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

THE FORMATION OF TRIPHENYLMETHYL PEROXIDE FROM CARBON DIOXIDE AND PHENYLMAGNESIUM BROMIDE

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Several years after the discovery by Grignard[1] that carboxylic acids can be prepared from carbon dioxide and alkyl magnesium halides Meyer and Tögel[2] undertook a detailed study of the action of carbon dioxide on phenyl magnesium bromide. They obtained benzoic acid and triphenylcarbinol as principal products and, in addition, varying amounts of benzene, biphenyl, triphenylmethane and phenol. Furthermore, a small amount of a colorless, crystalline, ether-insoluble material was found. This substance melted at 186° and remained unidentified. Meyer and Tögel also stated that their reaction mixtures were colored. Schroeter[3] was able to show that benzophenone is another product formed in this synthesis and he too obtained the ether-insoluble product. From the data which were given we suspected that the unidentified compound might have been triphenylmethyl peroxide, formed by oxidation of triphenylmethyl present in the reaction mixture.

We allowed carbon dioxide to react with phenylmagnesium bromide according to the directions of the above-mentioned investigators and proved conclusively that triphenylmethyl peroxide was present among the reaction products.

A number of unsuccessful experiments were performed in the attempt to discover the reaction by which triphenylmethyl was formed. For example, $C_6H_5COOMgBr$ and $(C_6H_5)_3COMgBr$ were heated, respectively, with phenylmagnesium bromide in ether and the effects of small amounts of magnesium and iodine[4] upon the reaction mixtures were tested. Although we were unable to determine just how the free radical was formed, it seems probable that triphenylmethyl was produced in some way from triphenylcarbinol, or rather from its MgBr derivative.[5]

By the interaction of carbon dioxide and a cold ether solution of α-naphthylmagnesium bromide, α-naphthoic acid was obtained in good yield. By the use of a hot solution of the Grignard reagent, we hoped that the reaction would proceed further with the formation of the tertiary carbinol

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[1] Grignard, *Ann. chim. phys.*, (7) **24**, 255 (1901).

[2] Meyer and Tögel, *Ann.*, **347**, 55 (1906).

[3] Schroeter, *Ber.*, **36**, 3006 (1903).

[4] (a) Gomberg and Bachmann, THIS JOURNAL, **49**, 236 (1927); (b) Boyd and Hatt, *J. Chem. Soc.*, **131**, 904 (1927).

[5] Stadnikoff, *Ber.*, **57**, 5 (1924), obtained triphenylmethyl peroxide from the interaction of the MgBr derivative of triphenylcarbinol and ethyl formate. The exact mechanism of this reaction has not been established.

and possibly the free radical. A compound claimed to be tri-α-naphthylcarbinol has been described by Schmidlin and co-workers[6] and also by Tschitschibabin;[7] the former investigator allowed naphthoyl chloride to react with more than two equivalents of naphthylmagnesium bromide, the latter added naphthylmagnesium bromide to dinaphthyl ketone. However, judging from the remarkable properties ascribed to this compound, it seems to us that these investigators could not have had the pure carbinol. Schmidlin and Massini state that the compound contains a very unreactive hydroxyl group and that the usual reagents which convert tertiary carbinols into their respective chlorides are without action. Tschitschibabin maintains that at ordinary temperature the carbinol spontaneously absorbs oxygen and is oxidized by potassium permanganate to α-naphthyl-di-α,α-naphthofluoryl alcohol. When treated with iodine the carbinol iodide is said to have been formed. As Schmidlin[8] himself points out it is strange that it was found impossible to convert the carbinol iodide, or bromide, into either the original carbinol or into the free radical. Judging from the properties of diphenyl-α-naphthylcarbinol[9] and phenyl-di-α-naphthylcarbinol,[10] it might be predicted that tri-α-naphthylcarbinol would possess a very reactive hydroxyl, so reactive, in fact, that the carbinol as well as its derivatives such as $(C_{10}H_7)_3COMgBr$, a compound which would result from the Grignard synthesis, would tend to undergo very readily various types of changes, especially fluorenation. The absorption of oxygen and iodine and the decolorization of potassium permanganate at ordinary temperature are reactions which are foreign to any simple tertiary aromatic carbinols hitherto described. Finally, tri-α-naphthylcarbinol might be expected to yield an intense blue or violet solution when treated with concentrated sulfuric acid; Schmidlin and Tschitschibabin state that their compounds are colored orange-red or yellow by this reagent.

From the interaction of carbon dioxide and a hot ether solution of α-naphthylmagnesium bromide we obtained naphthoic acid and a red oil from which no crystalline products could be obtained.

We then attempted to prepare the carbinol from naphthylmagnesium bromide and di-α-naphthyl ketone. After decomposition of the reaction mixture with ice and ammonium chloride, a colorless material quickly deposited from the ether layer. This substance decolorized solutions of iodine and of potassium permanganate at ordinary temperature and dissolved in sulfuric acid with the formation of a red solution. These ob-

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[6] (a) Schmidlin and Massini, *Ber.*, **42**, 2397 (1909); (b) Schmidlin and Bergman, *ibid.*, **45**, 3203 (1912).

[7] Tschitschibabin, *J. prakt. Chem.*, **84**, 769 (1911).

[8] Schmidlin, "Das Triphenylmethyl," Ferdinand Enke, Stuttgart, **1913**, p. 163.

[9] (a) Gomberg, *Ber.*, **37**, 1637 (1904); (b) Acree, *Ber.*, **37**, 624 (1904).

[10] Schoepfle, THIS JOURNAL, **44**, 188 (1922).

servations correspond to those of Tschitschibabin but in our opinion the material is not tri-α-naphthylcarbinol, or it contains only very little of this substance.

Since further work on this compound seems impossible at present we are obliged to present our results in an unfinished state.

Experimental Part

The Formation of Triphenylmethyl Peroxide.—Phenylmagnesium bromide was prepared from 6.2 g. of magnesium turnings, 40 g. of bromobenzene, 120 cc. of ether and a crystal of iodine. A rapid stream of dry carbon dioxide was then passed through the solution. At first no noticeable change took place; later the mixture became somewhat warm and colorless crystals were deposited upon the walls of the flask. After one and one-half hours a considerable amount of gummy precipitate had formed. The mixture was then decomposed with ice and slightly more than the calculated amount of dilute hydrochloric acid. After decomposition had been effected a deep orange ether layer was obtained. A small amount of crystalline substance floated between the ether and water layers. When the clear ether solution was separated and shaken with air it became noticeably lighter in color and a colorless, crystalline material precipitated. This was washed with ether and recrystallized twice from xylene; m. p. 184°. A portion of this substance was mixed with triphenylmethyl peroxide obtained from triphenylchloromethane, silver and air; the mixture melted at 185–186°. The largest yields of peroxide were obtained when the solution of phenylmagnesium bromide was heated during the addition of carbon dioxide; the reaction mixture then turned a permanganate color during the course of the reaction. The crude peroxide, varying in weight from 1 to 2 g., contained a considerable amount of magnesium salts which could only be removed by several recrystallizations. When the solution of the Grignard reagent was cooled with ice, the mixture remained colorless during the reaction with carbon dioxide, and upon the addition of water and dilute mineral acid, benzoic acid and some triphenylcarbinol were obtained as the principal reaction products but no peroxide seems to have been formed.

α-Bromonaphthalene.—The bromonaphthalene used in our experiments was carefully purified material. At first a technical grade of this substance was purchased and subjected to several fractional distillations. However, the separation of the monobromonaphthalene from naphthalene, dibromonaphthalene and bromine and hydrogen bromide addition products which were present in the technical product required considerable time. We finally prepared the bromonaphthalene by the following method which differs in several essential respects from the methods commonly used.[11] Carbon tetrachloride was substituted for the poisonous and inflammable carbon disulfide; $^3/_4$ of a molecular equivalent of bromine was used instead of one whole equivalent; the crude bromonaphthalene was fractionated under ordinary pressure instead of under diminished pressure. The use of carbon tetrachloride as a solvent enabled us to brominate in a one-phase system, hence mechanical stirring was unnecessary. By the use of the above amount of bromine the yield of monobromonaphthalene, based on bromine, was as large as that obtained in other processes in which

[11] "Organic Syntheses," John Wiley and Sons, Inc., 1921, Vol. I, p. 36.

one whole equivalent of bromine is used; moreover, dibromonaphthalene, a product which represents a loss of both bromine and naphthalene, was formed only in negligible amount. The bromine and hydrogen bromide addition products formed during bromination are surprisingly difficult to decompose; the desired decomposition of these products is always effected by distillation under ordinary pressure but they often remain undecomposed, to some extent at least, during distillation under diminished pressure.

One thousand g. of technical naphthalene and 1500 cc. of carbon tetrachloride were put into a 5-liter flask, the stopper of which was fitted with a reflux condenser and a dropping funnel. The hydrogen bromide evolved during the reaction was led through the condenser into water. One hundred and fifty cc. of bromine was added in 25cc. portions during the course of two hours and the flask was shaken occasionally. A slow, regular evolution of hydrogen bromide began and all of the naphthalene soon dissolved. The remainder of the bromine, 150 cc., was added in 25cc. portions during the course of twenty-four hours. After all of the bromine had been added the mixture was allowed to stand for one day. Two hundred g. of technical sodium hydroxide dissolved in 400 cc. of hot water was then added and the alkaline mixture subjected to steam distillation. After the solvent had been removed, the oily residue was separated and dried with solid sodium hydroxide. The crude product was fractionated under ordinary pressure into four portions and, since hydrogen bromide and bromine were evolved, each fraction was treated with hot concentrated sodium hydroxide solution and then refractionated several times. Most of the unchanged naphthalene was removed from the lowest-boiling portion by filtration. The fourth fractionation of the portion which had boiled at 270–275° under 740 mm. yielded 730 g. of monobromonaphthalene which was collected at 271–274°. From other experiments the yields of bromonaphthalene were 755 g. and 760 g., respectively. Small fractions of low- and high-boiling material obtained from three experiments were united and refractionated. One hundred and fifty g. of pure bromonaphthalene was obtained. The yields given above, therefore, are increased by approximately 50 g., respectively, and correspond to 63, 65 and 65%, respectively, of the calculated amounts based on bromine.

α-Naphthoic Acid.—Acree[12] claims to have obtained an almost theoretical yield of α-naphthoic acid from naphthylmagnesium bromide and carbon dioxide but gives no experimental details regarding the process. According to Gilman and co-workers[13] α-naphthylmagnesium bromide is formed only to the extent of 70% under optimum conditions. We have prepared α-naphthoic acid a great many times and found that the yields of crude acid, which had been washed free from inorganic salts and thoroughly dried, varied from 65–70% of the calculated amount.

Naphthylmagnesium bromide was prepared from 18 g. of magnesium, 156 g. of α-bromonaphthalene, 400 cc. of ether and a crystal of iodine. The oily Grignard reagent[14] and the supernatant ether were poured into a 2-liter, wide-mouthed bottle the stopper of which was fitted with a stirrer, a wide carbon dioxide inlet tube which extended almost to the bottom of the bottle and a reflux condenser to which a calcium chloride tube was attached. During the reaction with carbon dioxide the bottle was immersed in ice water but the Grignard reagent should not be cooled before the addition of

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[12] Acree, *Ber.*, **37**, 627 (1904).

[13] (a) Gilman and McCracken, THIS JOURNAL, **45**, 2462 (1923); (b) Gilman and Parker, *ibid.*, **46**, 2822 (1924).

[14] This material tends to solidify readily if allowed to stand at ordinary temperature.

carbon dioxide or the naphthylmagnesium bromide will solidify to a hard cake which reacts very slowly with the gas. A brass rod, bent in a zig-zag form was found to be much more satisfactory than a stirrer made from glass. The Grignard reagent was stirred very vigorously and the gas, dried by passing it through three wash bottles filled with sulfuric acid, was led through it at a rapid rate. The reaction mixture became more and more viscous and at the end of one and one-half hours the mixture was decomposed in the usual manner. The naphthoic acid was extracted from the ether layer with dilute sodium carbonate solution.

If the ether suspension of naphthylmagnesium bromide was refluxed during the addition of carbon dioxide the yield of naphthoic acid was decreased to about 35% of the calculated amount.

Di-α-naphthyl Ketone.—For the preparation of large amounts of this ketone the method of Schmidlin and Massini[15] is unsatisfactory, but we found that their method could be modified with advantage as follows. Naphthylmagnesium bromide, which had been freed from traces of unchanged magnesium by the subsequent addition of a small amount of α-bromonaphthalene, was added slowly, with stirring, to excess (2 equivalents) of cold naphthoyl chloride[16] dissolved in ether. In this way the possible production of the tertiary carbinol was prevented to a considerable extent and the formation of the red impurity mentioned by Schmidlin and Massini was eliminated entirely. In spite of the fact that carefully purified materials had been used, the yield of pure ketone never exceeded 40% of the calculated amount. It was finally found that di-α-naphthyl ketone could be prepared easily, in large amounts, from the interaction of naphthylmagnesium bromide and naphthyl cyanide.

Naphthylmagnesium bromide (1.4 equivalents) was prepared in a liter flask from 45.5 cc. of α-bromonaphthalene, 7.5 g. of magnesium and 300 cc. of ether. Any unchanged magnesium was brought into solution by the subsequent addition of a few drops of bromonaphthalene. Thirty-three g. of naphthyl cyanide dissolved in ether was then added. Since the Grignard reagent had precipitated to a large extent in the form of a viscous oil, intimate contact of this substance with the cyanide was obtained by refluxing the mixture vigorously on a steam-bath. After a short time a granular precipitate began to form. The mixture was then heated for eight hours longer at a less vigorous rate. The ether, which contained binaphthyl, was decanted from the precipitate and the latter decomposed with ice and ammonium chloride. The ketone imine was extracted with ether, the solvent removed and the imine, in order to hydrolyze it to the ketone, was refluxed for twenty-four hours on a steam-bath with a mixture composed of 50 cc. of acetone, 100 cc. of water and 30 cc. of hydrochloric acid. After removal of the acetone by evaporation the granular product, which had been well washed with water, was dissolved in the least possible amount of hot alcohol. Upon cooling a brown oil was deposited. The alcoholic solution was decanted from this material and upon further cooling the ketone (23 g.) precipitated in crystalline form and in a quite pure state. The ketone was finally recrystallized from ether. From the brown oil, which soon solidified, a further amount (23 g.) of material was obtained which was recrystallized successively from acetic acid, alcohol and ether. The total yield of ketone was 75% of the calculated. Schmidlin and Massini[15] state that di-α-naphthyl ketone, recrystallized from ether, is a colorless substance which melts at 103°. Tschitschibabin,[7] who prepared the ketone by oxidation of the corresponding secondary carbinol, reported that the material, recrystallized from acetic acid, melted at 98°. We found that the ketone was often slightly yellow even after several recrystallizations

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[15] Ref. 6 a, p. 2388.

[16] In order to prepare pure naphthoyl chloride, naphthoic acid was refluxed with 6 equivalents of thionyl chloride for two hours.

from ether and frequently yielded a deep yellow solution; in other instances the compound was obtained in a colorless condition after only one recrystallization and melted at 99–100°. The yellow color of the ketone is undoubtedly due to some impurity which is removed with difficulty.

α-Naphthoic Anhydride.—To a mixture of 4 g. of thoroughly dried, anhydrous sodium carbonate and 8 g. of naphthoyl chloride, there was added 2.5 cc. of pure pyridine. Apparently no reaction took place even when the mixture was warmed. However, upon the addition of a few drops of water to the cold mixture a vigorous reaction began. The mass was stirred thoroughly and then allowed to cool. After the addition of water the insoluble residue was dried and recrystallized from benzene. The compound melted at 145–146°. This anhydride had previously been prepared from calcium naphthoate and naphthoyl chloride.[17] The yield of pure product was 5.3 g. or 80% of the calculated.

α-Naphthyl Cyanide.—α-Naphthoyl chloride was added to cold, concentrated ammonia water which was stirred vigorously and the acid amide formed was dried and then warmed gently for a short time with one equivalent of phosphorus pentachloride. The phosphorus oxychloride was removed by distillation; the residue was poured on ice, pulverized and thoroughly washed with water to remove phosphorus compounds. The crude cyanide was purified by distillation under ordinary pressure. The yield was practically quantitative.[18]

Di-α-naphthylcarbinol.—In the preparation of this carbinol according to the directions given in the literature,[19] difficulty was encountered because of the formation of oily by-products; the use of excess ethyl formate seemed to be responsible for the formation of the oily material. Since naphthylmagnesium bromide can be obtained only in 70% yield,[13] 0.7 of an equivalent of the ester (instead of 1 equivalent) should be used for 2 equivalents of the Grignard reagent. The Grignard reagent was prepared from 69 g. of bromonaphthalene, 7.2 g. of magnesium, 200 cc. of ether and a crystal of iodine. Seven and eight-tenths g. of freshly-distilled ethyl formate was added, a few drops at a time, during the course of half an hour and the mixture was thoroughly shaken and cooled after each addition of the ester. The carbinol, in the form of its magnesium bromide addition product, precipitated almost completely. After twenty-four hours the ether was decanted and the precipitate decomposed with ice and the calculated amount of dilute hydrochloric acid. The crystalline product was washed with a small amount of dilute hydrochloric acid, dried and then triturated with a small quantity of ether several times. The yield of pure product was 22 g.; m. p. 144°.

The carbinol can be converted easily into di-α-naphthylmethane as follows. Three g. of the carbinol was dissolved in 60 cc. of hot acetic acid and 25 g. of hydriodic acid (sp. gr. 1.96) was added to the hot solution, a small amount at a time. The mixture was then boiled for a few minutes. After twelve hours the methane, which had separated in the form of colorless needles, was filtered. The compound melted at 107–108° after recrystallization from alcohol.

Summary

It has been shown that under certain conditions triphenylmethyl is formed in the interaction of carbon dioxide and phenylmagnesium bromide.

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[17] Hofmann, *Ber.*, 1, 42 (1868).

[18] By a modification of the Sandmeyer synthesis of nitriles, Clarke and Read, This Journal, **46**, 1003 (1924), obtained a 55% yield of α-naphthonitrile from α-naphthylamine. West, *ibid.*, **42**, 1661 (1920), prepared the nitrile from sodium α-naphthalene sulfonate and potassium cyanide.

[19] Ref. 6 a, p. 2381; Tschitschibabin and Magidson, *J. prakt. Chem.*, **90**, 170 (1914).

Methods are given for the preparation of α-bromonaphthalene, α-naphthoic acid, di-α-naphthylketone and di-α-naphthylcarbinol.

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THE POLARITY OF THE CARBON-HALOGEN BOND

I. DEVELOPMENT OF A QUANTITATIVE METHOD FOR THE DETERMINATION OF RELATIVE RATES FOR THE ACID HYDROLYSIS OF POSITIVE HALOGENS

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Recently Nicolet and collaborators[1] have studied the different degrees of polarity that are shown by halogens attached to carbon in the aromatic series. The present investigation was undertaken with a two-fold purpose: to develop a more quantitative method for the determination of the rate of removal of positive halogens and to determine to what extent halogens in halogen naphthols show different degrees of polarity. The reaction which Nicolet has found useful as a preliminary test for positive halogens, that of the action of stannous chloride in acid solution on the organic halide, is one which has been applied in a qualitative way to the removal of halogen atoms from halogen amines and phenols[2] and to a less extent to the removal of bromine from bromo-β-naphthols and bromo-β-naphthylamines.[3] The method described below differs from those referred to in that the hydrolysis was carried out in an oxygen-free atmosphere, and that the amount of halogen removed was determined by titration of the excess stannous chloride solution with standard iodine solution.[4] It is thus considerably more convenient and rapid.

Method of Hydrolysis

The standard solution of stannous chloride was prepared by dissolving 60 g. of $SnCl_2\cdot 2H_2O$ in 1000 g. of hydrochloric acid (37%) and the solution was diluted to 3700 cc. with 95% alcohol (the alcohol was added to make the organic halides soluble). This solution was stored in an atmosphere of hydrogen to prevent oxidation; after twenty-four hours the oxygen in the gases above the solution had disappeared and the stannous chloride maintained its strength unaltered during the time required to make the hydrolyses. The apparatus used for the storage of the solution and for the titration was

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[1] (a) Nicolet, This Journal, **43**, 2081 (1921); (b) Nicolet and Sampey, *ibid.*, **49**, 1796 (1927); (c) Nicolet and Ray, *ibid.*, **49**, 1801 (1927); (d) Nicolet and Sandin, *ibid.*, **49**, 1806 (1927); (e) Nicolet, *ibid.*, **49**, 1810 (1927).

[2] Burton and Kenner, *J. Chem. Soc.*, 121, 675 (1922).

[3] (a) Franzen, *J. prakt. Chem.*, 101, 58 (1920); (b) **103**, 352 (1922); (c) Fries, *Ann.*, **334**, 342 (1904).

[4] Treadwell and Hall, "Analytical Chemistry," John Wiley and Sons, Inc., New York City, **1919**, p. 698.