

solved in 5 cc. of acetone and dilute sodium hydroxide added. The acetone was removed by boiling, the alkaline solution treated with norit and filtered. A solution containing 2 g. of potassium ferricyanide was added to the cold filtrate and the typical red resinoid was filtered off, dried and weighed: sample, 4.372 g.; chromo-resinoid 0.113 g., corresponding to 3.7% di-iodothymol.

Anal. (Carius). Calcd. for $(C_{10}H_{11}IO)_n$: I, 46.32. Found: I, 44.75.

Summary

Di-iodothymol and its benzoate have been prepared.

Di-iodothymol salts have been shown to be precursors of the chromo-resinoid formed when iodine acts on alkaline solutions of thymol according to the equation $nC_{10}H_{11}I_2ONa = (C_{10}H_{11}IO)_n + nNaI$.

Di-iodothymol has been shown to be present in U. S. P. thymol iodide.

UNIVERSITY, MISSISSIPPI

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

THE POLYMERIZATION OF ASYMMETRICAL DIPHENYLETHYLENE. THE PREPARATION OF 1,1,3-TRIPHENYL-3-METHYLHYDRINDENE

BY C. S. SCHOEPPLE AND J. D. RYAN¹

RECEIVED JUNE 30, 1930

PUBLISHED OCTOBER 6, 1930

Bergmann and Weiss, in a paper recently published,² have shown that the saturated dimer of asymmetrical diphenylethylene is 1,1,3-triphenyl-3-methylhydrindene and not tetraphenylcyclobutane, as previously supposed, and have stressed the importance of this fact in connection with the views of Staudinger and others on the mechanism of polymerization and the structure of high molecular weight compounds. In a study of the properties of this saturated dimer in this Laboratory, its identity has been established, independently, from its oxidation products. Our investigation, which is still in progress, is concerned chiefly with the mechanism of the reaction by which triphenylmethylhydrindene and other indenenes are formed, but the work has paralleled that of Bergmann and Weiss in many respects and therefore it is considered advisable to publish the results which have been obtained at this time.

Polymerization of asymmetrical diphenylethylene (I) by the use of catalysts yields two dimeric compounds, one unsaturated (III) and the other saturated (XII). The unsaturated dimer, m. p. 113°, was prepared first by Hildebrand³ and shown by Lebedev⁴ to be 1,1,3,3-tetraphenyl-1-butene,

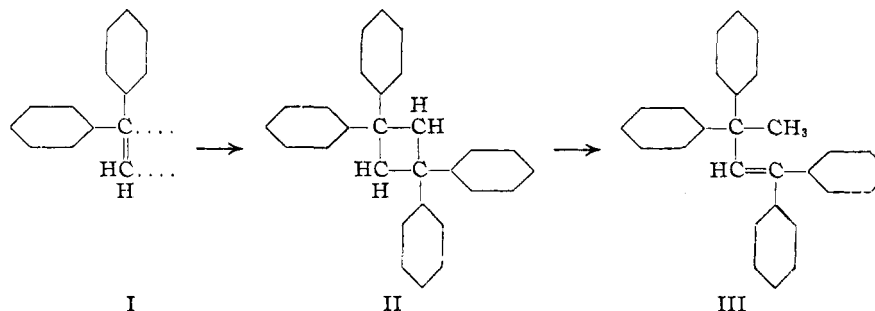
¹ This paper represents part of a dissertation to be submitted to the Graduate School by Mr. Ryan in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

² Bergmann and Weiss, *Ann.*, **480**, 49 (1930).

³ Dissertation by Hildebrand, Strassburg, 1909.

⁴ Lebedev, Andreievskii and Matiushkina, *Ber.*, **56**, 2349 (1923).

which structure was confirmed by Schlenk and Bergmann.⁵ The formation of this compound may be explained by assuming that two molecules of asymmetrical diphenylethylene combine under the influence of catalysts such as sulfuric acid, iodine, stannic chloride, etc., to give 1,1,3,3-tetraphenylcyclobutane (II), which being unstable rearranges to 1,1,3,3-tetraphenyl-1-butene (III). The intermediate product cannot be 1,1,4,4-



tetraphenylcyclobutane, since it appears from the work of Schlenk and Bergmann⁶ that this compound, prepared by the action of mercury on 1,4-disodium-1,1,4,4-tetraphenylbutane, reverts to diphenylethylene.

The saturated dimer, m. p. 143° , was prepared first by Lebedev,⁴ who obtained a mixture of the two isomers by treating diphenylethylene with concentrated sulfuric acid or with fuller's earth. He concluded that this compound was tetraphenylcyclobutane, since it did not add bromine nor react with ozone, and gave only benzophenone on oxidation. The compound is very stable toward oxidation and Bergmann and Weiss state that long treatment with a considerable excess of chromic acid in acetic acid oxidized only a part of the material and that this part was completely destroyed. By regulating the conditions of the oxidation, however, it is possible to control the reaction so that over a 40% yield of the crude oxidation product is obtained. This product contains a large number of acids and ketones of which about ten have been isolated in pure form. Only two of these were readily identified, namely, benzoic acid and *o*-dibenzoylbenzene. In addition, benzophenone was isolated as the oxime in small amounts, substantiating the observation of Lebedev. The two latter oxidation products were sufficient to establish the identity of the hydrocarbon, since of the various structures which might be assigned to a dimer of diphenylethylene, only one, namely, 1,1,3-triphenyl-3-methylhydrindene could give both *o*-dibenzoylbenzene and benzophenone on oxidation and could readily be formed by the rearrangement of 1,1,3,3-tetraphenyl-1-butene, which rearrangement had been effected by Lebedev⁴

⁵ Schlenk and Bergmann, *Ann.*, **463**, 239 (1928).

⁶ Ref. 5, p. 7.

with fuller's earth at high temperature and with stannic chloride plus hydrochloric acid at room temperature in our work. A synthesis of this hydrindene was in progress at the time when Bergmann and Weiss² reported their excellent synthesis, which removed any possible doubt concerning its structure.

1,1,3-Triphenyl-3-methylhydrindene can be readily prepared in practically quantitative yield by adding anhydrous stannic chloride to a benzene solution of methyldiphenylchloromethane, obtained by the action of dry hydrogen chloride on the corresponding carbinol, and allowing the mixture to stand at room temperature for one week. The reaction is apparently a general one and has been extended to several other carbinol chlorides. For example, dimethylphenylchloromethane gave the dimer, m. p. 52.5°, first described by Grignard,⁷ and dimethyl-*p*-tolylchloromethane and dimethyl- α -naphthylchloromethane gave compounds melting at 122 and 199°, respectively.⁸ The structures of these compounds remain to be proved. Zinc chloride, ferric chloride, antimony pentachloride and aluminum chloride have been used in the reaction in place of stannic chloride, and it is probable that other agents such as boron trichloride and titanium tetrachloride will also be effective.

Inasmuch as tetraphenylbutene can be rearranged to the hydrindene by concentrated sulfuric acid at room temperature, it seems probable that the former is an intermediate step in the preparation of the latter compound from diphenylethylene. As suggested by Bergmann and Weiss, the rearrangement of the unsaturated dimer would consist in the addition of the sulfuric acid to the double bond and the subsequent removal of the acid to form the stable five-membered ring. The unsaturated dimer may also be rearranged by means of stannic chloride, provided hydrogen chloride is present. A benzene solution of this compound in the presence of stannic chloride showed no appreciable rearrangement after one week at room temperature, but when the solution was partially saturated with hydrogen chloride, the rearrangement to the saturated dimer was practically complete in the same period of time. Again, diphenylethylene in benzene solution under the influence of stannic chloride polymerized almost exclusively to the unsaturated dimer, while in the presence of hydrogen chloride the saturated isomer was formed. These results apparently favor the theory that an intermediate compound is formed by the addition of hydrogen chloride to the unsaturated dimer, which compound then reacts to give the hydrindene, but there is some evidence which points to a different mechanism of reaction when stannic chloride is used.

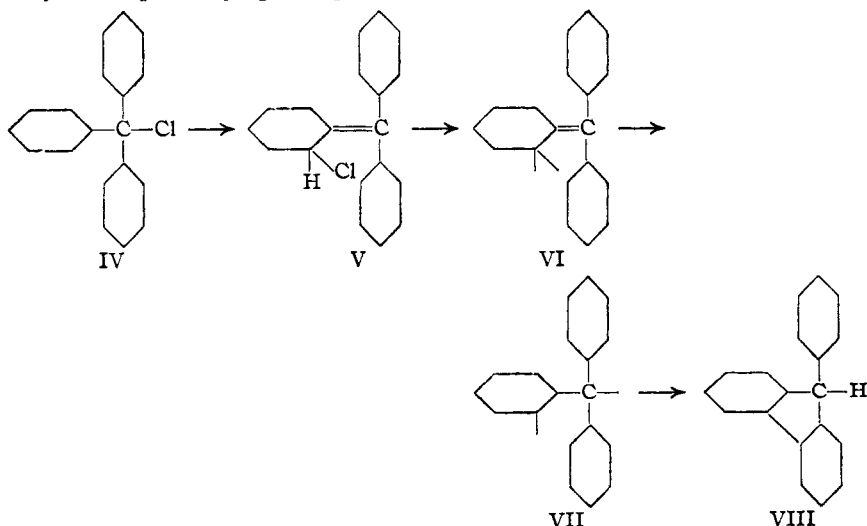
If the preparation of 1,1,3-triphenyl-3-methylhydrindene from methyl-

⁷ Grignard, "Ann. de l'Univ. of Lyon," 1901, p. 57; *Ann. chim. phys.*, [7] 24, 485 (1901).

⁸ These compounds were prepared by R. F. Ruthruff.

diphenylchloromethane is compared with the preparation of fluorenes from triarylmethyl halides, it is found that the two reactions have much in common. In each case the product is an indene derivative, and in each case the same reagents may be used to bring about the reaction, namely, stannic chloride, aluminum chloride, zinc chloride, etc. These reagents incidentally give definite colored addition products with the triarylmethyl halides which have been shown to be quinonoid in character.⁹ The ease with which fluorenes are formed from triarylmethyl halides varies greatly with different individuals. Triphenylmethyl chloride and bromide give phenylfluorene (VIII) only upon heating above 200°. ¹⁰ Phenyl- α -naphthofluorene, however, may be prepared by refluxing an acetic acid solution of α -naphthyldiphenylcarbinol in the presence of a small amount of hydrochloric acid, sulfuric acid, zinc chloride, etc.;¹¹ the solution first acquires a dark green color which rapidly disappears, indicating that the intermediate product is a quinonoid chloride, sulfate, etc. Di- α -naphthylphenylmethyl chloride or bromide is still more reactive. These halides give addition products of a deep purple color with stannic, aluminum, ferric, zinc and mercuric chlorides, which are unstable and decompose within a short time at room temperature with the formation of di- α -naphthofluorene.¹²

The reaction, for example, in the case of triphenylchloromethane, probably takes place by splitting off the chlorine atom and a hydrogen atom



⁹ Gomberg, *Ber.*, 40, 1847 (1907); 42, 406 (1909); Anderson, *THIS JOURNAL*, 52, November, 1930.

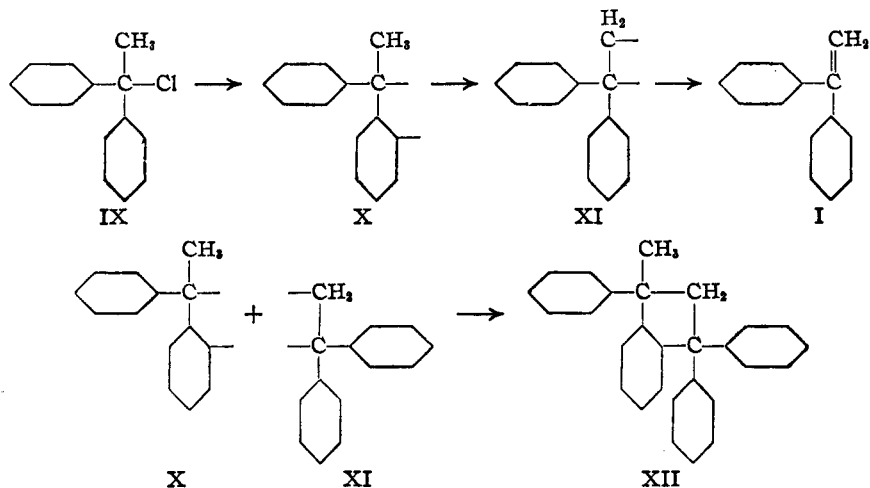
¹⁰ Hemilian, *Ber.*, 7, 1208 (1874); 11, 837 (1878); E. and O. Fischer, *Ann.*, 194, 257 (1878); Schwarz, *Ber.*, 14, 1522 (1878).

¹¹ Ullmann and Mourawiew-Winogradoff, *ibid.*, 38, 2213 (1905).

¹² Schoepfle, *THIS JOURNAL*, 44, 188 (1922).

from an ortho position in the ring to give an unstable intermediate product (VII) which rearranges to the stable fluorene (VIII). Since the reagents or the conditions used in the reaction result in quinoidation of the triaryl-methyl halide, the formation of the intermediate compound (VII) may be postulated as being due to splitting off hydrogen chloride from the ortho quinonoid compound, (V), to give the quinonoid residue (VI), which would, of course, rearrange to the benzenoid configuration (VII). In general, the triarylmethyl halides assume the para-quinonoid form but some of the ortho-quinonoid form may also be present, and, indeed, certain compounds would be expected to assume the ortho-quinonoid form more readily than others, which might account for the greater ease with which naphthyl derivatives react in comparison with phenyl derivatives.

In the case of methyldiphenylchloromethane (IX), hydrogen chloride may be split off in accordance with the mechanism proposed above to give



the intermediate product (X), which then tends to rearrange not to methylfluorene but to asymmetrical diphenylethylene, a rearrangement which is not possible in the case of the triarylmethyl derivatives. Actually, however, the rearrangement does not proceed thus far, due to the coupling of the two intermediate products (X) and (XI) to give the stable triphenylmethylhydrene.

Methyldiphenylcarbinol and concentrated sulfuric acid give a red color which is also characteristic of the addition compounds of methyldiphenylchloromethane with stannic chloride, aluminum chloride, ferric chloride, etc. In the polymerization of diphenylethylene to the hydriene in the presence of stannic chloride and hydrochloric acid, and in the rearrangement of the unsaturated dimer under these conditions, the same red color always appears. In the absence of hydrochloric acid, the ethylene and the

unsaturated dimer give a light green color instead of the red color and in each case practically no hydrindene is obtained. In other words, it seems that the preparation of the hydrindene may be dependent on the formation

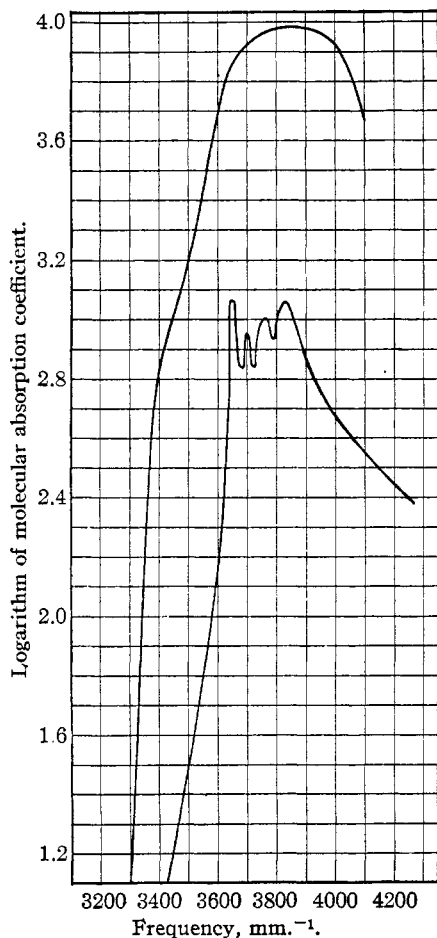


Fig. 1.—Upper curve, 1,1,3,3-tetraphenyl-1-butene; lower curve, 1,1,3-triphenyl-3-methylhydrindene.

of methyldiphenylchloromethane as the intermediate product. The formation of this compound is readily explainable with the ethylene which may add hydrochloric acid under the influence of the stannic chloride, and is also plausible in the case of the unsaturated dimer, which evidently dissociates readily to the ethylene, since Hildebrand³ found that bromine and nitric acid in boiling acetic acid react with the unsaturated dimer to give dibromodiphenylethylene and diphenylvinyl nitrite, respectively, while Lebedev⁴ found that with excess of ozone at 0°, diphenylethylene ozonide was obtained from the dimer. Moreover, it was observed that the unsaturated dimer in benzene solution and in the presence of stannic chloride depolymerized to an appreciable extent at room temperature.

An attempt was made to establish the identity of the red intermediate compound formed in the various reactions by means of absorption spectra in the visible region, using a Nutting photometer and a Hilger wave length spectrometer. The following solutions were investigated: (1) methyldiphenylcarbinol in concentrated sulfuric acid, (2) methyldiphenylchloromethane and stannic chloride in benzene, (3) diphenylethylene, stannic chloride and hydrochloric acid in benzene, and (4) tetraphenylbutene, stannic chloride and hydrochloric acid in benzene. All showed a rapid increase in absorption in the violet region and gave an indication of a band with its peak near the edge of the visible part of the spectrum. The location of this peak could not be definitely determined, due to the limitations

of the apparatus at wave lengths below 4500 Å. Spectrographic measurements of the absorption spectra of these solutions are to be undertaken in order to obtain this information.

In many of our preliminary experiments mixtures of the unsaturated and saturated dimers of diphenylethylene were obtained and it was desirable to determine the amount of each isomer present, but the separation by means of fractional crystallization was tedious and unsatisfactory. The mixtures did not melt sharply and did not crystallize readily on cooling, so that the melting point and solidification point were of no value for this purpose. The index of refraction of a concentrated solution of the material could not be used, due to the fact that the indices of refraction of the pure isomers were too nearly alike. The absorption curves of the two dimers are quite different though, as will be seen from Fig. 1, and therefore the composition of a mixture could be quite accurately determined from the molecular absorption coefficient at frequencies between 3425 and 3600. The absorption curves should also prove of value in establishing the structure of other indene derivatives which are not readily synthesized.

The measurements of the absorption spectra were made with a Judd-Lewis sector photometer and a Hilger quartz spectrograph, size C, by Dr. L. C. Anderson of this Laboratory, for whose assistance we wish to express our appreciation.

Experimental

Methyldiphenylchloromethane.—This compound was prepared by treating a benzene solution of the carbinol with dry hydrochloric acid gas at a temperature below 10° in the presence of anhydrous calcium chloride to remove the water formed in the reaction. Attempts to isolate the chloride by concentrating the solution gave a colorless oil which could not be crystallized, although an analysis for chlorine showed that no appreciable decomposition had taken place. A sample of the chloride was prepared in low-boiling petroleum ether, the solvent removed under reduced pressure at 0° and a stream of dry air passed through the residual oil to remove traces of hydrochloric acid. On analysis, 16.0% of chlorine was obtained, the calculated value being 16.4%. At room temperature the chloride decomposes slowly to give the ethylene and hydrochloric acid, a small amount of the unsaturated dimer of diphenylethylene being formed.¹³

1,1,3-Triphenyl-3-methylhydrindene.—Twenty-five grams of methyldiphenylcarbinol was dissolved in 250 cc. of benzene and converted into the chloride as described above. Ten grams of anhydrous stannic chloride was then added and the solution maintained below 10° for several hours, after which it was allowed to stand at room temperature. Upon the addition of the stannic chloride, the solution acquired a deep red color which gradually faded to a light brown. After one week it was washed thoroughly with water, dried and concentrated, and the residue dissolved in absolute alcohol, from which the triphenylmethylhydrindene was obtained in colorless crystals melting at 143°; yield, 95-97%. If the reaction is stopped after one day at room temperature, the yield is about 80%. An attempt to accelerate the reaction by heating on the steam-bath gave a decreased yield due to the formation of diphenylethylene and the unsaturated dimer.

¹³ Blicke and Powers, *THIS JOURNAL*, 51, 3383 (1929).

Saturated Dimer of α -Methylstyrene.—This compound was prepared from dimethylphenylcarbinol by the method described above. The oily product from the concentration of the solution was rubbed with a small amount of alcohol, whereby a solid separated which was filtered and recrystallized. An additional amount of the product was obtained by distilling the oily residue and crystallizing the fraction which boiled at 128–135° at 3 mm. from alcohol. The combined yield of the dimer was 88% and the melting point 52°. The same compound is obtained if the stannic chloride used in the reaction is replaced by ferric chloride, aluminum chloride, antimony pentachloride or zinc chloride; stannic chloride and antimonious chloride have the advantage over the other reagents in that they are soluble in benzene. Staudinger and Breusch¹⁴ have previously prepared this compound in 72% yield by the action of stannic chloride on α -methylstyrene.

Oxidation of 1,1,3-Triphenyl-3-methylhydrindene.—Five grams of the hydrocarbon was dissolved in 100 cc. of glacial acetic acid and 25 g. of chromic acid was cautiously added. The reaction was allowed to proceed rapidly with just enough cooling to prevent it from becoming violent, and was usually complete in about half an hour. After one hour the solution was poured into water, cooled to 0° with ice and partially neutralized by adding a solution of 50 g. of sodium hydroxide, which seemed to change the character of the precipitate so that it was easier to filter. The product was washed with water on the filter and air dried. No further material could be recovered from the filtrate by extraction with ether.

The crude oxidation products obtained from a number of runs were combined and extracted with hot water. From the water solution a small amount of oil was obtained by extraction with ether and evaporation of the solvent. Crystallization of the oil from alcohol gave a mixture of colorless, thin plates which after recrystallization melted at 95°, and colorless serrated tables which melted at 146°. A small amount of benzoic acid was obtained by sublimation of that portion of oil which failed to crystallize.

The residual oxidation product was then treated under rapid stirring with warm 25% sodium hydroxide solution and the mixture allowed to settle. The supernatant liquid was decanted or siphoned off and the operation repeated twice to insure removal of all of the alkali-soluble material. The product which was insoluble in alkali was steam distilled and the distillate extracted with ether. A small amount of oil was obtained from the ether solution which upon crystallization from alcohol gave the 146° compound along with long thin colorless needles which melted after recrystallization at 279°. The portion of oil which did not crystallize was treated with hydroxylamine hydrochloride and deposited benzophenone-oxime, which was identified by a mixed melting point. Extraction with ether of the non-volatile residue from the steam distillation, evaporation of the solvent and crystallization of the product from alcohol gave an additional quantity of the 146° compound.

The material soluble in 25% sodium hydroxide solution was precipitated with dilute hydrochloric acid, and the precipitate washed with water and air dried. The yield of this product was 40% of the weight of hydrocarbon oxidized. The material was stirred with a slight excess of dilute sodium hydroxide solution in which about 20% remained insoluble. This was filtered, washed with water, air dried and dissolved in alcohol. Two compounds were recovered from the solution, the 146° compound and large colorless needles which after recrystallization melted at 120°. The solution obtained by re-dissolving the oxidation product in dilute sodium hydroxide solution was treated with ether and the extracted material crystallized from alcohol. More of the 120° compound was obtained and also a small amount of small colorless needles which melted at 295° after recrystallization. The alkaline solution was then precipitated with dilute hydro-

¹⁴ Staudinger and Breusch, *Ber.*, **62**, 450 (1929).

chloric acid and the precipitate dissolved in alcohol. The solution deposited a considerable amount of colorless prisms melting at 225°. Since most of this product failed to crystallize, it was dissolved in excess of ammonium hydroxide, the solution diluted several times and then concentrated to its original volume on the hot-plate, when part of the material separated as an oil. The fraction which remained in solution was precipitated with dilute hydrochloric acid and the precipitate dissolved in ethyl alcohol, from which colorless needles were obtained which melted at 245° after recrystallization. The fraction which was precipitated was also dissolved in alcohol and gave very fine colorless needles which after recrystallization melted at 285°. The portion which did not crystallize was then dissolved in ether and extracted with 0.25 *N* ammonium hydroxide solution. The extracted material was precipitated from the ammoniacal solution by dilute hydrochloric acid and dissolved in alcohol from which a considerable quantity of colorless rhombohedral prisms melting at 190° was deposited. From the ether solution, more of the 285° compound was obtained.

The compounds melting at 95 and 295°, respectively, were not obtained in sufficient quantities for macro analysis. The analyses of the other compounds and the solubility in hot 5% sodium hydroxide solution and hot 5% ammonium hydroxide solution are given in Table I. It will be seen that in general the oxidation products which were isolated have a complex structure. Only traces of benzoic acid and benzophenone were obtained. The compound melting at 146° was identified as *o*-dibenzoylbenzene, and gave no depression in melting point when mixed with a sample of this compound prepared by the oxidation of *o*-dibenzylbenzene. The other compounds have not as yet been identified.

TABLE I

ANALYSES AND SOLUBILITY DATA OF THE OXIDATION PRODUCTS OF 1,1,3-TRIPHENYL-3-METHYLHYDRINDENE

| M. p. of compound, °C. (uncorr.) | Soly. in hot 5% NaOH soln. | Soly. in hot 5% NH ₄ OH soln. | Formula | Calculated | | Found | |
|----------------------------------|----------------------------|------------------------------------------|------------------------------------------------|------------|------|-------|------|
| | | | | C, % | H, % | C, % | H, % |
| 120 | Insol. | Insol. | C ₁₆ H ₁₂ O ₂ | 81.32 | 5.12 | 81.16 | 5.06 |
| 146 | Insol. | Insol. | C ₂₀ H ₁₄ O ₂ | 83.88 | 4.93 | 83.73 | 4.96 |
| 190 | Sol. ^a | Sol. | C ₂₂ H ₂₀ O ₂ | 84.10 | 6.14 | 83.99 | 6.19 |
| 225 | Slightly ^b | Insol. | C ₂₁ H ₁₄ O ₃ | 80.23 | 4.49 | 79.98 | 4.49 |
| 245° | Sol. | Sol. | C ₂₄ H ₂₂ O ₄ | 76.97 | 5.93 | 76.92 | 5.89 |
| 279 | Insol. | Insol. | C ₂₂ H ₁₆ O ₃ | 80.45 | 4.92 | 80.47 | 4.89 |
| 285 ^d | Sol. | Insol. | C ₁₆ H ₁₂ O ₂ | 81.32 | 5.12 | 81.14 | 5.09 |

^a The sodium salt is insoluble in concentrated NaOH solution. ^b Dissolves slowly in hot concentrated NaOH solution. ^c This compound may be α -methyl- α,γ,γ -triphenylglutaric acid. ^d The properties of this compound agree with those described for an anhydro derivative of β -benzoyl- α -phenylpropionic acid. Anschütz and Montfort, *Ann.*, **284**, 5 (1895); Hann and Lapworth, *J. Chem. Soc.*, **85**, 1362 (1904).

Polymerization of Asymmetrical Diphenylethylene.—Ten grams of the ethylene was dissolved in 75 cc. of benzene and treated with 4 g. of anhydrous stannic chloride at room temperature. The solution developed a light green color which faded to a light brown during the course of a day or two. After seven days at room temperature the solution was washed thoroughly with water, dried and concentrated. The product was dissolved in alcohol, from which the unsaturated dimer, 1,1,3,3-tetraphenyl-1-butene was obtained in 77% yield, the residue being unchanged ethylene. Heating the reaction mixture on the steam-bath decreased the yield.

A similar reaction was carried out at room temperature using benzene which had been partially saturated with dry hydrochloric acid. The same light green color ap-

peared initially, but after two hours the solution had become dark red, which color persisted for about a day and then faded to a light brown. Crystallization of the product from absolute alcohol gave a 90% yield of the saturated dimer, 1,1,3-triphenyl-3-methylhydrindene.

Rearrangement and Depolymerization of 1,1,3,3-Tetraphenyl-1-butene.—This compound in benzene solution is not rearranged under the influence of stannic chloride but is partially depolymerized. Five grams of the butene in 40 cc. of benzene was treated with 2 g. of stannic chloride, whereupon the solution acquired a light green color which persisted for about a day. After seven days at room temperature the solution was washed with water, dried and concentrated, and the product dissolved in alcohol, from which 80% of the butene was recovered. The residue was distilled in vacuum and gave 0.7 g. of asymmetrical diphenylethylene. No appreciable rearrangement was observed with stannic chloride in boiling benzene, toluene or xylene, but when 5 g. of the butene was added to 50 cc. of stannic chloride and the solution refluxed for one week, a 90% yield of the saturated isomer was obtained.

The rearrangement is effected readily at room temperature provided hydrochloric acid is present. Five grams of the butene was dissolved in 40 cc. of benzene which was partially saturated with dry hydrochloric acid gas and 2 g. of stannic chloride was added. The solution first became light green and then dark red, the latter color fading after a day to a light brown. The solution was allowed to stand for a week at room temperature and was then washed with water, dried and concentrated. The residue was crystallized from absolute alcohol and gave a 90% yield of the saturated isomer, triphenylmethylhydrindene.

Summary

The saturated dimer of asymmetrical diphenylethylene has been identified as 1,1,3-triphenyl-3-methylhydrindene by means of its oxidation products.

The preparation of triphenylmethylhydrindene from methyldiphenylchloromethane has been described, and the method shown to be of general application.

The influence of stannic chloride on the polymerization of diphenylethylene and on the rearrangement and depolymerization of 1,1,3,3-tetraphenyl-1-butene has been described.

A reaction mechanism has been postulated for the formation of fluorene derivatives from triarylmethyl halides and for the formation of hydrindene derivatives from alkylarylmethyl halides.

ANN ARBOR, MICHIGAN