evaporated under reduced pressure to 400 cc. Upon cooling, most of the acid crystallized. This fraction melted at 156–158°. Two more fractions from this solution obtained by further evaporation melted at 157–158°.

Two fractions were obtained from the first benzene extraction. Both melted at 157–158°.

4,4-Dimethylcyclohexane-1,1-diacetic Acid.—A. The acid (17 g.) was dissolved in aqueous ammonia, and this solution evaporated to dryness on a steam-bath. The dry salt formed was dissolved in 120 cc. of boiling absolute alcohol and the solution allowed to cool to room temperature. The crystalline precipitate formed was filtered and washed with cold absolute alcohol and then converted to the acid. This fraction melted at 227° (bloc Maquenne). The acid (13 g.) was then dissolved in 100 cc. of hot alcohol and the solution allowed to cool when part of the acid crystallized. This fraction melted at 230°. By gradual evaporation of the mother liquor three more fractions were obtained, and they melted at 230, 229 and 228°, respectively.

The first fraction of the acid from alcohol was dissolved in 30 cc. of hot alcohol and part of it recrystallized on cooling. This fraction melted at 230°. The mother liquor from this fraction was used to dissolve the second fraction from alcohol, etc. This procedure was followed until a total of nine fractions had been obtained, all of which melted at 230°. The seventh fraction was converted to the anhydride and fractionated from ligroin. All of the fractions melted at 85–86°.

The original mother liquor from the ammonium salt was evaporated to dryness, and the salt converted to the acid (34 g.) which melted at 224° (bloc Maquenne). This portion of the acid was dissolved in 60 cc. of boiling alcohol, and three fractions were obtained from this solution by alternate evaporation and cooling. They all melted at 230°. The second fraction was converted to the anhydride which was fractionally crystallized from 80 cc. of ligroin. The fractions obtained all melted at 85°.

Summary

1. 4,4-Dimethyl-1-carboxycyclohexylacetic acid, 4,4-dimethylcyclohexyl-1,1-diacetic acid and 4-methylcyclohexyl-1,1-diacetic acid have been prepared. Each was obtained in a single form only.

2. A discussion is given of the theoretical number of isomers in substituted cyclohexanes, on the assumption that multiplanar forms are possible.

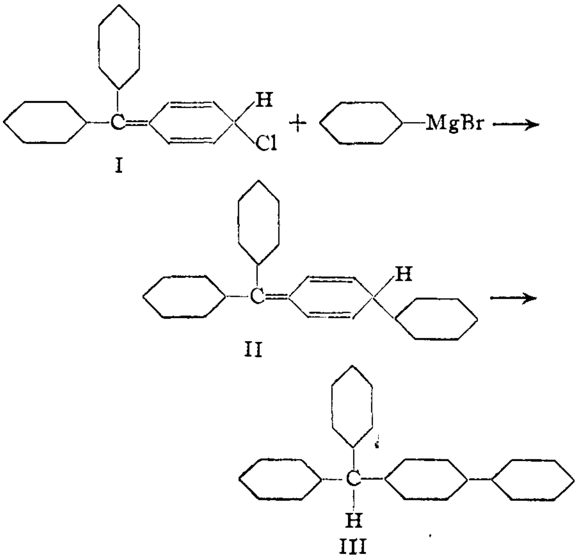
URBANA, ILLINOIS RECEIVED FEBRUARY 27, 1936

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

The Reaction between Triarylmethyl Halides and Phenylmagnesium Bromide. II

BY C. S. SCHOEPFLE AND S. G. TREPP

Tetraphenylmethane is commonly prepared by the reaction of triphenylchloromethane and phenylmagnesium bromide,[1] although the yield is very poor. Gilman and Jones[2] found that biphenyldiphenylmethane (biphenyl = 4-phenyl-phenyl) is also formed in this reaction and that this compound is actually the principal product. The explanation offered by the present authors[3] for the formation of the two compounds is that triphenylchloromethane reacts partly in a benzenoid modification giving tetraphenylmethane, and partly in a quinonoid modification (I) giving biphenyldiphenylmethane (III). The relative amounts of the two products will therefore be dependent upon the equilibrium between the two forms of triphenylchloromethane, and the rate of reaction of each form with the Grignard reagent; it is assumed that the rate of transformation of the benzenoid form to the quinonoid form is rapid in comparison with the rate of reaction of the quinonoid form.



It might be expected then that the reaction of a given triarylchloromethane would vary with dif-

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[1] (a) Gomberg and Cone, *Ber.*, **39**, 1461 (1906); (b) Freund, *ibid.*, **39**, 2237 (1906).

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

[3] Schoepfle and Trepp, *ibid.*, **54**, 4059 (1932).

ferent Grignard reagents, and it is well known that this is the case. Triphenylchloromethane in ether or ether–benzene solution reacts with phenylmagnesium bromide to give about a 6 to 7% yield of tetraphenylmethane, but with methylmagnesium iodide or benzylmagnesium chloride under the same conditions a quantitative yield of 1,1,1-triphenylethane and 1,1,1,2-tetraphenylethane, respectively, is obtained.[1a] Therefore, the benzenoid modification of triphenylchloromethane must react much less readily with phenylmagnesium bromide than with the other two Grignard reagents.

It is also known that the reaction will vary when a given Grignard reagent is used with different triarylchloromethanes under the same conditions. Although triphenylchloromethane and phenylmagnesium bromide give a yield of but 6 to 7% of tetraphenylmethane as stated, Gomberg and Forrester[4] have shown that certain methoxy derivatives of triphenylchloromethane give relatively good yields of the tetra-aryl compounds; for example, 2,5-dimethoxytriphenylchloromethane and phenylmagnesium bromide give a 58% yield of 2,5-dimethoxytetraphenylmethane. In the present work, we have prepared three trisubstituted tetraphenylmethanes with somewhat similar results. Starting in each case with the corresponding triarylchloromethane and phenylmagnesium bromide in ether or ether–benzene solution, the following compounds and yields were obtained: 4,4′,4″-tribromotetraphenylmethane, 44%; 4,4′,4″-trichlorotetraphenylmethane, 43%; 4,4′,4″-trimethyltetraphenylmethane, 35%. In the case of these trisubstituted tetra compounds, the higher yields are probably due largely to the lessened tendency of the triarylchloromethanes to become quinonoid rather than to an increased rate of reaction of the benzenoid modification.

It appeared likely therefore that an increased yield of tetraphenylmethane itself would result if a solvent were used which would lessen the tendency for the formation of the quinonoid modification of triphenylchloromethane. Heretofore, the reaction has been carried out in ether solution or in a solution containing ether. We have now found that if the Grignard reagent is freed from ether by heating under reduced pressure and the reaction then carried out in benzene, the yield of tetraphenylmethane is increased to about 25%, with occasional yields of 30%. The yield with ether-free Grignard reagent using toluene or bromobenzene as solvent was likewise about 25%, and in ethylene dichloride and in dioxane was about 20%.[5]

The results obtained with the ether-free Grignard reagent cannot be due to a repression of the quinonoidation of triphenylchloromethane by the solvent inasmuch as ethylene dichloride which is known to favor quinonoidation[6] nevertheless gives a much higher yield of tetraphenylmethane than is obtained in ether. Since the Grignard reagent has been shown to represent the equilibrium, $2C_6H_5MgBr = (C_6H_5)_2Mg + MgBr_2$,[7] and since ether is the only solvent used in which the Grignard reagent is soluble, it might be supposed that the enhanced yield in other solvents is due to a pronounced difference in the respective rates with which phenylmagnesium bromide and diphenylmagnesium react with either the benzenoid or the quinonoid modification of triphenylchloromethane. Such an explanation has been advanced by others[8] to account for Grignard reactions which proceed differently in ether and in benzene, but this explanation does not seem to be the most acceptable one in the present case.

Magnesium bromide, although perhaps less effective, behaves like zinc chloride, stannic chloride, etc., in that it forms a yellow quinonoid addition compound with triphenylchloromethane. When the phenylmagnesium bromide solution is added to the colorless ether or benzene solution of triphenylchloromethane, a yellow color instantly appears and when other triarylchloromethanes are used, the initial color is always that of the corresponding quinonoid addition compound; for example, diphenyl-1-naphthylchloromethane and phenylmagnesium bromide give a green color. The magnesium bromide formed in the reaction or present as part of the Grignard reagent must therefore add to the unchanged triphenylchloromethane, or perhaps phenylmagnesium bromide itself adds to the chloride before the true Grignard reaction takes place. This addition produces a marked increase in the concentration of the quinonoid modification with the result that mostly biphenyldiphenylmethane (III) is formed. When an ether-free Grignard reagent is used with a sol-

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[4] Gomberg and Forrester, This Journal, **47**, 2373 (1925).

[5] Preliminary experiments indicate that similar yields are obtained with phenylmagnesium chloride.

[6] Schoepfle and Ryan, This Journal, **54**, 3690 (1932); see also Dilthey, *J. prakt. Chem.*, [2] **109**, 273 (1925).

[7] Schlenk and Schlenk, Jr., *Ber.*, **62**, 920 (1929); Schlenk, Jr., *ibid.*, **64**, 734 (1931).

[8] Miller and Bachman, This Journal, **57**, 766 (1935).

vent such as benzene, there should be less tendency to favor the quinonoid modification because magnesium bromide and phenylmagnesium bromide are practically insoluble in benzene, and consequently a larger yield of tetraphenylmethane should result. The fact that not more than 30% of tetraphenylmethane is obtained even with ether-free Grignard reagent leads to the conclusion that the rate of reaction of the benzenoid modification is very slow in comparison with that of the quinonoid modification.

In the reaction between triphenylchloromethane and phenylmagnesium bromide, a number of products have been isolated in addition to tetraphenylmethane and biphenyldiphenylmethane. These products and the approximate yields obtained are as follows: triphenylmethane, 5%; dibiphenylphenylmethane, 3%; 4-phenyltetraphenylmethane, 0.6%; tribiphenylmethane, trace. It has previously been shown[8] that dibiphenylphenylmethane and 4-phenyltetraphenylmethane are the products formed from biphenyldiphenylchloromethane and phenylmagnesium bromide, and by analogy, tribiphenylmethane should be formed from dibiphenylphenylchloromethane and phenylmagnesium bromide. A probable explanation of the formation of these chlorides in the reaction is as follows. When the quinonoid modification of triphenylchloromethane reacts with the Grignard reagent, the intermediate product is a quinonoid modification of biphenyldiphenylmethane (II) which is unstable and rearranges to the stable benzenoid form. The intermediate compound must be very active and before or during the rearrangement may react to some extent with unchanged triphenylchloromethane to give triphenylmethane and biphenyldiphenylchloromethane. Dibiphenylphenylchloromethane would be formed in a similar manner from biphenyldiphenylchloromethane. Another example of this type of reaction will be discussed in a later paper.

Experimental

Triphenylchloromethane and Phenylmagnesium Bromide.—An ether solution of phenylmagnesium bromide in 50% excess was filtered through cotton and poured slowly, with swirling, into a benzene solution of triphenylchloromethane. The yellow color which appears instantly changes rapidly to a deep cherry red and then fades to a pale orange after several hours. The reaction proceeds rapidly without heating since no difference in yield was observed between runs allowed to stand only one-half hour and those allowed to stand for several days.

The reaction mixture was decomposed in the usual manner, and the product steam distilled and digested with ether which left most of the tetraphenylmethane undissolved. The solution was dried, concentrated, and a further amount of tetraphenylmethane recovered. The crude compound contained a trace of triphenylmethyl peroxide from which it was readily separated by crystallization from benzene. The ether filtrate was concentrated to a small volume, petroleum ether added and the solvent allowed to evaporate spontaneously, whereupon the biphenyldiphenylmethane crystallized. Several such evaporations increased the quantity of material recovered. The uncrystallized residue was distilled in a molecular still but only insignificant amounts of the two hydrocarbons could be crystallized from the distillate. The yields obtained in ten runs varied from 5 to 7.5% for tetraphenylmethane and from 50 to 77% for biphenyldiphenylmethane. An excess of Grignard reagent greater than 50% had no effect, nor was any difference observed when ether alone was used in the reaction.

Triphenylbromomethane gave the same yields as the chloride. When phenylmagnesium iodide was used, the yields of both hydrocarbons were considerably lower but, contrary to expectations, an appreciable quantity of triphenylmethyl peroxide was not obtained. This reaction has previously been found to yield a large amount of triphenylmethyl,[9] which suggests that the nature of the reaction may vary with slight changes in procedure.

Reaction with Ether-free Phenylmagnesium Bromide.—To prepare ether-free phenylmagnesium bromide, the ether solution of the Grignard reagent was filtered through cotton into a large test-tube and heated on the steam-bath under reduced pressure until no more ether was given off. At this point, the material was still liquid but very viscous. The test-tube was then immersed in an oil-bath and the heating continued under reduced pressure, the temperature being gradually raised. The largest amount of ether was given off at about 115° and the evolution of gas was complete at 150°. The material was kept at this temperature for three hours during which time any unchanged bromobenzene and most of the diphenyl present were removed. When cool, the product was readily broken up into a fine powder in the test-tube. The Grignard reagent was not changed appreciably by this treatment as it was still completely soluble in a mixture of ether and benzene, and in solution reacted with triphenylchloromethane to give tetraphenylmethane and biphenyldiphenylmethane in yields of 5.5 to 6% and 65 to 76%, respectively.

A sample of the ether-free Grignard reagent was placed in the thimble of a Soxhlet apparatus, the material being protected from the air, and a benzene solution of triphenylchloromethane placed in the flask. Upon heating, the Grignard reagent was slowly dissolved by the solvent. The solution in the flask developed a deep red color which gradually faded to a pale yellow. All experiments were allowed to proceed for two days, after which only a small amount of solid remained undissolved; approximately three times the theoretical amount of the Grignard reagent was used. The reaction product was treated in the usual manner. In one run, a 32% yield of tetraphenylmethane was obtained but in general the yield

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[9] Schmidlin, *Ber.*, **43**, 1141 (1910).

varied from 19 to 23%. Biphenyldiphenylmethane, if present, could not be recovered in these experiments due perhaps to difficulty in crystallization.

In another series of experiments, the powdered, ether-free Grignard reagent was suspended in the solvent, the triphenylchloromethane dissolved in the same solvent was added, and the mixture shaken at room temperature for at least two days. Approximately three times the theoretical amount of the reagent was used as before, and the same color effect was observed. Five solvents were tried and the yields of tetraphenylmethane and biphenyldiphenylmethane, respectively, were as follows: in benzene (8 runs), 21 to 29%, 13 to 35%; in toluene, 25, 9%; in bromobenzene, 24, 9%; in ethylene dichloride, 20, 8%; in dioxane (3 runs), 17 to 22%, 33 to 49%.

In several of the benzene runs, the uncrystallizable residues were distilled in a molecular still[10] at a temperature below 200° and at a pressure of 0.001 mm., no evidence of decomposition being noted. In addition to tetraphenylmethane and biphenyldiphenylmethane, the following compounds were isolated from the distillates and identified by mixed melting points with authentic samples: triphenylmethane, 2 to 14% yield; dibiphenylphenylmethane, 2.5 to 3.5% yield; 4-phenyl-tetraphenylmethane, 0.5 to 0.8% yield; tribiphenylmethane and three unidentified compounds in traces.

Trisubstituted Tetraphenylmethanes.—In each case, an ether solution of phenylmagnesium bromide in excess was added at room temperature to a benzene solution of the appropriate triarylchloromethane. The reaction mixture was decomposed in the usual manner, the product steam distilled and the residue crystallized from benzene plus petroleum ether. Only one compound was isolated in each case.

Tetraphenylmethane	Yield, %	M. p., °C.	Crystalline form
4,4′,4″-tribromo[a]	43–45	234–235	Needles
4,4′,4″-trichloro[a]	38–49	207–207.5	Needles
4,4′,4″-trimethyl[b]	31–41	177–178	Needles

	Analyses, %					
	Calcd.			Found		
Formula	C	H	Halogen	C	H	Halogen
$C_{25}H_{17}Br_3$	53.87	3.08	43.05	53.97	3.04	42.73
$C_{25}H_{17}Cl_3$	70.84	4.04	25.12	70.40	4.11	25.16
$C_{28}H_{26}$	92.76	7.24		92.40	7.17	

[a] Insoluble in ether and cold benzene, somewhat soluble in carbon tetrachloride, and slightly soluble in hot acetic acid. [b] Soluble in benzene and in hot acetic acid.

Summary

The reaction between triphenylchloromethane and phenylmagnesium bromide has been discussed. With ether-free Grignard reagent, a yield of 25 to 30% of tetraphenylmethane is obtained.

The difference in the yields of tetraphenylmethane obtained under different conditions is explained on the basis of a shifting of the equilibrium between the benzenoid and the quinonoid modification of triphenylchloromethane.

ANN ARBOR, MICHIGAN RECEIVED FEBRUARY 7, 1936

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

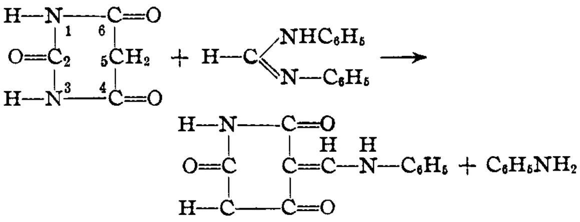
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY, UNIVERSITY OF MISSOURI]

Some Nitrogen Substituted Barbituric Acids and their Derivatives[1]

BY DOROTHY NIGHTINGALE AND CLAUDE H. ALEXANDER

In order to study some reactions of a series of aryl nitrogen substituted barbituric acids, it was necessary to prepare and identify a number of these acids not described in the literature. Whiteley[2] has prepared 1,3-diphenylbarbituric acid and 1,3-diphenyl-2-thiobarbituric acid. Macbeth, Nunan and Traill[3] have prepared 1-phenylbarbituric acid. For identification, the 5,5-bis-*p*-nitrobenzyl, 5-cinnamylidene and 5-anilinomethylene derivatives of these barbituric acids were prepared.

The reaction of barbituric acid and formamidines has been studied extensively in this Laboratory by Professor Sidney Calvert and his students, and was first described by W. N. Jones.[4] The 5-anilinomethylene barbituric acid is formed from barbituric acid and diphenylformamidine as follows



Experimental

The malonyl chloride procedure of Whiteley was used in preparing and purifying the nitrogen-

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[1] Abstract of a thesis submitted by Claude Hudson Alexander in partial fulfilment of the requirements for the degree of Master of Arts at the University of Missouri.

[2] Whiteley, *J. Chem. Soc.*, **91**, 1330 (1907); *Proc. Chem. Soc.*, **25**, 121 (1909).

[3] Macbeth, Nunan and Traill, *ibid.*, **1248** (1926).

[4] Webster N. Jones, Thesis, University of Missouri, 1909.