at 0° for 48 hours. Filtration removed 2.15 g. (66% yield) of *o*-benzoylbenzoic acid which melted at 129–130° after crystallization from benzene-cyclohexane. Its melting point was not depressed by admixture with authentic *o*-benzoylbenzoic acid. The acidic filtrate was extracted with ether, but no neutral product was obtained.

Another sample of the 9.5° indan was oxidized with anhydrous chromic acid-acetic acid as follows. Chromic acid (15 g.) was added to a stirred solution of 3.0 g. of 1-methyl-3-phenylindan in 35 cc. of glacial acetic acid at such rate that the temperature remained below 30°. The mixture was then stirred for 4 hours at 30°. After dilution with 500 cc. of water, the mixture was extracted with ether, and the ether solution was extracted with aqueous carbonate. Acidification of the carbonate extract, followed by ether extraction and evaporation of the ether, gave a 2.0 g. residue (62% yield) of *o*-benzoylbenzoic acid (m.p. and mixture m.p. 129–130° after crystallization from benzene-cyclohexane). Evaporation of the ether from the carbonate-washed ether extract left a 1.05 g. residue (33% yield) of *o*-acetylbenzophenone (white plates from *n*-hexane, m.p. 99–100°).

Anal. Calc'd for $C_{15}H_{12}O_2$: C, 80.3; H, 5.40.

Found: C, 80.3; H, 5.37.

The combined yields of acid and ketone accounted for 95% of the initial 1-methyl-3-phenylindan. Chromic acid oxidation of the ketone produced *o*-benzoylbenzoic acid.

Oxidation of saturated dimer fraction made in the absence of solvent or in n-heptane solution. Similar oxidation results were obtained with the saturated dimer mixture as with the 25.5° isomer isolated therefrom and the authentic 9.5° isomer.

Oxidation of 1-(p-ethylphenyl)-1-phenylethane (V). Oxidation of 3.0 g. of this hydrocarbon with aqueous chromic acid-acetic acid gave 2.8 g. (87% yield) of crude *p*-benzoylbenzoic acid (m.p. and mixture m.p. 198.5–199.5° after crystallization from toluene), but no neutral product. However, oxidation of 3.0 g. of the hydrocarbon with anhydrous chromic acid-acetic acid resulted in 0.55 g. (17% yield) of crude *p*-benzoylbenzoic acid and 2.7 g. (85% yield) of crude *p*-acetylbenzophenone (white needles from *n*-hexane, m.p. 85.5–86.5°).

Anal. Calc'd for $C_{15}H_{12}O_2$: C, 80.3; H, 5.40.

Found: C, 80.2; H, 5.20.

Oxidation of 3.0 g. of the 85.5–86.5° diketone with aqueous chromic acid (0.5 hour at 60° followed by 0.5 hour at 100°) gave an essentially quantitative yield of *p*-benzoylbenzoic acid. The weight of nonoxidized diketone was 0.2 g. The acid was converted to its methyl ester (m.p. 109.5–110.5°, plates from methanol), whose melting point was not depressed by admixture with authentic methyl *p*-benzoylbenzoate. The literature reports the melting point at 106–107° (20).

Oxidation of saturated "styrene dimer" made in ethylbenzene solution. Alkaline permanganate was first used for this purpose, but the results were confusing for two reasons: (a) the oxidation products were too small to fix the structure of the antecedent hydrocarbon; (b) the simultaneous presence of 1-methyl-3-phenylindan and aralkylated ethylbenzene (at that time not suspected) made for a multiplicity of oxidation products. The latter included phenylphthalide, benzoic acid, benzoylformic acid, phthalonic acid, terephthalic acid, *o*-benzoylbenzoic acid, *p*-benzoylbenzoic acid, *o*-acetylbenzophenone, *p*-acetylbenzophenone, and an unidentified white solid, crystallized from cyclohexane and melting at 154–155°, perhaps an indandiol (hydroxyl groups indicated by infrared scanning), which dissolved in concentrated sulfuric acid with the production of a red solution.

Anal. Calc'd for $C_{16}H_{16}O_2$: C, 80.0; H, 6.71; Mol. wt., 240.

Found: C, 80.1; H, 6.58; Mol. wt., 256.

Chromic acid oxidation gave larger oxidation fragments, but the composition of the mixture of saturated dimer and aralkylated ethylbenzene was too complicated to establish by oxidation. A typical oxidation experiment with chromic acid follows.

Three g. of "dimer fraction" (b.p. 171–173°/20 mm., n_D^{20} 1.5690, d_4^{20} 0.9978) was oxidized at reflux temperature with aqueous chromic acid-acetic acid, and the reaction mixture was stored at 0° for 48 hours. Filtration of the cold solution through a fritted glass funnel removed 0.5 g. (16% yield) of *p*-benzoylbenzoic acid, and the filtrate quickly deposited a second crop of crystals, 0.8 g. (25% yield) of *o*-benzoylbenzoic acid. Both crops of crystals were essentially pure. This remarkable separation was obtained in several experiments.

The filtrate was extracted with ether, the extract was washed with aqueous carbonate, and the ether was evaporated. The residual white solid was crystallized from *n*-hexane. By repeated fractionation it was possible to separate *p*-acetylbenzophenone (long needles) and *o*-acetylbenzophenone (thin plates). The latter colors the skin blue-green.

Spectrometric analysis. Mixtures of the 1-methyl-3-phenylindan isomers were analyzed for the 9.5° isomer by infrared absorption at 13.64 microns. In the presence of other components, the 9.5° and 25.5° isomers were determined by ultraviolet absorption at 266 and 277 millimicrons, respectively. Unsaturated dimer was determined by ultraviolet absorption at 293 millimicrons, and 1-(*p*-ethylphenyl)-1-phenylethane was determined by infrared absorption at 11.98 microns.

SUMMARY

The dimerization of styrene in the absence of solvent or in *n*-heptane solution resulted in a mixture of unsaturated dimer (1,3-diphenyl-1-butene) and saturated dimer (1-methyl-3-phenylindan). The latter was found to exist in two stereoisomeric forms (*cis-trans*), one melting at 9.5°, the other at 25.5°.

The structure of the saturated dimer was established by (a) the identity of the infrared spectrum of its 9.5° isomer with authentic 1-methyl-3-phenylindan, (b) the conversion of the 9.5° isomer to the 25.5° isomer, and (c) the oxidation of both indan isomers, in good yield, to a mixture of *o*-acetylbenzophenone and *o*-benzoylbenzoic acid.

The dimerization of styrene in the presence of benzene or ethylbenzene is complicated by the simultaneous production of aralkylation coproducts — 1,1-diphenylethane in the case of benzene and 1-(*p*-ethylphenyl)-1-phenylethane in the case of ethylbenzene. The identity of these two coproducts was established by their infrared spectra and other physical constants. The identity of 1-(*p*-ethylphenyl)-1-phenylethane was established also by its oxidation products.

p-Acetylbenzophenone and 1-phenyl-1-(*p*-ethylphenyl)ethane have not previously been described.

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