

butyl compound. A number of conclusions previously arrived at with regard to the cleavage of simple 1,3-diketones have been found also to hold for these more complex 1,3-diketones which are also β -keto esters.

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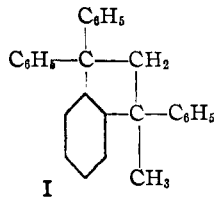
THE ABSORPTION SPECTRUM OF METHYLDIPHENYL-
CHLOROMETHANE PLUS STANNIC CHLORIDE. THE
PREPARATION OF 9,10-DIPHENYLPHENANTHRENE FROM
TETRAPHENYLETHYLENE DICHLORIDE¹

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In an earlier communication² it was shown that 1,1,3-triphenyl-3-methylhydrindene (I) is obtained in practically quantitative yield by adding anhydrous stannic chloride to a benzene solution of methyldiphenylchloromethane at room temperature. It was also shown that the reaction is a general one and can be used with other alkylarylmethyl halides and that other reagents such as antimony pentachloride, aluminum chloride, etc., can replace the stannic chloride. The reaction mechanism which was suggested postulated the formation of a quinonoid salt as an intermediate step, and in support of this assumption it was noted that the reaction is always accompanied by a transitory color and that the reagents used are those which are known to produce quinoidation of the triarylmethyl halides.



Preliminary absorption spectra measurements in the visible region failed to establish the identity of the intermediate colored compound or compounds since the point of maximum absorption was found to lie beyond the range of the visual apparatus. Spectrographic measurements of the absorption in the ultraviolet region have now been made which confirm the existence of a quinonoid modification of methyldiphenylchloromethane in the reaction mixture.

The quantitative absorption curves for methyldiphenylcarbinol, methyldiphenylchloromethane and asymmetrical diphenylethylene are shown in Fig. 1. (The curve for diphenylethylene was determined inasmuch as this compound is readily formed by loss of hydrogen chloride from methyldiphenylchloromethane.) The curves for the carbinol and the chloride

¹ This paper represents the second part of a dissertation 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 Schoeffle and Ryan, *THIS JOURNAL*, **52**, 4021 (1930).

show a marked similarity to those of triphenylcarbinol and triphenylchloromethane.³

An absolute quantitative curve could not be obtained in the case of the methyl-diphenylchloromethane-stannic chloride mixture, due to the fact

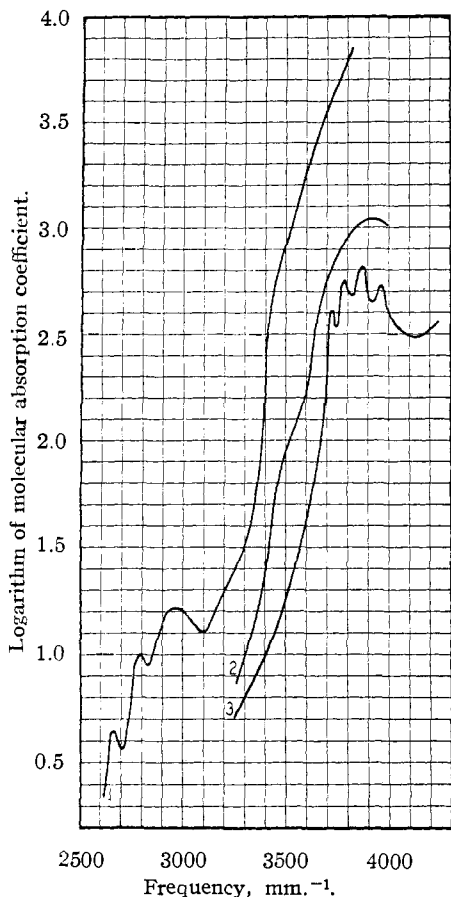


Fig. 1.—Curve 1, asymmetrical diphenylethylene in ether; Curve 2, methyl-diphenylchloromethane in petroleum ether; Curve 3, methyl-diphenylcarbinol in ether.

that the concentration of the chloride drops and other compounds are formed as the reaction proceeds. However, the absorption of the solution in ethylene chloride was measured directly after adding the stannic chloride and the resulting curve is shown in Fig. 2 (Curve 1). This curve is entirely different from that of the chloride in the absence of stannic chloride, but is very similar in some respects to the quantitative absorption curves for the triphenylchloromethane-stannic chloride addition compound (Curve 2) and for triphenylmethyl acid sulfate (Curve 3). (The absorption curve of the latter compound has been determined by Anderson⁴ and is inserted here to facilitate comparison.) Since the quinonoid character of triphenylmethyl acid sulfate has been established,^{4,5} it follows from a comparison of the three curves that the band in Curve 1 with maximum frequency 2300 mm^{-1} is due to a quinonoid addition compound of methyl-diphenylchloromethane.

The solution of methyl-diphenylchloromethane and stannic chloride is at first red in color but after standing a short time the color changes to a greenish-red due to an increase

³ Anderson, *THIS JOURNAL*, **50**, 208 (1928).

⁴ Anderson, *ibid.*, **52**, 4567 (1930).

⁵ (a) Gomberg, *Ber.*, **40**, 1853 (1907); (b) Gomberg and Blicke, *THIS JOURNAL*, **45**, 1770 (1923).

in intensity of the absorption band with maximum frequency 1660 mm.^{-1} . A benzene solution of asymmetrical diphenylethylene and stannic chloride develops a pure green color and shows an absorption band at approximately this same frequency. It is possible that this band is due to the presence of a quinonoid form of 1,1,3,3-tetraphenyl-1-chlorobutane which may result from the addition of hydrogen chloride to 1,1,3,3-tetraphenyl-1-butene, inasmuch as diphenylethylene is known to polymerize in the presence of stannic chloride to give the latter compound. Attempts to prepare 1,1,3,3-tetraphenyl-1-chlorobutane from the corresponding butanol were unsuccessful, the butene being obtained instead.

Bergmann and co-workers⁵ have shown that compounds similar to 1,1,3,3-tetraphenyl-1-chlorobutane in the presence of stannic chloride split off a molecule of acid with ring closure to give hydrindene derivatives. Since the absorption measurements of the methyldiphenylchloromethane-stannic chloride mixture indicate the possibility that a quinonoid form of 1,1,3,3-tetraphenyl-1-chlorobutane may be present in addition to the quinonoid form of methyldiphenylchloromethane, no definite conclusion can be drawn from these measurements as to which of the two chlorides is the intermediate product in the formation of triphenylmethylhydrindene.

Attention was called in the previous paper² to the striking resemblances to be found in comparing the preparation of hydrindene derivatives from alkylarylchloromethanes and the preparation of fluorene derivatives from triarylchloromethanes. Another reaction analogous to these is the prepa-

⁵ Bergmann, Taubadel and Weiss, *Ber.*, **64**, 1493 (1931).

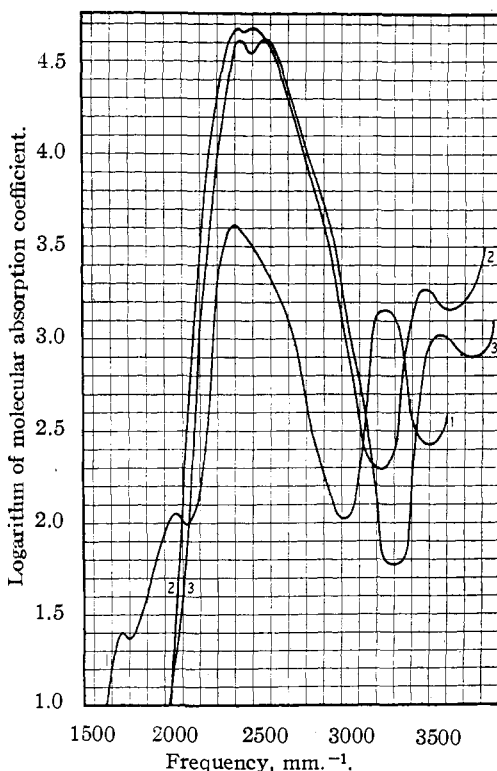
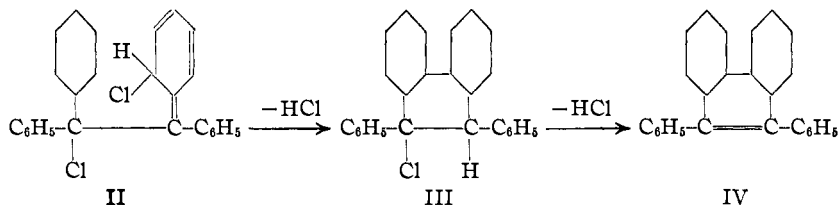


Fig. 2.—Curve 1, methyldiphenylchloromethane plus stannic chloride in ethylene chloride; Curve 2, triphenylchloromethane plus stannic chloride in ethylene chloride; Curve 3, triphenylmethyl acid sulfate in sulfuric acid (95%).

ration of 9,10-diphenylphenanthrene (IV) from tetraphenylethylene dichloride. This reaction as carried out by Schmidlin and Von Escher⁷ consists in treating tetraphenylethylene dichloride with aluminum chloride in benzene or carbon disulfide solution, and according to Prins⁸ is an example of an intramolecular Friedel-Crafts reaction. It has now been found that in solvents favoring quinoidation the aluminum chloride may be replaced with advantage by stannic chloride, so that in this respect the reaction differs from the usual Friedel-Crafts reaction. A possible explanation of the reaction mechanism is that the ortho quinonoid modification of tetraphenylethylene dichloride (II) loses a molecule of hydrochloric acid to give a radical which rearranges to 9,10-diphenyl-9-chloro-(9,10-dihydrophenanthrene) (III), which compound then loses another molecule of hydrochloric acid to give 9,10-diphenylphenanthrene (IV). Or perhaps two rings become quinonoid and both molecules of hydrochloric acid are split off simul-



taneously. In general, a para quinonoid form reacts in preference to the corresponding ortho form but this need not hold for reactions in which a stable product can result from the ortho but not from the para modification.

Tetraphenylethylene dichloride dissolved in chloroform and treated with stannic chloride was found to give an intensely colored purple solution which gradually becomes colorless after a few hours, a 95% yield of 9,10-diphenylphenanthrene being obtained. The purple color is undoubtedly due to the formation of the quinonoid modification of tetraphenylethylene dichloride. This conclusion is supported by the fact that tetrakis-(dimethylaminophenyl)-ethylene adds chlorine directly to give a violet colored chloride⁹ to which Kehrmann¹⁰ and Recsei¹¹ assign a quinonoid configuration.

A study of the reaction of tetraphenylethylene dichloride and stannic chloride in various solvents showed that the character of the solvent has a marked effect on the formation of diphenylphenanthrene. In ethylene chloride, chloroform, nitrobenzene and benzonitrile, a quinonoid salt is produced, as manifested by the development of an intense purple color, and excellent yields of diphenylphenanthrene are obtained. On the other

⁷ Schmidlin and von Escher, *Ber.*, **43**, 1153 (1910).

⁸ Prins, *J. prakt. Chem.*, [2] **89**, 438 (1914).

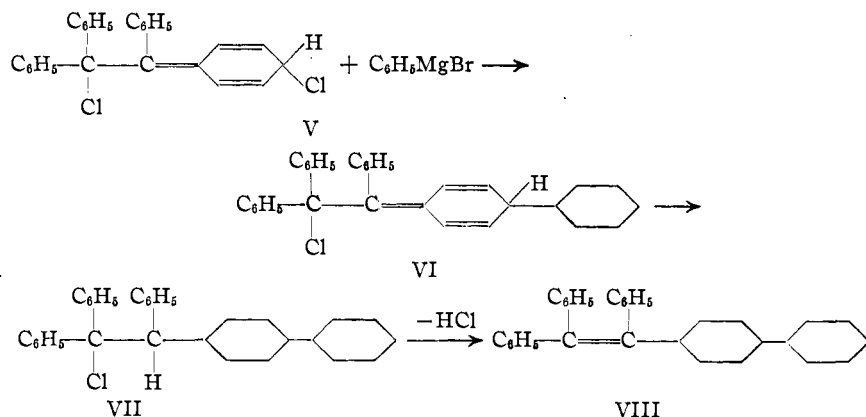
⁹ Wizinger, *Ber.*, **60**, 1383 (1927).

¹⁰ Kehrmann, *ibid.*, **60**, 1913 (1927).

¹¹ Recsei, *ibid.*, **60**, 2383 (1927); see also Madelung and Oberwegner, *ibid.*, **60**, 2469 (1927).

hand, under the same conditions no color is developed in benzene, carbon tetrachloride or carbon disulfide and little or no diphenylphenanthrene is obtained, most of the tetraphenylethylene dichloride being recovered unchanged. Since color develops in polar solvents and not in non-polar solvents, it is evident that the former favor quinoidation.¹² And while the fact that the reaction proceeds only in solvents which favor quinoidation does not necessarily indicate that a quinonoid salt must be an intermediate step in the preparation of diphenylphenanthrene, it does nevertheless lend plausibility to such an hypothesis.

Further support for the suggested mechanism is found in the reaction of tetraphenylethylene dichloride and phenylmagnesium bromide. Norris¹³ carried out this reaction in the hope of preparing hexaphenylethane, but instead obtained tetraphenylethylene and 4-phenyltetraphenylethylene. No attempt was made to interpret the mechanism of formation of the latter compound, and yet it can be logically explained by the assumption that the para quinonoid modification of tetraphenylethylene dichloride (V) reacts with phenylmagnesium bromide. The resulting product (VI) rearranges to 1,1,2-triphenyl-2-biphenyl-1-chloroethane (VII), which then yields 4-phenyltetraphenylethylene (VIII) by loss of a molecule of hydrochloric acid.



Other Grignard reactions which substantiate this hypothesis will be discussed in a separate communication.

9,10-Diphenylphenanthrene may also be prepared in 25% yield by treating tetraphenylethylene in chloroform solution with bromine at -40° in the presence of stannic chloride. The reaction is of interest since the addition of bromine to the double bond must be postulated as an intermediate step, and tetraphenylethylene has repeatedly been cited as a classi-

¹² See also Dilthey, *J. prakt. Chem.*, [2] 109, 273 (1925).

¹³ Norris, Thomas and Brown, *Ber.*, 43, 2955 (1910).

cal example of a compound which would not add bromine although it does add chlorine, and also sodium.

The measurements of the absorption spectra were made with the assistance of Dr. L. C. Anderson of this Laboratory to whom we wish to express our appreciation.

Experimental

Absorption Spectra Data.—For the measurement of quantitative absorption spectra in the ultraviolet region, a Judd-Lewis sectorphotometer and a Hilger quartz spectrograph, size C, were employed. Absorption spectra in the visible region were determined by the use of a Nutting photometer and a Hilger constant wave length spectrometer. The procedure was that described by Anderson and Gomberg.¹⁴

Asymmetrical diphenylethylene was prepared by the action of 30% sulfuric acid on methyldiphenylcarbinol¹⁵ and was fractionated several times under reduced pressure; b. p. 148° at 17 mm.; f. p. 8°.

Methyldiphenylcarbinol was prepared by the action of phenylmagnesium bromide upon ethyl acetate and was purified by recrystallization from ether plus petroleum ether, m. p. 81°.

Methyldiphenylchloromethane could not be isolated in crystalline form. It was prepared by saturating a petroleum ether solution of the corresponding carbinol with dry hydrogen chloride at 0° in the presence of anhydrous calcium chloride. The calcium chloride was filtered off and a stream of dry air passed through the solution under reduced pressure at 0° to remove the solvent and excess hydrogen chloride. An analysis of the residual oil gave 98% of the theoretical amount of chlorine, indicating that no appreciable decomposition had taken place. Preliminary measurements showed that hydrogen chloride had no effect on the absorption of methyldiphenylchloromethane when dissolved in petroleum ether; therefore the solutions used for obtaining the absorption (Fig. 1, Curve 2) were made in the following manner. A weighed amount of the carbinol was dissolved in about 5 cc. of pure petroleum ether and the solution cooled and diluted to 25 cc. with cold petroleum ether saturated with hydrogen chloride, after which anhydrous calcium chloride was added and the mixture allowed to stand overnight at 0°. Five cc. of the solution was then pipetted off, diluted with petroleum ether to the proper concentration and the absorption measured. A sample which had been kept for three days at 0° gave results identical with those obtained with a sample which had been allowed to stand for eighteen hours.

The solution used for obtaining the absorption of methyldiphenylchloromethane plus stannic chloride (Fig. 2, Curve 1) was prepared in a similar manner using ethylene chloride as the solvent, except that the final dilution was made with ethylene chloride which was saturated with hydrogen chloride and contained 1% by volume of anhydrous stannic chloride. The entire curve was obtained with a 0.0025 molar solution since the absorption differs somewhat with different concentrations.

9,10-Diphenylphenanthrene.—Tetraphenylethylene dichloride was prepared by passing dry chlorine through a carbon tetrachloride solution of tetraphenylethylene at 0°¹⁶ and recrystallizing the product thus obtained from a mixture of carbon disulfide and ethyl acetate.¹⁷ One gram of the dichloride was dissolved in 40 cc. of pure chloroform and cooled in a freezing mixture to a temperature of -5 to -10°. Two cc. of

¹⁴ Anderson and Gomberg, *THIS JOURNAL*, 50, 203 (1928).

¹⁵ Lebedev, Andreevskii and Matiushkina, *Ber.*, 56, 2349 (1923).

¹⁶ Finkelstein, *Ber.*, 43, 1534 (1910).

¹⁷ Norris, *THIS JOURNAL*, 38, 707 (1916).

anhydrous stannic chloride was added, whereupon the solution assumed a deep purple color which gradually faded. After a few hours, the solution became colorless and was then washed thoroughly with water, dried and concentrated. Crystallization of the solid residue from absolute alcohol gave 9,10-diphenylphenanthrene in 90–95% yield, m. p. 235°. When mixed with an authentic specimen, no lowering in melting point was observed. Schmidlin and von Escher,⁷ who carried out this reaction using aluminum chloride, obtained a 60% yield. At higher temperatures the reaction proceeds more rapidly but chlorinated products are formed which decrease the yield of diphenylphenanthrene.

Repetition of the experiment described above using ethylene chloride, nitrobenzene or benzonitrile as the solvent instead of chloroform gave a similar result. When benzene, carbon disulfide or carbon tetrachloride was used, however, no color was observed and only a trace of diphenylphenanthrene was obtained. About 60–70% of the tetraphenylethylene dichloride was recovered unchanged, along with an appreciable amount of chlorinated products.

Diphenylphenanthrene was also prepared from tetraphenylethylene and bromine. Five grams of tetraphenylethylene was dissolved in 100 cc. of chloroform and treated with 7 cc. of anhydrous stannic chloride. The green solution thus obtained was cooled to -40° and 2.4 g. (1 mole) of bromine was added. A deep purple color developed which had not disappeared after two hours, whereupon the solution was treated with a calcium chloride freezing mixture. Addition of the aqueous solution resulted in the disappearance of the purple color but considerable bromine was still present which was removed by washing with bisulfite solution. When the chloroform layer was dried and concentrated, a crystalline product was obtained which after repeated crystallization gave a 25% yield of pure 9,10-diphenylphenanthrene melting at 235°. The remainder of the material consisted of unchanged tetraphenylethylene and a small amount of brominated products. At room temperature a mixture of tetraphenylethylene and various bromination products of tetraphenylethylene and diphenylphenanthrene was obtained.

When the reaction was carried out in ethylene dichloride, the results were similar to those obtained in chloroform, but in carbon disulfide or carbon tetrachloride the purple color was not developed and little or no diphenylphenanthrene was obtained.

1,1,3,3-Tetraphenyl-1-butanol.—Five grams of finely ground β,β -diphenylbutyrophene prepared by the method of Kohler¹⁸ was added to an ether solution of phenylmagnesium bromide made from 3 g. of magnesium. The mixture was refluxed for one hour, then decomposed with ice and acid, and the ethereal layer washed, dried and concentrated. The solid residue crystallized from alcohol in plate-like prisms melting at 124–125°; yield, 75%. The carbinol is readily soluble in the common organic solvents except petroleum ether.

Attempts to prepare the corresponding chloride, 1,1,3,3-tetraphenyl-1-chlorobutane, by saturating a benzene solution of the carbinol with dry hydrogen chloride at -5° in the presence of anhydrous calcium chloride gave instead a quantitative yield of 1,1,3,3-tetraphenyl-1-butene.

The butene is also obtained if the butanol is dissolved in glacial acetic acid at room temperature and a few drops of concentrated sulfuric acid added. However, if 1 g. of the powdered butanol is treated with 25 cc. of concentrated sulfuric acid, 1,1,3-triphenyl-3-methylhydrindene is formed in approximately 25% yield, the remaining product consisting principally of asymmetrical diphenylethylene with a small amount of tetraphenylbutene. The triphenylmethylhydrindene appears to be formed from the carbinol and not by rearrangement of the butene, for when 3 g. of the butene was treated

¹⁸ Kohler, *Am. Chem. J.*, **31**, 657 (1904); *ibid.*, **33**, 558 (1907).

with 15 cc. of concentrated sulfuric acid and the mixture allowed to stand for forty-eight hours at room temperature, the product obtained proved to be unchanged butene, a small amount of diphenylethylene, and water-soluble sulfonated products. No triphenylmethylhydrindene could be isolated. When a similar mixture was allowed to stand for six weeks, only about 0.1 g. of the hydrindene was obtained, although Bergmann and Weiss¹⁹ state that the hydrindene can be readily prepared from the butene by means of sulfuric acid.

Summary

1. The quantitative absorption spectra of the following compounds have been obtained: asymmetrical diphenylethylene, methyldiphenylcarbinol, methyldiphenylchloromethane, methyldiphenylchloromethane plus stannic chloride, and triphenylchloromethane plus stannic chloride.

2. The preparation of 9,10-diphenylphenanthrene from tetraphenylethylene dichloride and stannic chloride has been investigated and the effect of polar and non-polar solvents noted.

3. A reaction mechanism involving quinoidation has been postulated to explain the formation of 9,10-diphenylphenanthrene from tetraphenylethylene dichloride and also the formation of 4-phenyltetraphenylethylene from tetraphenylethylene dichloride and phenylmagnesium bromide.

¹⁹ Bergmann and Weiss, *Ann.*, **480**, 49 (1930).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]
**ORGANIC REACTIONS WITH BORON FLUORIDE. III. THE
CONDENSATION OF PROPYLENE WITH PHENOL**

BY F. J. SOWA, H. D. HINTON AND J. A. NIEUWLAND

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The condensation of unsaturated hydrocarbons with phenols in the presence of condensing agents has been studied by various investigators. Amylene, di-isobutylene,¹ cyclohexane,² styrene,³ isoprene,⁴ acetylene,⁵ and propylene^{6,7} have been condensed with phenol or phenolic type compounds to yield substituted phenols, phenyl ethers or substituted phenyl ethers.

In an earlier publication a study was made of the rearrangement of isopropyl phenyl and cresyl ethers⁸ in an attempt to determine the position occupied by the isopropyl group after the rearrangement. The results

¹ Niederl and Natelson, *THIS JOURNAL*, **53**, 272 (1931).

² Liebermann and Hartmann, *Ber.*, **25**, 957 (1892).

³ König, *ibid.*, **24**, 3889 (1891).

⁴ Claisen, German Patent 374,142, 1923.

⁵ Wenzke and Nieuwland, *THIS JOURNAL*, **46**, 177 (1924).

⁶ Howard and Blagden, British Patent 214,866, 1923.

⁷ Sowa, Sc. M. Dissertation, University of Notre Dame, 1930.

⁸ Sowa, Hinton and Nieuwland, *THIS JOURNAL*, **54**, 2019 (1932).