3. The heat of activation of the enolization is about 14 ± 1 kg. cal. The free energy of enolization of the acetophenone derivatives is estimated to be between +5 and +14 kg. cal.

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THE REACTION BETWEEN TRIARYLMETHYL HALIDES AND PHENYLMAGNESIUM BROMIDE. I

BY C. S. SCHOEPFLE AND S. G. TREPP[1]

In a previous communication[2] the apparently abnormal reaction of tetraphenylethylene dichloride and phenylmagnesium bromide, which results in the formation of p-phenyltetraphenylethylene and tetraphenylethylene,[3] was explained on the assumption that the dichloride reacts in the para quinonoid form. Another Grignard reaction of this type has been described by Gilman and Jones,[4] who treated triphenylchloromethane with phenylmagnesium bromide and obtained a 47% yield of biphenyldiphenylmethane in addition to a small amount of the expected product, tetraphenylmethane. Again, as in so many other reactions of the triarylmethyl salts, the products of this reaction can be readily explained by a simple mechanism involving quinoidation of the triphenylchloromethane. If the quinonoid modification of triphenylchloromethane (I) reacts
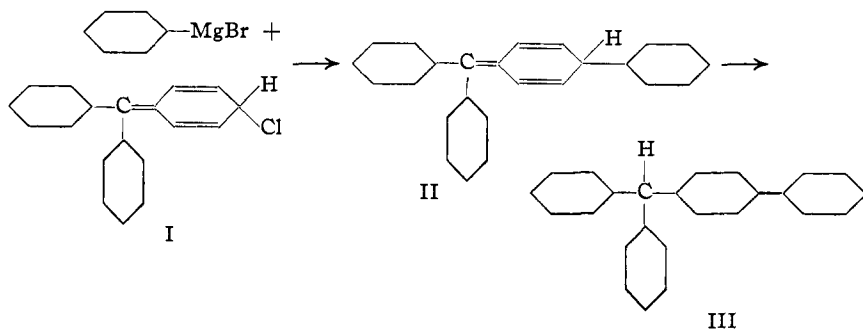
with the Grignard reagent, there will be formed an unstable intermediate product (II) which will rearrange to give biphenyldiphenylmethane (III); the benzenoid modification of the chloride of course gives tetraphenyl-

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[2] Schoepfle and Ryan, THIS JOURNAL, 54, 3687 (1932).

[3] Norris, Thomas and Brown, Ber., 43, 2955 (1910).

[4] Gilman and Jones, THIS JOURNAL, 51, 2840 (1929).

methane. The fact that biphenyldiphenylmethane is the principal product indicates that the reaction with the quinonoid modification predominates.
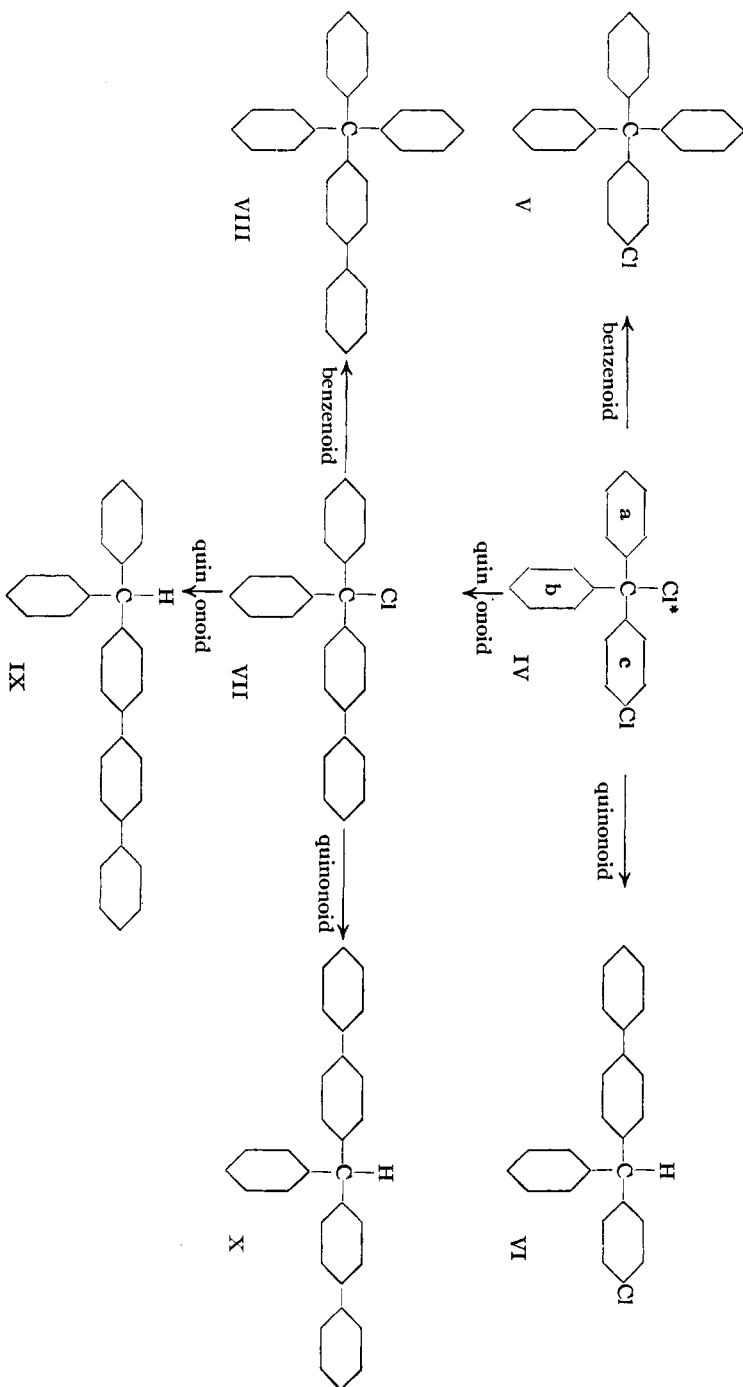
The purpose of the present investigation was to show that the suggested mechanism of the reaction between triarylmethyl halides and phenylmagnesium bromide is correct.[5] If, instead of triphenylchloromethane, 4-chlorotriphenylchloromethane (IV) were used, then in the reaction with excess phenylmagnesium bromide not only the chlorine on the central carbon atom but also some of the chlorine in the ring should be removed, resulting in an increased number of reaction products. Assuming that only para quinoidation takes place, one intermediate and five final products should be formed. The chloride may react in the benzenoid form to give 4-chlorotetraphenylmethane (V), or it may react in the quinonoid form, in which case there are two possibilities. If a ring (a or b) not containing chlorine becomes quinonoid and reacts, 4-chloro-4'-phenyltriphenylmethane (VI) will result. Since this compound no longer has a halogen atom attached to the central carbon atom, it cannot react further with the Grignard reagent, which fact was established by experiment. However, if in the original chloride the ring (c) containing the chlorine atom becomes quinonoid and reacts with one mole of phenylmagnesium bromide, the chlorine atom remaining will migrate back to the central carbon atom to give biphenyldiphenylchloromethane (VII).[6] This compound may then react further with the Grignard reagent in one of three ways; (1) in the benzenoid form to give 4-phenyltetraphenylmethane (VIII); (2) in the quinonoid form where the halogen has migrated to the biphenyl ring to give terphenyldiphenylmethane (IX); or (3) in the other quinonoid form where the halogen has migrated to a benzene ring, in which case dibiphenylphenylmethane (X) should result.

This reaction has been studied with the result that the following compounds have been isolated, the average yields being stated: 4-chlorotetraphenylmethane (V), 10%; 4-chloro-4'-phenyltriphenylmethane (VI), 28%; dibiphenylphenylmethane (X), 9%. Approximately the same results were obtained with 4-chlorotriphenylbromomethane, the average yields of the three products being 9, 27 and 17%, respectively. 4-Bromotriphenylchloromethane and phenylmagnesium bromide also were found

[5] It may be remarked that in this work we are interested in quinoidation of the triarylmethyl halides and not in quinoidation of the Grignard reagent. Several examples of quinonoid Grignard reagents have been recorded and their structures established by experimental evidence. See Schmidlin,"Das Triphenylmethyl," Ferdinand Enke, Stuttgart, Germany, 1914, p. 204.
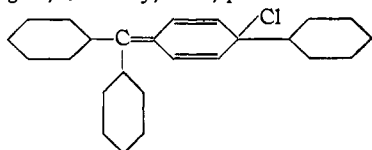
[6] The possibility exists that the intermediate product, of structure indicated, might react with another molecule of phenylmagnesium bromide before it has time to rearrange to VII, but such a reaction is not considered likely.

VIII

V

benzenoid

IV

a

b

c

Cl*

Cl

quinonoid

quinonoid

benzenoid

benzenoid

VII

Cl

quinonoid

IX

H

quinonoid

X

H

VI

H

Cl

Cl

* The structures of the intermediate quinonoid forms are omitted.

to react in a similar manner. The products obtained and the average yields were: 4-bromotetraphenylmethane, 13%; 4-bromo-4'-phenyltriphenylmethane, 7%; and dibiphenylphenylmethane, 20%. 4-Bromo-4'-phenyltriphenylmethane, however, was isolated in only a few runs due to the difficulty with which it crystallizes even when pure.

Inasmuch as 4-phenyltetraphenylmethane (VIII) and terphenyldiphenylmethane (IX) could not be isolated in the above experiments, it was necessary to determine whether these products are formed in appreciable amounts in the reaction between biphenyldiphenylchloromethane and phenylmagnesium bromide. It was found that dibiphenylphenylmethane (X) is the principal product, being obtained in yields of 60 to 70%, while the yield of 4-phenyltetraphenylmethane was less than 10%; terphenyldiphenylmethane could not be isolated at all from the reaction mixture. Since terphenyldiphenylmethane is formed by the quinoidation of the biphenyl group and dibiphenylphenylmethane by the quinoidation of the phenyl group, it follows that a phenyl group apparently becomes quinonoid more easily than a biphenyl group when the two are present in the same molecule.

In the light of these results, it is not at all surprising that terphenyldiphenylmethane is not found among the reaction products of the mono para halogenated triphenylchloromethanes, for it probably is formed only in extremely small amounts; 4-phenyltetraphenylmethane should be present, but again is formed in such small amounts that failure to crystallize it from the complex reaction mixture is readily understood.

The experimental evidence obtained in these reactions is thus in entire agreement with the quinonoid interpretation of the reaction mechanism. Since 4-bromo- or 4-chloro-triphenylchloromethane presumably exists in ether or benzene solution principally or entirely in the benzenoid form, it is probable that the reacting product is a quinonoid addition compound of the chloride with either magnesium bromide or phenylmagnesium bromide itself. This question will be discussed further in a separate communication which concerns a study of the wide variation in yield in the preparation of different tetraaryl methanes by the Grignard reaction.

It should be noted that the reaction between triarylmethyl halides and phenylmagnesium bromide can also be explained on the theory of the formation of intermediate free radicals, but only on the basis that the free radicals themselves exist partly in the quinonoid form.

Experimental

4-Chlorotriphenylchloromethane and Phenylmagnesium Bromide.—An ether solution of phenylmagnesium bromide (3 moles) was rapidly filtered through a small piece of cotton and then slowly poured, with swirling, into a benzene solution of 4-chlorotriphenylchloromethane. The usual sized sample of chloride was 15 g. The reaction mixture assumed a red color, considerable heat was developed, and a flocculent precipi-

tate of magnesium salts settled out. Although the reaction proceeds rapidly, the mixture was usually allowed to stand for a day or two at room temperature, after which it was decomposed with ice and dilute acid in the usual manner. The ether–benzene layer was washed with sodium carbonate solution and with water, and then concentrated and steam distilled. The residue was dissolved in benzene, and the solution dried and concentrated, whereupon 4-chlorotetraphenylmethane crystallized in fairly pure form and was separated. Addition of ligroin to the mother liquor gave a further small amount of this compound, the total yield being 8.5–10.5%. The solution was then allowed to concentrate by spontaneous evaporation of the solvent, and deposited fairly pure crystals of dibiphenylphenylmethane. When no further material could be crystallized, the residue was distilled in a high vacuum still designed by Hickman and Sanford.[7] The temperature was usually about 200° and never exceeded 225°, and there was no evidence of decomposition during the distillation. The distilled product was dissolved in benzene, ligroin added and the solution concentrated as before by spontaneous evaporation. By this means, a trace of 4-chlorotetraphenylmethane and a further quantity of dibiphenylphenylmethane were recovered, giving a total yield of 6.5–10.0% of the latter compound. In addition, 4-chloro-4'-phenyltriphenylmethane was obtained from the distillate in a yield of 27–28%.

The 4-chlorotetraphenylmethane was purified by recrystallization from benzene, from which it is obtained in colorless needles which melt at 227–227.5°. It is soluble in carbon tetrachloride, somewhat soluble in benzene, and insoluble in ether, petroleum ether and acetic acid.

Anal. Calcd. for $C_{25}H_{19}Cl$: C, 84.60; H, 5.40; Cl, 10.00. Found: C, 84.49; H, 5.46; Cl, 10.00.

Dibiphenylphenylmethane and 4-chloro-4'-phenyltriphenylmethane were identified by mixed melting point determinations with authentic samples.

Several experiments were also carried out with 4-chlorotriphenylbromomethane, which was prepared from the corresponding carbinol by treating a benzene solution of the latter with acetyl bromide. After concentrating the solution and adding ligroin, the bromide crystallized in colorless prisms which after recrystallization melted at 111–112°.

Anal. Calcd. for $C_{19}H_{14}BrCl$: Br, 22.36. Found: Br, 22.72.

The reaction of 4-chlorotriphenylbromomethane and phenylmagnesium bromide was similar to that of the chloride except that no precipitate of magnesium salts was formed when the reactants were mixed. The same products were isolated, the following yields being obtained: 4-chlorotetraphenylmethane, 6–9%; dibiphenylphenylmethane, 16.5–18%; and 4-chloro-4'-phenyltriphenylmethane, 18–35%.

4-Bromotriphenylchloromethane and Phenylmagnesium Bromide.—The procedure was the same as described in the preceding experiments, and upon crystallization of the product, dibiphenylphenylmethane in 15–25% yield, and 4-bromotetraphenylmethane in 10–18% yield were obtained. The latter compound melted at 245°;[8] its solubility is similar to that of 4-chlorotetraphenylmethane.

Anal. Calcd. for $C_{25}H_{19}Br$: C, 75.17; H, 4.80; Br, 20.03. Found: C, 74.77; H, 4.75; Br, 19.78.

The non-crystallizable residue was distilled in the Hickman still, and from the distillate a trace of 4-bromotetraphenylmethane and a few tenths of a gram of dibiphenylphenylmethane were recovered. In a few runs, 4-bromo-4'-phenyltriphenylmethane was also obtained from the distillate in a yield of 5–10%. Failure to isolate this com-

[7] Hickman and Sanford, *J. Phys. Chem.*, **34**, 643 (1930), Fig. 6.

[8] Gomberg and Cone, *Ber.*, **38**, 2456 (1905).

pound in other runs is undoubtedly due to the fact that it crystallizes with great difficulty. It was identified by a mixed melting point with an authentic sample.

Biphenyldiphenylchloromethane and Phenylmagnesium Bromide.—The reaction was carried out by mixing a benzene solution of the chloride with an ether solution of phenylmagnesium bromide (2 moles) at room temperature. As in the other reactions studied, a heating effect was observed, the solution became cherry-red in color, and a precipitate of magnesium salts was obtained. After standing for several hours, the reaction mixture was decomposed in the usual manner, the organic layer separated, washed, evaporated to dryness and steam distilled. The product was fractionally crystallized from benzene plus ligroin by gradual concentration of the solution. The only products which could be isolated were 4-phenyltetraphenylmethane in 7–10% yield, and dibiphenylphenylmethane in 58–70% yield. Both compounds were identified by mixed melting point determinations with authentic samples.

Synthesis of 4-Chloro-4'-phenyltriphenylmethane.—4-Chloro-4'-phenylbenzophenone was prepared by the method used by Gomberg and Bailar[9] for the corresponding bromo derivative. The acid chloride obtained from 10.4 g. of 4-chlorobenzoic acid was dissolved in 150 cc. of carbon disulfide, and 30 g. of biphenyl added, followed by 25 g. of anhydrous aluminum chloride in small portions. The reaction mixture was warmed on the steam-bath for three days, and then hydrolyzed. The excess of biphenyl was distilled off under reduced pressure, and the residue dissolved in benzene, from which the ketone crystallized in 63% yield. Upon recrystallization from alcohol, colorless plates were obtained which melted at 169.5–170.5°. The compound is fairly soluble in hot benzene and somewhat soluble in hot alcohol.

Anal. Calcd. for $C_{19}H_{13}OCl$: C, 77.94; H, 4.48; Cl, 12.12. Found: C, 77.65; H, 4.44; Cl, 12.17.

4-Chloro-4'-phenyltriphenylcarbinol was prepared by adding 15 g. of 4-chloro-4'-phenylbenzophenone to a slight excess of phenylmagnesium bromide. The ketone was added as a solid because of its limited solubility in cold solvents. The mixture was refluxed for six hours, and hydrolyzed and worked up in the usual manner. The carbinol did not crystallize readily, therefore the impure product was reduced by shaking the benzene solution for two days with an excess of 57% hydriodic acid. The benzene layer was washed with sodium bisulfite solution and water, and then dried and concentrated. The residue was dissolved in petroleum ether, from which 4-chloro-4'-phenyltriphenylmethane crystallized in colorless rosets in 62% yield. The compound melts at 102–103° and is soluble in the common organic solvents except cold alcohol and cold petroleum ether.

Anal. Calcd. for $C_{25}H_{19}Cl$: C, 84.60; H, 5.40; Cl, 10.00. Found: C, 84.80; H, 5.38; Cl, 9.83.

Synthesis of 4-Bromo-4'-phenyltriphenylmethane.—4-Bromo-4'-phenyltriphenylcarbinol was prepared from 4-bromo-4'-phenylbenzophenone[9] and phenylmagnesium bromide, but could not be made to crystallize. It was therefore treated with hydriodic acid, following the procedure just described. The product obtained was dissolved in petroleum ether, from which 4-bromo-4'-phenyltriphenylmethane crystallized after long standing, a 53% yield being obtained. After recrystallization from petroleum ether or from a mixture of benzene and absolute alcohol, it melted at 82–84°. It is soluble in the common organic solvents except cold alcohol and cold petroleum ether. The compound crystallizes with difficulty even when pure; it may not begin to crystallize until twenty-four hours after being seeded and crystallization from a concentrated petroleum ether solution is seldom complete in less than three or four days. This is in contrast to the corresponding chloro derivative, which crystallizes readily.

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[9] Gomberg and Bailar, THIS JOURNAL, **51**, 2233 (1929).

Anal. Calcd. for $C_{25}H_{19}Br$: C, 75.17; H, 4.80; Br, 20.03.   Found: C, 75.52; H, 4.95; Br, 20.30.

Synthesis of 4-Phenyltetraphenylmethane.—This compound was prepared by diazotizing 4-amino-4'-phenyltetraphenylmethane and treating the diazonium salt with absolute alcohol to replace the amino group by hydrogen.   The method is analogous to that used by Ullmann and Münzhuber[10] for the synthesis of tetraphenylmethane.

To prepare 4-amino-4'-phenyltetraphenylmethane, 20 g. of biphenyldiphenylchloromethane and 35 g. of aniline hydrochloride were dissolved in acetic acid and the solution refluxed for several hours.   The solution was then poured into water, neutralized with sodium carbonate, heated to boiling and the precipitated amine filtered off.   The compound crystallized from toluene on addition of ligroin in long thin colorless prisms which melted at 192°.   The yield was 90%.   It is soluble in toluene, benzene and acetic acid when hot, but insoluble in these solvents when cold.

Anal. Calcd. for $C_{31}H_{25}N$: N, 3.41.   Found: N, 3.51.

Four grams of 4-amino-4'-phenyltetraphenylmethane was diazotized by means of amyl nitrite at 30°[10] and the solid diazonium sulfate, obtained by precipitation with ether, was washed and dried; yield, 3 g.   This was added in small quantities to 200 cc. of boiling absolute alcohol, and upon concentration of the solution, 4-phenyltetraphenylmethane crystallized in 70% yield.   Recrystallization from benzene plus ligroin gave colorless rosets which melted at 197–198°.   The compound is soluble in carbon tetrachloride, slightly soluble in benzene and in hot acetic acid, and insoluble in acetone, ether and alcohol.

Anal.   Calcd. for $C_{31}H_{24}$: C, 93.89; H, 6.11.   Found: C, 93.99; H, 6.23.

In connection with this work, N-phenyl-biphenyldiphenylmethylamine was desired.   Ten grams of biphenyldiphenylchloromethane and 10 g. of aniline were dissolved in separate portions of benzene, and then mixed.   The mixture was heated on the steambath for a few minutes after which the precipitated aniline hydrochloride was filtered off, the solution concentrated and ether added.   The anilide was obtained in long colorless prisms, which upon recrystallization melted at 154–155°.   The yield was 86%.   It is soluble in benzene, very slightly soluble in ether and insoluble in alcohol.

Anal.   Calcd. for $C_{31}H_{25}N$: N, 3.41.   Found: N, 3.36.

N-Biphenyl-triphenylmethylamine was prepared in a similar manner from triphenylchloromethane and 4-aminobiphenyl in 84% yield.   Recrystallized from benzene plus alcohol, colorless hexagonal prisms were obtained, which melted at 179.5–180.5°.   It agrees with N-phenyl-biphenyldiphenylmethylamine in solubility.   Attempts to rearrange this compound to 4-(4-aminophenyl)-tetraphenylmethane were unsuccessful.

Anal. Calcd. for $C_{31}H_{25}N$: N, 3.41.   Found: N, 3.40.

Summary

A theory postulating quinoidation of triarylmethyl halides has been advanced to explain the supposedly abnormal reaction of these compounds with phenylmagnesium bromide.

The reaction of 4-chloro- and 4-bromotriphenylchloromethane with phenylmagnesium bromide has been studied and the reaction products are shown to be in agreement with this theory.

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[10] Ullmann and Münzhuber, *Ber.*, **36**, 404 (1903).