

The oxidized celluloses obtained have been extracted with 18.5% sodium hydroxide and the optical rotations determined.

The alkaline extract has been separated into fractions soluble and in soluble in dilute acetic acid.

The optical rotations of insoluble portions were determined in 17.5% sodium hydroxide.

The optical rotations of the soluble portions were determined in dilute acetic acid and in alkaline solutions.

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CONDENSATIONS BY SODIUM INSTEAD OF BY THE GRIGNARD REACTION. III. TERTIARY CARBINOLS AND ACIDS

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In previous papers¹ we have emphasized the fact that sodium will bring about the same condensations as are normally brought about by the Grignard reaction with the advantages that with sodium one may use aryl chlorides and solvents other than ether. In addition, the reaction can be carried out in one step rather than through the intermediate formation of the Grignard reagent. These advantages are of considerable laboratory and practical value since the metal, the halide and the solvent are far cheaper than for the corresponding materials with the Grignard reaction. The importance of this has led us to further studies and in this paper we shall report some preparations which show the possibilities of this synthesis.

Tribiphenylcarbinol was prepared by Schlenk and Weickel² by a round-about method involving the initial preparation of iodobiphenyl and paraphenylbenzoic acid. The preparation of these intermediates is in itself a laborious process. We have succeeded in preparing tribiphenylcarbinol from chlorobiphenyl, diethyl carbonate and sodium in benzene solution in one step with a yield of 46% crude material, from which we obtained pure material amounting to 23% of the theoretical. This simplification in preparation and cost makes available this interesting and somewhat rare compound.

In further studies on chlorobenzene which is unreactive to a large number of reagents, we have been able to bring about its reaction with diethyl carbonate, forming triphenylcarbinol in benzene solution with a yield of 66% of crude material. With benzoyl chloride and benzophenone the yields were 79 and 98%, respectively.

¹ Morton and Stevens, *THIS JOURNAL*, **53**, 2244, 2769 (1931).

² Schlenk and Weickel, *Ann.*, **368**, 295 (1909).

Chlorodimethylaniline reacted with diethyl carbonate in benzene solution in the presence of sodium, forming crystal violet. Since chlorodimethylaniline is rather difficult to prepare, we made a large number of experiments with bromodimethylaniline. The reaction proceeded very smoothly and a yield of 53% was obtained. When the reaction was carried out with ethyl benzoate instead of diethyl carbonate, malachite green was isolated in 69% yields. This is a new and interesting synthesis of these dyes and offers possibilities in the synthesis of other dyes which are not now obtainable.

The use of sodium in the preparation of acids from chlorides and carbon dioxide in the presence of benzene is also possible. Para- and meta-toluic acid, benzoic acid, *p*-phenylbenzoic acid and *p*-dimethylaminobenzoic acid (the last from the bromide) were prepared under 30 lb. pressure of carbon dioxide. The yields varied from 76% in the case of *p*-toluic acid to 12% for phenylbenzoic acid.

In the course of this work we have observed several points of interest in the use of sodium. Chief among these is the formation of a surface film over the metal which inhibits the reaction. This film can be broken in a number of ways. A trace of diphenyl mercury often serves. Small quantities of substances such as *n*-butyl chloride or *p*-chlorotoluene, which react very vigorously, may be used. In very many cases the reaction is started by increasing the concentration of the halide in the mixture. It is obvious that the reaction is more apt to start the greater the surface exposed and we have found that sodium ribbon 0.2 mm. in thickness will react under conditions which give no reaction with sodium wire 1.6 mm. in diameter. Heat may be applied, even to the melting point of the sodium, but the difficulty in this case is that the reaction is exothermic and once started at a higher temperature sometimes becomes uncontrollable. Even in cases where the reaction is quickly brought under control, the yield is usually smaller. In general it is desirable to initiate the reaction at a low temperature.

A wide variety of solvents is possible. We have used anhydrous ether, petroleum ether, gasoline, benzene, toluene, xylene, diethylaniline and chlorobenzene, the last being a reactant.

Considerable caution must be exercised in carrying out these reactions, particularly when ideal conditions, such as concentrated solutions, starters, thin strips of sodium, etc., are employed. When a reaction once gets beyond control it proceeds with explosive violence. Consequently all experiments were run under conditions permitting of easy disposal of the reaction mixture or with such precautions that no damage was done to other apparatus nearby.

Experiments

Preparation of Tribiphenylcarbinol.—Chlorobiphenyl, 0.1 mole, diethyl carbonate, 0.42 mole and 0.22 gram atom of sodium wire, 1.6 mm. in diameter, were put into a

flask with 100 cc. of benzene. The mixture was gently heated to start the reaction and the burner then withdrawn to allow the initial heat to dissipate. Heating was then continued on an oil-bath until the total time was ten hours. After cooling, alcohol was added to decompose any unchanged sodium. The mixture was then treated with water and the benzene solution diluted with ligroin. The crude triphenylcarbinol precipitated in 46% yield. It was purified by dissolving in hot acetic acid in the presence of decolorizing carbon, filtering and allowing to crystallize, m. p. 207°. The value recorded by Schlenk and Weickel³ is 207–208°. The yield of the pure product was 23%. When the quantity and concentration of the chlorobiphenyl were increased to 0.27 mole in 50 cc. of benzene, the reaction with diethyl carbonate, 0.42 mole, and sodium wire, 0.22 gram atom, started at room temperatures. The yield was the same as given in the foregoing experiment. A reaction was carried out in diethylaniline as a solvent (100 cc.), using the same quantities as in the first experiment above recorded. The mixture was allowed to stand until the sodium had disappeared. Upon decomposing and purifying in the usual manner, an 18% yield was obtained.

Preparation of Triphenylcarbinol.—Chlorobenzene, 0.15 mole, reacted very easily with 0.042 mole of diethyl carbonate and 0.22 gram atom of sodium in 80 cc. of benzene. The mixture was allowed to stand for three days, after which a little alcohol was added to decompose the unchanged sodium. The mixture was then steam distilled. Crude triphenylcarbinol remained as an insoluble residue in the distilling flask. It was washed and dried, giving a yield of 66% of crude carbinol. Upon digestion with a little alcohol 52% of material melting at 158–160° was obtained. In a similar manner chlorobenzene, benzoyl chloride, and sodium (0.2 mole, 0.1 mole and 0.43 gram atom, respectively) reacted together in 200 cc. of benzene giving 79% of crude triphenylcarbinol. Chlorobenzene, benzophenone and sodium (0.05 mole, 0.05 mole and 0.12 gram atom) reacted together in 100 cc. of benzene giving 98% of crude product. When chlorobenzene, ethyl benzoate and sodium (0.10 mole, 0.50 mole and 0.22 gram atom) reacted in 100 cc. of diethylaniline as a solvent, 62% of crude triphenylcarbinol was obtained. Experiments conducted on the effect of increasing the quantity and concentration of the chlorobenzene in its reaction with diethyl carbonate showed that the chief result was to accelerate the rate at which the reaction occurred, with a slight decrease in the yield.

Preparation of Crystal Violet.—Chlorodimethylaniline, 0.05 mole, was put into a bottle with 0.034 mole of diethyl carbonate, 0.13 gram atom of sodium, and 100 cc. of benzene. The mixture was allowed to stand for four days, after which any unchanged sodium was decomposed with alcohol and water in the usual manner. The crystal violet was then isolated and purified in the manner described by Gattermann;³ yield, 22%.

With bromodimethylaniline, 0.05 mole, the mixture of diethyl carbonate, 0.025 mole, sodium, 0.13 gram atom and benzene, 100 cc., was heated for six hours. After decomposing and purifying in the usual manner, a 53% yield of the dye was obtained. With exactly twice the quantity of reagents but in 50 cc. of benzene the mixture was shaken in a machine for twenty-four hours. At the end of that time the mass was a thick sludge from which a yield of 49% of the dye resulted. A run exactly similar to the run in the shaker but using chloroethylformate instead of diethyl carbonate and 100 cc. of benzene gave a yield of 40%. Still another run using diethyl oxalate, 0.041 mole, with 0.05 mole of the bromodimethylaniline and 0.26 gram atom of sodium in 50 cc. of benzene gave a 32% yield. When 100 cc. of ether was used as a solvent with 0.05 mole of bromodimethylaniline, 0.034 mole of diethyl carbonate and 0.13 gram atom of sodium, the mixture was allowed to stand for three days. The yield of crystal violet was 64%.

Preparation of Malachite Green.—Bromodimethylaniline, 0.05 mole, ethyl benzo-

³ Gattermann, "Practical Methods of Organic Chemistry," The Macmillan Company, New York, 1921, p. 364.

ate, 0.027 mole, and sodium, 0.13 gram atom, were heated with 100 cc. of benzene. After the initial vigor of the reaction had subsided, the heating was continued for a total time of ten hours. The mixture was then decomposed with alcohol and water in the usual manner and malachite green obtained as the oxalate in the manner described by Lambrecht and Weil;⁴ yield, 69%.

Preparation of Dibiphenylphenylcarbinol.—Chlorobiphenyl, ethyl benzoate and sodium (0.10 mole, 0.05 mole and 0.22 gram atom, respectively), were put into a flask and set in an ice-bath. The whole was allowed to warm gradually as the reaction proceeded. When the sodium had disappeared the mixture was decomposed with alcohol, water and acid. The carbinol was isolated by adding ligroin to the solution, after which it was crystallized from hot acetic acid. A 7.3% yield of dibiphenylphenylcarbinol was obtained, m. p. 149–150°. The value obtained by Schlenk and Weickel⁵ was 151°. An exactly similar run in 100 cc. of benzene gave only 1% yield.

Preparation of Biphenylnaphthylphenylcarbinol.—Alpha-chloronaphthalene, 0.1 mole, was put into a flask with 0.1 mole of phenyl diphenyl ketone, 0.22 gram atom of sodium, and 200 cc. of anhydrous ether. The flask was set aside in the usual manner to allow the sodium to react. Upon decomposition and evaporation of the solvent a tarry mass was obtained. The viscous product was dissolved in ether, the solution filtered, and saturated with dry hydrogen chloride. Upon evaporation of the solvent in a desiccator, a semi-crystalline residue was formed. After digesting with a little benzene and drying on a porous tile, crude solids were secured which gave a fairly good product when treated with hot acetyl chloride and then hot benzene. It was finally recrystallized from benzene, m. p. 190–192°. The value recorded by Schlenk⁵ is 194.5°; yield, 7.4%. A similar run with α -bromonaphthalene gave a 4.5% yield of chlorobiphenylnaphthylphenylmethane.

Tribenzylcarbinol from Benzyl Chloride.—Benzyl chloride reacted with diethyl carbonate in the presence of sodium (0.1 mole, 0.042 mole and 0.261 gram atom, respectively) in 50 cc. of benzene, the mixture being allowed to stand for one day. After decomposing and acidifying the reaction mixture, the tribenzylcarbinol crystallized from the benzene solution, m. p. 115°; yield, 0.25 g. or 2.5%. Klages and Heilmann⁶ record 115°.

The Preparation of Acids from Carbon Dioxide and Halides.—Attempts to prepare acids by bubbling carbon dioxide through a mixture of a halide and sodium in benzene did not result in good yields. The reaction was very difficult to start because of the coating over the sodium. The formation of this film could be avoided by allowing the sodium to begin reacting upon the halide alone and then passing carbon dioxide rapidly through the mixture, but the solubility of the carbon dioxide was so low that the sodium reacted chiefly with the halide to form the product of a Wurtz-Fittig synthesis. Benzoic, *p*-phenylbenzoic and valeric acids were prepared in this manner from the corresponding chlorides and sodium in benzene solution in yields varying from 6 to 1% based on the quantity of sodium.

To increase the solubility of the carbon dioxide in the solvent, the reaction was next tried under pressure, using for this purpose a Burgess-Parr hydrogenation apparatus, capable of being used safely with pressures up to 50 lb. The ordinary glass bottle and wire protector were replaced by a similar bottle wound with asbestos, nichrome wire and asbestos impregnated with sodium silicate so that the whole would be of a size to fit into the shaker. With this apparatus the heating could be regulated by an external resistance so that the temperature was raised slowly to the point where black spots ap-

⁴ Lambrecht and Weil, *Ber.*, 37, 3059 (1904).

⁵ Schlenk, *Ann.*, 394, 196 (1912).

⁶ Klages and Heilmann, *Ber.*, 37, 1456 (1904).

peared on the sodium, indicating that a reaction was taking place. The heating was then stopped but on account of the exothermic nature of the reaction the mixture usually became hotter, sometimes enough to melt the sodium. In extreme cases the benzene was observed to reflux even under pressure of about 30 lb. of carbon dioxide. This back pressure of benzene undoubtedly cut down the yield, since it would prevent intimate contact of carbon dioxide with the reacting mass. In one experiment with chlorobenzene the reaction became uncontrollable and exploded. Fortunately, because of the wrapping on the bottle, the force of the explosion was mostly upward so that no damage occurred. The table summarizes the experiments. The yields are based on the quantity of sodium used. The pressure of carbon dioxide was 30 lb. in all cases.

TABLE I
SUMMARY OF DATA (BENZENE AS SOLVENT)

Halide	Moles	Sodium, gram atom	Solvent, cc.	Acid product	Yield, %
<i>p</i> -Chlorotoluene	0.24	0.13	25	Toluic ^a	76
<i>p</i> -Chlorodiphenyl	.27	.13	50	<i>p</i> -Phenylbenzoic ^b	12
<i>p</i> -Bromodimethylaniline	.05	.10	25	<i>p</i> -Dimethylaminobenzoic ^c	28
<i>m</i> -Chlorotoluene	.24	.13	25	<i>m</i> -Toluic	58
Chlorobenzene	.51	.22	50	Benzoic ^a	45

^a The reaction required no external heat but became warm of its own accord.

^b M. p., 222°; the melting point obtained by Schlenk and Weickel² was 222°. ^c M. p., 233°; Michler, *Ber.*, 9, 400 (1876), obtained 235°.

It should be noted in the table that the meta- and para-chlorotoluenes reacted with carbon dioxide very smoothly and with good yields. With diethyl carbonate the chlorotoluenes gave tarry products. The difference is probably due to the fact that the sodium salt resulting from the reaction with carbon dioxide was insoluble in the organic solvent and was therefore removed from the possibility of reacting further. This fact would indicate that the reaction with carbon dioxide was an especially favored one since fewer by-products would be obtained. It also suggests that in cases where tarry products resulted in other reactions, a change of solvent so as to obtain less solubility of the product would be beneficial. Further studies on such factors are in progress.

Conclusions

Sodium will cause condensations similar to those obtained regularly by the Grignard reaction.

Sodium is better than magnesium in many reactions since aryl chlorides and solvents other than ether may be used.

The preparation of tribiphenylcarbinol, triphenylcarbinol, crystal violet, malachite green and other tertiary compounds is described.

The synthesis of a number of acids from the halide, carbon dioxide and sodium in benzene is described.

The formation of a surface film on the metal and methods of removing it are discussed.

Warning is given of the possibility of reactions taking place with explosive violence.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PURDUE UNIVERSITY]

ORGANIC COMPOUNDS OF SELENIUM. II. THE ACTION OF SELENIUM OXYCHLORIDE UPON ETHERS¹

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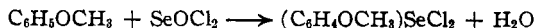
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Selenium oxychloride is a very reactive compound and, therefore, lends itself readily to the synthesis of organic compounds. The action on ketones was reported² in the first paper of this series. In this investigation selenium oxychloride was allowed to act on the following ethers: anisole, phenetole, propyl phenyl ether, butyl phenyl ether, diphenyl ether, *o*-methyl cresyl ether, *o*-bromoanisole, *p*-bromoanisole, *o*-nitroanisole and *p*-nitroanisole.

Kunckell has reported the action of selenium oxychloride upon anisole and phenetole.³ Kunckell stated that two products were formed in the action of selenium oxychloride on anisole in ethereal solution. He reports bis-(*p*-methoxyphenyl)-selenium dichloride and bis-(*p*-methoxyphenyl) selenide. Kunckell used water in the purification of his products, which leads to the hydrolysis of the chlorine attached to the selenium. The second product could have been formed by the reduction of the first product during the purification. In our experiments we did not find the selenides among the primary products of the selenium dichlorides.

The first seven ethers, upon reacting with selenium oxychloride in anhydrous ether at room temperature, form the selenium dichlorides according to the following equation in which anisole is used as a typical example



The last three ethers listed did not react under these conditions and could be quantitatively recovered unchanged after hydrolysis of the selenium oxychloride. By raising the temperature, and without a solvent, the *p*-bromoanisole formed a 2-chloro-4-bromoanisole, just as has been reported for the action of thionyl chloride on the same compound.

The selenium dichlorides are light yellow solids and react readily with cold water. These compounds are soluble in chloroform, hot glacial acetic

¹ Based upon a thesis submitted by F. N. Alquist to the Faculty of the Graduate School of Purdue University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy.

² Nelson and Jones, *THIS JOURNAL*, **52**, 1588 (1930).

³ Kunckell, *Ber.*, **28**, 609 (1895).