terization of the fractions through their molecular weights, boiling points, refractive indices and hydrogen–carbon ratios has given an approximate distribution of the various sized units in the extract and in the residue.

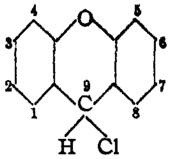
PITTSBURGH, PENNA. RECEIVED DECEMBER 18, 1936

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

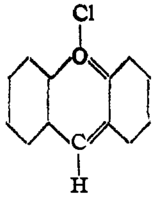
The Reaction between Triarylmethyl Halides and Phenylmagnesium Bromide. III. 9-Phenylxanthyl Chloride[1]

BY C. S. SCHOEPFLE AND J. H. TRUESDAIL

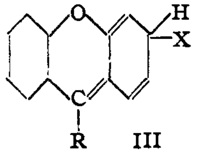
In 1901, Werner[2] found that xanthenol gave a colored solution with hydrochloric acid and concluded that a colored xanthyl chloride was formed. Since the benzenoid structure (I) would not account for the color of this salt, he accepted the oxonium structure (II) which had been assigned to such compounds the year before by Hewitt.[3] Bünzly and Decker[4] later prepared phenylxanthenol which likewise formed colored salts with mineral acids to which they assigned oxonium structures. Neither Werner nor Bünzly and Decker obtained the pure chlorides but they were able to isolate colored addition products with metallic salts such as ferric chloride and mercuric chloride. Xanthyl chloride and phenylxanthyl chloride were first prepared in pure form by Gomberg and Cone[5] and found to be colorless. With dry hydrochloric acid gas, however, phenylxanthyl chloride gave a red addition product containing one molecule of hydrogen chloride. The color observed by Werner and by Bünzly and Decker when xanthenols were treated with hydrochloric acid was, therefore, not due to the chlorides but to the chloride–hydrochlorides which were formed.



I

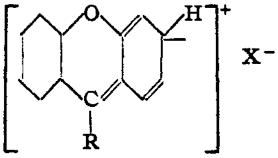


II



III

or



IV

X = Cl·HCl, Cl·FeCl$_3$, etc.

Gomberg and Cone assigned a quinonoid structure (III) to the colored addition products of xanthyl chlorides because of the close agreement in the properties of these compounds with the corresponding addition products of the triarylmethyl halides. One of the many arguments cited in favor of the quinonoid structure of the latter compounds was the fact that a bromine atom in the para position in bromotriphenylmethyl chloride is labile and is readily replaced when shaken with silver chloride in a sulfur dioxide solution,[6] while a bromine atom in the ortho or meta position is not replaced under any conditions. The same situation was found to exist with the xanthyl halides.[5] If the bromine atom in bromophenylxanthyl halides was in the 3-position, it was readily replaced by chlorine either by shaking with silver chloride in a benzene solution containing a small amount of hydrogen chloride, or merely by treating with excess of dry hydrochloric acid gas at room temperature. However, the bromine atom could not be replaced if it was in the phenyl group which is not a part of the xanthene ring, which showed that the phenyl group does not become quinonoid.

Further evidence that triarylmethyl halides can exist in two modifications was obtained from the reaction of triphenylchloromethane with phenylmagnesium bromide,[7] where the chloride reacts partly in the benzenoid form to give tetraphenylmethane (usually 5–8% yield), and partly in the quinonoid form to give biphenyldiphenylmethane (50–80% yield).[8] In the present paper it is shown that 9-phenylxanthyl chloride likewise reacts in two forms with phenylmagnesium bromide.

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(1) From the Ph.D. dissertation of J. H. Truesdail.

(2) Werner, *Ber.*, **34**, 3300 (1901).

(3) Hewitt, *Z. physik. Chem.*, **34**, 1 (1901); *Ber.*, **34**, 3819 (1901).

(4) Bünzly and Decker, *ibid.*, **37**, 2931 (1904).

(5) Gomberg and Cone, *Ann.*, **370**, 142 (1909); *ibid.*, **376**, 183 (1909).

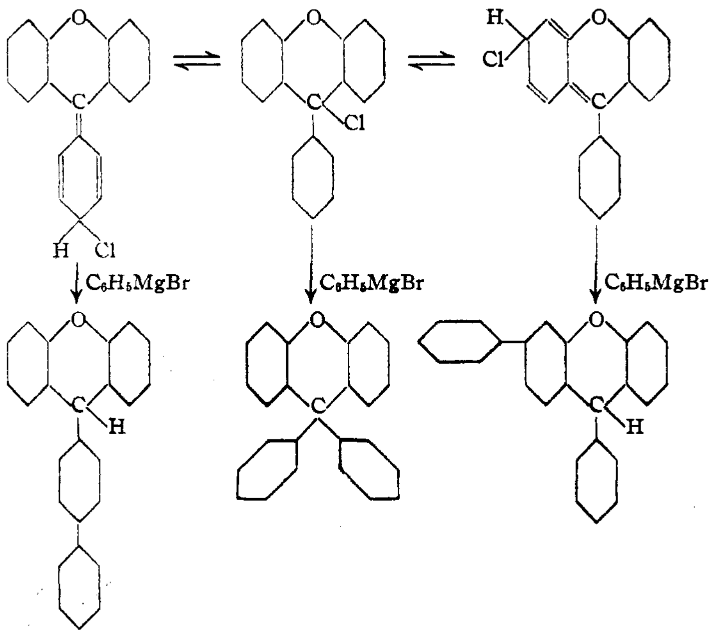
(6) Gomberg, *Ber.*, **40**, 1861 (1907).

(7) Gilman and Jones, THIS JOURNAL, **51**, 2840 (1929).

(8) Schoepfle and Trepp, (a) *ibid.*, **54**, 4059 (1932); (b) *ibid.*, **58**, 791 (1936).

Theoretically, it is possible for 9-phenylxanthyl chloride to exist in a benzenoid modification (VI), and in two quinonoid modifications, one in which the 9-phenyl group assumes a quinonoid structure (V), and the other in which part of the xanthene ring assumes a quinonoid structure (VII). If the benzenoid form (VI) reacts with phenylmagnesium bromide, 9,9-diphenylxanthene (IX) will be obtained. However, if the quinonoid form (V) reacts, the replacement of the chlorine atom by the phenyl group gives an intermediate unstable molecule which will rearrange to 9-biphenylxanthene (VIII). Finally, if the quinonoid form (VII) reacts, then the intermediate compound obtained will rearrange to give 3,9-diphenylxanthene (X).

V VI VII

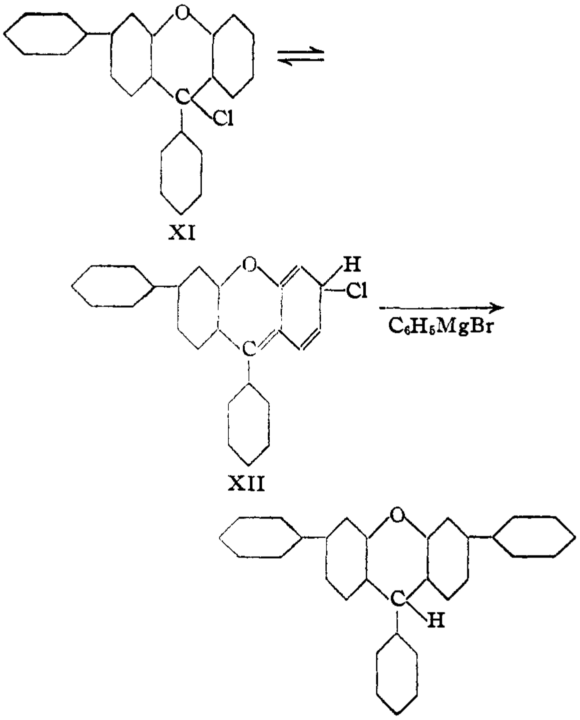


VIII IX X

Only two of these three compounds were actually isolated from the reaction between 9-phenylxanthyl chloride and phenylmagnesium bromide, namely, 9,9-diphenylxanthene (IX) in traces, and 3,9-diphenylxanthene (X) in 34–51% yield. In addition, however, there were obtained 3,6,9-triphenylxanthene (XIII) in 3–14% yield and 9-phenylxanthene in 13–21% yield. (The variations in yields are due no doubt to experimental difficulty in isolating the crystalline compounds rather than to variations inherent in the reaction itself.)

3,6,9-Triphenylxanthene and 9-phenylxanthene evidently are secondary rather than primary products of the reaction. Corresponding compounds were obtained in small amounts in the reaction of triphenylchloromethane and phenylmagnesium bromide, and their formation was explained by assuming an intermolecular oxidation–reduction reaction between unreacted triphenylchloromethane and the primary reaction product, biphenyldiphenylmethane.[8b] In the present case, a similar explanation is offered. During the course of the reaction, a part of the 3,9-diphenylxanthene at the moment of formation (or the intermediate compound from which the xanthene is obtained) reacts with unchanged 9-phenylxanthyl chloride to give 9-phenylxanthene and 3,9-diphenylxanthyl chloride (XI). The latter compound will now react further with phenylmagnesium bromide and, by analogy with 9-phenylxanthyl chloride, it should react mainly in the quinonoid form (XII) to give 3,6,9-triphenylxanthene (XIII).

It has been found that in the reaction of triphenylchloromethane with phenylmagnesium bromide,[8b] the magnesium bromide present in solution favors the formation of the



XI

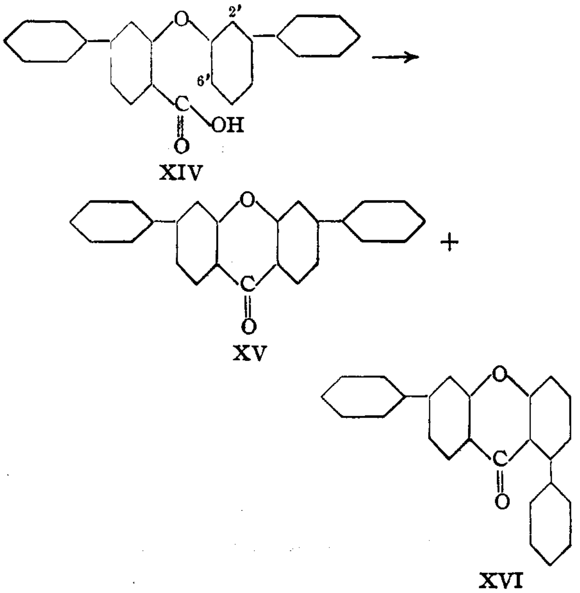
XII

XIII

quinonoid modification. This effect is shown clearly by the fact that a much higher yield of tetraphenylmethane may be obtained if triphenylchloromethane is allowed to react with diphenylmagnesium[9] in place of phenylmagnesium bromide. Magnesium bromide should induce an even higher concentration of the quinonoid modification of 9-phenylxanthyl chloride than of triphenylchloromethane, since the former becomes quinonoid more readily than the latter. However, because only a small amount of 9,9-diphenylxanthene and a large amount of 3,9-diphenylxanthene are obtained in the reaction of phenylmagnesium bromide with 9-phenylxanthyl chloride, it must not be inferred that the chloride exists principally in the quinonoid form. Instead, the probable explanation is that the rate of reaction of the benzenoid form of 9-phenylxanthyl chloride with phenylmagnesium bromide is exceedingly slow in comparison to the rate of reaction of the quinonoid form. At present, the relative rates of reaction cannot be determined because of the disturbing effect of the magnesium bromide on the equilibrium between the two forms. It is of interest to note that no 9-biphenylxanthene was isolated in the reaction, indicating that the phenyl group does not become quinonoid, which is in agreement with the results of Gomberg and Cone who found that halogens in the phenyl group were not labile.

In order to identify the products of the reaction between 9-phenylxanthyl chloride and phenylmagnesium bromide, it became necessary to synthesize 3,9-diphenylxanthene and 3,6,9-triphenylxanthene. Acetyl-4-aminobiphenyl was chlorinated in acetic acid solution and the product hydrolyzed to give 3-chloro-4-aminobiphenyl.[10] The position of the chlorine atom in this compound was established definitely by a synthesis in which diazotized 3-chloro-4-nitroaniline was coupled with benzene to give 3-chloro-4-nitrobiphenyl which was reduced to 3-chloro-4-aminobiphenyl. The products from the two procedures were identical. The Sandmeyer reaction was used to prepare 3-chloro-4-cyanobiphenyl from 3-chloro-4-aminobiphenyl and the cyanide hydrolyzed to 2-chloro-4-phenylbenzoic acid. The remaining steps in the synthesis of 3,9-diphenylxanthene were the preparation of 2-phenoxy-4-phenylbenzoic acid from 2-chloro-4-phenylbenzoic acid by the Ullmann reaction, ring closure to give 3-phenylxanthone, treatment with phenylmagnesium bromide to give 3,9-diphenylxanthenol, and finally reduction to the xanthene.

3,6,9-Triphenylxanthene was synthesized in a similar manner. 2-(3′-Phenylphenoxy)-4-phenylbenzoic acid (XIV) was obtained by the Ullmann reaction from potassium 2-chloro-4-phenylbenzoate and sodium-3-phenylphenolate. Ring closure gave two compounds, 3,6-diphenylxanthone (XV) and 1,6(or 3,8)-diphenylxanthone (XVI), of which only the one occurring in the larger amount was isolated in pure form. This compound was assigned the first structure (XV), inasmuch as ring closure of the acid should take place largely in the 6′-position since this position is para to the phenyl group and since the activity of the 2′-position should be decreased due to the blocking effect of the adjacent phenyl group. Moreover, the properties of the compound isolated were in agreement with the expectation that 3,6-diphenylxanthone would have a higher melting point and a lower solubility than the less symmetrical 1,6-diphenylxanthone. The final steps in the synthesis were the preparation of 3,6,9-triphenylxanthenol by treating 3,6-diphenylxanthone with phenylmagnesium bromide, and the reduction of the xanthenol to 3,6,9-triphenylxanthene (XIII).



XIV

XV

XVI

Experimental

9-Phenylxanthyl Chloride and Phenylmagnesium Bromide.—9-Phenylxanthyl chloride[11] was prepared by sus-

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[9] Unpublished results of J. Taras in this Laboratory.

[10] Scarborough and Waters, *J. Chem. Soc.*, 559 (1926); Bell, Kenyon and Robinson, *ibid.*, 1247 (1926).

[11] Gomberg and Cone, *Ann.*, **370**, 155 (1932).

pending 15 g. of the corresponding carbinol in 150 cc. of petroleum ether, adding 20 cc. of freshly distilled acetyl chloride and refluxing the mixture until all of the carbinol had dissolved. The solution was concentrated to about 75 cc. and the chloride allowed to crystallize. Moisture was excluded rigorously at all times. One recrystallization from petroleum ether gave pure colorless crystals of the chloride.

An ether solution of from 10 to 15 g. of 9-phenylxanthyl chloride was poured with swirling into an ether solution of twice the theoretical amount of phenylmagnesium bromide which was cooled in ice. Several minutes were required for the addition. At first, the Grignard solution in the vicinity of each entering drop of the chloride solution acquired an orange color which immediately disappeared, but as the reaction proceeded the solution became dark green. The mixture was refluxed for an hour, cooled and decomposed with ice and ammonium chloride. The ether extract was washed, concentrated and the product steam distilled, after which the residue was dissolved in ether and the solution dried over calcium chloride.

When the ether solution of the reaction product was allowed to evaporate spontaneously and slowly, a mass of white solid material formed which was found to be a mixture of 3,9-diphenylxanthene and 3,6,9-triphenylxanthene. The solid was filtered and washed with small amounts of cold ether, and the filtrate allowed further to evaporate very slowly. A second lot of white material was thus formed which was again composed chiefly of the above-mentioned compounds but which in some cases also contained very small amounts of 9,9-diphenylxanthene. No other substances could be isolated following this particular procedure.

The solubilities of 3,9-diphenylxanthene and 3,6,9-triphenylxanthene are very similar, hence they are difficult to separate. If the mixture was dissolved in hot acetic acid, a mass of crystals formed on cooling. When these crystals were digested with hot alcohol, a beady precipitate remained in the bottom of the flask and a flocculent precipitate became suspended in the solution, the two being separated by decantation. The flocculent precipitate was impure 3,6,9-triphenylxanthene, which could be obtained pure by repeated crystallization from ether, benzene or butanol. The beady precipitate and the material which dissolved in the alcohol was impure 3,9-diphenylxanthene, which could be obtained pure by crystallization from benzene.

Experiments indicated that no other compounds were present in appreciable amounts. Therefore, a melting point curve of known mixtures of these two compounds was prepared and the melting point of the unknown mixture was taken as a guide in estimating the percentage composition. In four typical runs, the estimated yields of 3,9-diphenylxanthene and 3,6,9-triphenylxanthene, respectively, were as follows: 34%, 14%; 43%, 3%; 51%, 6%; 51%, 14%. As mentioned previously, the variations in yield are due to experimental difficulty in isolating the crystalline compounds.

Molecular distillation with a Hickman still[12] was used in an attempt to better the yields, and if possible to isolate other products from the reaction mixture. Molecular distillation at a temperature of about 125° gave a large amount of material, part of which sublimed to the top of the still and part of which distilled into the receiver. Crystallization of the sublimed material from alcohol gave well formed crystals melting at 140–141° which showed no lowering in melting point when mixed with authentic 9-phenylxanthene. The distillate in the receiver was found to be a mixture of 9-phenylxanthene and 3,9-diphenylxanthene, from which the latter could be obtained in pure state by repeated recrystallization from alcohol. 3,6,9-Triphenylxanthene could not be recovered in this manner since when the temperature of the still was raised to 150°, decomposition occurred as was evidenced by blackening of the residue and evolution of gas.

The amount of 9-phenylxanthene present in the reaction mixture was determined by removing it by sublimation at 0.001 mm. pressure and 100°. The molecular sublimation apparatus was patterned after the still described by Carothers.[13] The quantities obtained in three experiments were 21, 13 and 19%, respectively.

9-(*p*-Biphenyl)-xanthenol.—Xanthone was added to an ether solution of excess *p*-biphenylmagnesium bromide and the mixture refluxed overnight. After chilling in an ice-salt-bath, the precipitate was filtered and decomposed with ice and hydrochloric acid. The ether extract was filtered to remove a small amount of insoluble dibiphenyl, then concentrated and steam distilled, and the residue dissolved in benzene from which practically pure biphenylxanthenol crystallized. Recrystallized from ether, the compound melted at 178–179°; yield, 85%. The carbinol gives a deep red color with concentrated sulfuric acid.

Anal. Calcd. for $C_{25}H_{18}O_2$: C, 85.69; H, 5.18. Found: C, 85.38; H, 5.23.

9-(*p*-Biphenyl)-xanthene.—One gram of 9-(*p*-biphenyl)-xanthenol and 10 g. of dry sodium formate were added to 30 cc. of anhydrous formic acid and the mixture refluxed for one hour. At first, a deep red color was obtained but this soon disappeared and the xanthene crystallized. After dilution with water, the product was filtered and dried. Recrystallization from benzene gave colorless crystals which melted at 206–207°; yield, 95%.

Anal. Calcd. for $C_{25}H_{18}O$: C, 89.78; H, 5.43. Found C, 89.65; H, 5.49.

3-Bromo-4-methylbiphenyl.—Forty-four grams of 2-bromo-4-aminotoluene hydrochloride was treated with 25 cc. of concentrated hydrochloric acid, the mixture cooled in an ice-salt-bath and 18 cc. of water added. When cold a saturated solution of 16 g. of sodium nitrite was added dropwise to the mechanically stirred solution. Following the procedure of Gomberg and Bachmann,[14] the solution of the diazonium chloride was poured into 150 cc. of pure benzene at 5°, and 25 cc. of 40% sodium hydroxide solution added drop by drop over two hours, keeping the temperature below 9°; nitrogen was evolved. The stirring was continued for two to three hours. The resulting mixtures from two such runs were combined, the benzene layer concentrated and the product steam distilled at a temperature of 170–190°. About eight liters of distillate were caught, extracted with ether and the extract concentrated.

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

[13] Carothers and Hill, THIS JOURNAL, **54**, 1557 (1932).

[14] Gomberg and Bachmann, *ibid.*, **46**, 2339 (1924); Gomberg and Pernert, *ibid.*, **48**, 1372 (1926).

Distillation at 2 mm. pressure gave a light yellow oil which boiled at 123–123.5° and melted at 9°; yield 30%.

Anal. Calcd. for $C_{13}H_{11}Br$: Br, 32.36. Found: Br, 32.18.

Various attempts to oxidize 3-bromo-4-methylbiphenyl to 2-bromo-4-phenylbenzoic acid gave unsatisfactory yields.

3-Chloro-4-nitrobiphenyl.—Nineteen grams of 3-chloro-4-nitroaniline was heated to 70° with 45 cc. of concentrated hydrochloric acid, cooled, and diazotized by introducing a concentrated solution of sodium nitrite below the surface of the acid. The diazonium chloride solution was poured into 75 cc. of benzene, and 45 cc. of 40% sodium hydroxide solution added dropwise to the vigorously stirred mixture. The benzene solution was concentrated and the product distilling at 160–180° at 2 mm. pressure was crystallized from alcohol. Yellowish needles were obtained, melting at 78.5–79.5°; yield, 20%.

Anal. Calcd. for $C_{12}H_8ClNO_2$: Cl, 15.15. Found: Cl, 14.97.

3-Chloro-4-aminobiphenyl.—A solution of 10 g. of hydrated stannous chloride in 10 cc. of concentrated hydrochloric acid was poured slowly into a solution of 2 g. of 3-chloro-4-nitrobiphenyl in 15 cc. of alcohol. Repeated crystallization of the amine from dilute alcohol gave a compound melting at 69–69.5°. A mixed melting point showed that this compound was identical with the compound which Scarborough and Waters[10] obtained by chlorinating acetyl-4-aminobiphenyl and hydrolyzing the product. The latter method was therefore used for the preparation of further amounts of this amine.

3-Chloro-4-cyanobiphenyl.—This compound was obtained from 3-chloro-4-aminobiphenyl by the Sandmeyer reaction. The cuprous cyanide solution (150 cc.) was prepared in the usual manner from 18 g. of sodium cyanide, and was covered with 100 cc. of benzene and cooled to 5°. Twenty-four grams of 3-chloro-4-aminobiphenyl hydrochloride was suspended in 15 cc. of concentrated hydrochloric acid plus a small amount of ice and diazotized with a concentrated solution of sodium nitrite. The excess acid was made neutral to congo red paper with sodium bicarbonate solution and then added slowly to the vigorously stirred cuprous cyanide solution. The products of several such runs were combined and the benzene layer separated and washed with sodium carbonate solution and with water. Distillation at 2 mm. pressure followed by crystallization from alcohol gave the pure cyanide melting at 101–101.5°; yield 30%.

Anal. Calcd. for $C_{13}H_8ClN$: Cl, 16.60. Found: Cl, 16.39.

2-Chloro-4-phenylbenzoic Acid.—Twenty grams of 3-chloro-4-cyanobiphenyl was dissolved in 240 cc. of alcohol and 75 g. of 40% sodium hydroxide solution, and refluxed about six hours. The solution was cooled, poured into a liter of water, filtered, and the acid precipitated with hydrochloric acid. Crystallization from alcohol after treatment with norite gave white needles melting at 166.5–167°; yield 90%.

Anal. Calcd. for $C_{13}H_9ClO_2$: Cl, 15.25. Found: Cl, 15.19.

2-Phenoxy-4-phenylbenzoic Acid.—The potassium salt of 2-chloro-4-phenylbenzoic acid was prepared by dissolving the equivalent weights of the acid and of potassium carbonate in water, filtering the solution and concentrating to dryness on the sand-bath. To 3.5 g. of the salt was added 3.0 g. of phenol and a solution of sodium methylate prepared from 0.4 g. of sodium and 40 cc. of methanol, and the mixture refluxed until all the salt had dissolved. About 0.1 g. of copper powder was added and the methanol removed by distillation, after which the flask was placed in an oil-bath and the temperature slowly raised to 150°. At this temperature the reaction takes place rapidly and the temperature of the melt may reach 165–170°. After a few minutes the melt was cooled and digested with about 20 cc. of cold 5% sodium hydroxide solution. The phenol and original acid are quite soluble while the sodium salt of 2-phenoxy-4-phenylbenzoic acid is practically insoluble even in 1% sodium hydroxide solution. If necessary, the sodium salt may be purified readily by recrystallization from water. The acid was obtained by adding hydrochloric acid to a water solution of the sodium salt. Crystallization from alcohol or benzene gave colorless leaflets or small plates which melted at 169.5–170°; yield 80%.

Anal. Calcd. for $C_{19}H_{14}O_3$: C, 78.59; H, 4.87. Found: C, 78.51; H, 4.99.

3-Phenylxanthone.—When ring closure of 2-phenoxy-4-phenylbenzoic acid was attempted using hot concentrated sulfuric acid as the agent, a very poor yield of the xanthone was obtained; most of the product was water soluble and had a high melting point, indicating that sulfonation had occurred. The following procedure proved to be more satisfactory. Three grams of 2-phenoxy-4-phenylbenzoic acid was dissolved in 35 cc. of dry benzene, 3 g. of phosphorus pentachloride was added and the mixture heated. The solution thus obtained was cooled, 4 g. of anhydrous aluminum chloride added, and the mixture refluxed until no more hydrogen chloride was evolved. After treatment with ice, the product was steam distilled and the residue crystallized from alcohol or petroleum ether. Colorless needles were obtained melting at 141–141.5°; yield 95%.

Anal. Calcd. for $C_{19}H_{12}O_2$: C, 83.80; H, 4.45. Found: C, 83.50; H, 4.55.

3,9-Diphenylxanthenol.—A benzene solution of 3-phenylxanthone was added to an ether solution of excess phenylmagnesium bromide, the mixture refluxed for one hour and then decomposed with ice and ammonium chloride. The benzene–ether layer was concentrated, steam distilled and the residue dissolved in hot petroleum ether. Colorless crystals were obtained which upon recrystallization from benzene–petroleum ether melted at 128.5–129°; yield 90%. With concentrated sulfuric acid, the carbinol gives a light red color with yellow-green fluorescence.

Anal. Calcd. for $C_{25}H_{18}O_2$: C, 85.69; H, 5.18. Found: C, 85.49; H, 5.24.

3,9-Diphenylxanthene.—This compound was obtained by the reduction of 3,9-diphenylxanthenol with formic acid following the procedure described for the preparation of 9-biphenylxanthene. Crystallization from alcohol or petroleum ether gave colorless needles which melted at 146.5–147°; yield 95%.

Anal. Calcd. for $C_{25}H_{18}O$: C, 89.78; H, 5.43. Found: C, 89.53; H, 5.43.

2-(3′-Phenylphenoxy)-4-phenylbenzoic Acid.—3-Nitrobiphenyl was prepared by coupling diazotized *m*-nitraniline with benzene in alkaline solution,[15] and was reduced to 3-aminobiphenyl which was diazotized and added to boiling 30% sulfuric acid[16] to give 3-hydroxybiphenyl.

Four grams of potassium 2-chloro-4-phenylbenzoate, 3 g. of 3-hydroxybiphenyl and a methanol solution of sodium methylate prepared from 0.35 g. of sodium were placed in a flask, sufficient methanol being used so that the contents dissolved on refluxing. About 0.1 g. of copper powder was then added and the methanol removed by distillation, after which the flask was placed in an oil-bath and the temperature gradually raised. The reaction takes place readily at 150° and when the temperature of the bath reached 180° the flask was removed and the contents dissolved in about two liters of water containing a few grams of potassium hydroxide, after which the solution was filtered and the 2-(3′-phenylphenoxy)-4-phenylbenzoic acid precipitated with hydrochloric acid. Recrystallization from benzene or alcohol gave small, colorless needles which melted at 186–187°; yield 50–60%.

Anal. Calcd. for $C_{25}H_{18}O_3$: C, 81.93; H, 4.95. Found: C, 81.52; H, 4.95.

3,6-Diphenylxanthone.—Ring closure of 2-(3′-phenylphenoxy)-4-phenylbenzoic acid was accomplished with phosphorus pentachloride and aluminum chloride following the procedure described for the preparation of 3-phenylxanthone. A quantitative yield of crude material was obtained which appeared to be a mixture of 3,6-diphenylxanthone and 1,6-diphenylxanthone. Crystallization of this mixture from 1:1 methanol–benzene gave about a 35% yield of colorless needles which melted at 193.5–194.5°. The reasons for believing this compound to be 3,6-diphenylxanthone have been stated previously. The isomeric 1,6-diphenylxanthone was not obtained in pure form.

Anal. Calcd. for $C_{25}H_{16}O_2$: C, 86.18; H, 4.63. Found: C, 85.56; H, 4.64.

3,6,9-Triphenylxanthenol.—3,6-Diphenylxanthone, dissolved in benzene, was added to an ether solution of excess phenylmagnesium bromide and the mixture refluxed for about an hour. The product was decomposed with ammonium chloride and ice, and the ether extract concentrated and steam distilled.* Crystallization of the residue from benzene gave colorless crystals which decomposed at 238–239°; yield 90%. With concentrated sulfuric acid, the carbinol gives a light red color with yellow-green fluorescence.

Anal. Calcd. for $C_{31}H_{22}O_2$: C, 87.29; H, 5.20. Found: C, 86.90; H, 5.32.

3,6,9 - Triphenylxanthene.—3,6,9 - Triphenylxanthenol was reduced to 3,6,9-triphenylxanthene by formic acid using the procedure previously described. Crystallization from benzene–petroleum ether gave small colorless plates which decomposed at 220°; yield 95%.

Anal. Calcd. for $C_{31}H_{22}O$: C, 90.69; H, 5.41. Found: C, 90.24; H, 5.42.

Summary

The reaction between 9-phenylxanthyl chloride and phenylmagnesium bromide has been studied, and it has been found that the chloride reacts largely in a quinonoid form and only to a limited extent in the benzenoid form. A number of xanthene derivatives have been prepared and described.

ANN ARBOR, MICH. RECEIVED DECEMBER 21, 1936

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[15] Blakey and Scarborough, *J. Chem. Soc.*, 3000 (1927).

[16] Jacobsen and Loeb, *Ber.*, **36**, 4083 (1903).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

The Structure of Metal Ketyls. V. The Conductance Function

BY CHARLES BUSHNELL WOOSTER

I. Introduction

Previous papers in this series[1] have reported some studies of the chemical reactions of monosodium benzophenone in liquid ammonia solution. It has become increasingly evident that such solutions comprise a system of rather complex equilibria and that further progress on the problem of the structure of metal ketyls would be facilitated greatly by more accurate information regarding the nature and interrelations of these equilibria. It is the purpose of the present paper to show that the conductance of sodium benzophenone in liquid ammonia as measured by Kraus and Bien[2] may be described quantitatively by assuming the presence of the following equilibria

$$[(C_6H_5)_2CO]Na \rightleftharpoons [(C_6H_5)_2CO]^- + Na^+ \quad (1)$$

$$2[(C_6H_5)_2CO]Na \rightleftharpoons (C_6H_5)_2C(ONa)—C(ONa)(C_6H_5)_2 \quad (2)$$

$$(C_6H_5)_2C(ONa)—C(ONa)(C_6H_5)_2 \rightleftharpoons Na^+ + Na[(C_6H_5)_2CO]_2^- \quad (3a)$$

$$[(C_6H_5)_2CO]Na + [(C_6H_5)_2CO]^- \rightleftharpoons Na[(C_6H_5)_2CO]_2^- \quad (3b)$$

that is, simple ionization of the metal ketyl (1), association of the metal ketyl molecules (ion pairs) to the un-ionized pinacolate (2), and formation of

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[1] (a) Wooster, THIS JOURNAL, **51**, 1858 (1929); (b) Wooster, *ibid.*, **56**, 2436 (1934); (c) Wooster and Holland, *ibid.*, **56**, 2438 (1934); (d) Wooster and Dean, *ibid.*, **57**, 112 (1935).

[2] (a) Kraus and Bien, *ibid.*, **55**, 3609 (1933); (b) Bien, Dissertation, Brown University, 1932.