130° at 43 mm. (71–72° at 2.5 mm.), was secured; yield 25%.

*Anal.* Calcd. for $C_{11}H_{14}$: C, 90.29; H, 9.64. Found: C, 90.13; H, 9.63.

**Attempted Oxidation of the Carbinol.**—To 8 g. of the carbinol in 20 cc. of glacial acetic acid was added slowly a solution of 2 g. of chromium trioxide in 3 cc. of water with 0.5 cc. of sulfuric acid. Heat was evolved and a green color was produced, but the temperature did not exceed 50°. The solution was shaken well for one-half hour, and was then poured into 200 cc. of water. The resulting mixture was extracted with four 50-cc. portions of benzene. The extract was washed with water and dilute sodium hydroxide. It was dried over calcium chloride and distilled. The product boiled at 225–230° at 1.5 mm. The yield was 6 g. (75%). In another experiment, similar treatment of 2 g. of carbinol gave 1.8 g. (90%) of the product. Larger quantities gave lower yields.

*Anal.* Calcd. for the ketone, $C_{22}H_{20}O$: C, 87.94; H, 6.72. Calcd. for the ether, $C_{44}H_{42}O$: C, 90.10; H, 7.22. Found: C, 90.19,[10] 90.51,[11] 90.47;[11] H, 7.26,[10] 7.55,[11] 7.6.[11]

**Pyrolysis of the Ether.**—From 1.8 g. of the above product, pyrolyzed at 410–415° for half an hour, was obtained 1.3 g. of crude hydrocarbon and when purified from benzene, 0.56 g. (33%) of ethylcholanthrene, melting at 179–180° (corr.).

## Summary

20-Ethylcholanthrene has been synthesized by a general method previously developed by Fieser and Seligman. Some modifications of this procedure directed toward improving the yields and simplifying the operations for the preparation of this substance have been studied.

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(10) Microanalysis by W. F. B.

(11) Microanalyses by Mrs. Verna R. Keevil, at Harvard University, by courtesy of Professor L. F. Fieser.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 167]

# Pyrolysis of Organomagnesium Compounds. I. A New Agent for the Reduction of Benzophenone

BY DANIEL B. CLAPP AND ROBERT B. WOODWARD

By the pyrolysis of ethylmagnesium bromide at 220°, *in vacuo*, a gas, which proved to be ethylene, was evolved, leaving a residual gray powder. The powder reacted vigorously with water, and with various alcohols, and sometimes caught fire in moist air. It possesses a peculiar, garlic-like odor, very similar to that observed with calcium hydride. The powder is practically insoluble in organic solvents with which it does not react.

By treatment of the pyrolysis product in suspension in an ether–benzene mixture with benzophenone, it has been possible to obtain a 66% yield of benzhydrol. No other products except unchanged benzophenone were isolated. This reduction of benzophenone cannot be due to any ethylmagnesium bromide which may be present in the pyrolysis product, since the gas evolved on hydrolysis of the product contains no ethane. Also, Noller and Hilmer[1] report that ethylmagnesium bromide reduces benzophenone only to the extent of 2%.

The composition of the pyrolysis product and the mode of its reducing action are being investigated. The product may well be similar to that obtained by Jolibois,[2] by the pyrolysis of ethylmagnesium iodide at 175° *in vacuo*. Jolibois claims that the following reaction takes place

$$2C_2H_5MgI \longrightarrow 2C_2H_4 + (2HMgI) \longrightarrow H_2Mg + MgI_2$$

The pyrolysis of methylmagnesium iodide was carried out like that of ethylmagnesium bromide. A product was obtained which was only slightly soluble in ether, indicating a reaction had taken place, but on treatment of this product with benzophenone, no benzhydrol could be isolated, and most of the benzophenone was recovered unchanged.

The pyrolysis of other organomagnesium compounds is being studied, and the reducing action of this new reagent with various classes of organic compounds is being investigated.

## Experimental

**Pyrolysis of Ethylmagnesium Bromide.**—Ethylmagnesium bromide was prepared in the usual way from magnesium (8 g.) and ethyl bromide (36 g.). The Grignard solution was filtered under nitrogen through a sintered glass filter to remove any undissolved magnesium. The ether was removed according to the direction of Schoepfle and Trepp[3] for the preparation of ether-free phenylmag-

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(1) Noller and Hilmer, THIS JOURNAL, **54**, 2503 (1932).

(2) Jolibois, *Compt. rend.*, **155**, 353 (1912).

(3) Schoepfle and Trepp, THIS JOURNAL, **58**, 793 (1936).

nesium bromide. The pyrolysis was carried out in a large test-tube, connected with a manometer and an oil-pump. The system was evacuated to 0.5 mm. and the tube heated with an oil-bath. The pyrolysis was carried out at 220° for four hours. At the end of this period, the pressure no longer tended to rise, indicating that the evolution of gas was complete. A gray, vesicular powder remained in the tube.

In another experiment the evolution of ethylene was detected by bleeding bromine vapor into the system next to the pyrolysis tube, and condensing out the ethylene dibromide formed. After distillation, a 30% yield of ethylene dibromide was obtained, b. p. 130.5–131° at 758 mm.; density$^{25}{}_4$ 2.182.

*Anal.* Calcd. for $C_2H_4Br_2$: Br, 85.08. Found: Br, 85.1.

The gas evolved on hydrolysis of the pyrolysis product was found to be completely absorbed by a palladium chloride solution, indicating that it could not contain ethane or saturated hydrocarbons.

**Reaction of Pyrolysis Product with Benzophenone.**—The gray powder (15 g.) was suspended in an ether–benzene mixture, and benzophenone (10 g.) added. A precipitate gradually formed on the walls of the vessel. The mixture was refluxed with stirring for ten hours, and allowed to stand overnight. The mixture was hydrolyzed with ice and hydrochloric acid, and on concentration of the organic layer, benzhydrol (5 g.), m. p. 57–61.5°, was isolated. This gave on recrystallization from ligroin (b. p. 70–90°) 4.7 g., m. p. 64.5–65.5°. The substance was identified by mixed melting point with an authentic sample of benzhydrol, and by the preparation of dibenzhydryl succinate,[4] m. p. 135–137.5°. On working up the mother liquors and repeated crystallization an additional 2 g. of benzhydrol was obtained. About 1 g. of unchanged benzophenone was also obtained.

**Pyrolysis of Methylmagnesium Iodide and Treatment of Product with Benzophenone.**—The pyrolysis was carried out in exactly the same way as with ethylmagnesium bromide. The residual product reacted with water, a gas being evolved. The product was treated with benzophenone as above, and, after hydrolysis, 82% of the benzophenone was recovered. No benzhydrol could be isolated.

## Summary

1. Ethylmagnesium bromide has been pyrolyzed at 220° *in vacuo*, ethylene being evolved.

2. The pyrolysis product reduces benzophenone to benzhydrol in a yield of 66%.

3. The pyrolysis product of methylmagnesium iodide does not reduce benzophenone.

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[4] Linnemann, *Ann.*, **133**, 23 (1865).

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[CONTRIBUTION FROM MELLON INSTITUTE OF INDUSTRIAL RESEARCH, AND E. R. SQUIBB & SONS]

# Halogeno-alkyl Glycosides. I. Monohalogeno-alkyl Derivatives

BY HAROLD W. COLES,[1] MARY L. DODDS[1] AND FRANK H. BERGEIM[2]

Halogeno-alkyl glycosides were required for another project. A search of the literature revealed that, while sugars had been condensed with numerous glycols, similar condensations had not been attempted with the halogenohydrins. Ethylene chlorohydrin had indeed served as a solvent in reactions of glucose with aldehydes.[3] Carbohydrates such as starch and cellulose have been depolymerized by treatment with chlorohydrin.[4] Reduced sugars such as mannitol and sorbitol can be condensed with chlorohydrin but the condensation does not involve carbon 1 of the sugar chain.[5]

The initial attempts to prepare the glucosides by the condensation of glucose with ethylene bromohydrin in the presence of gaseous hydrochloric acid failed to give a crystalline product. A hygroscopic sirup was obtained. Successful results were, however, obtained with the method of Fischer[6] whereby acetohalogeno sugars are condensed with glycols in the presence of silver carbonate. It was found that the halogenohydrins condensed readily at room temperature with acylhalogeno sugars in the presence of silver carbonate, provided the reactants were purified carefully. Under these conditions, the silver carbonate did not react with the halogen of the halogenohydrins.

The acylhalogeno sugars were purified by recrystallization until all free acid was removed, and they were used at once. The halogenohydrins were allowed to stand over calcium oxide until neutral to litmus, filtered, and distilled in a vacuum, the middle fraction being selected. They were likewise used immediately. It was not found necessary to reprecipitate the silver carbonate.

The preparation of tetraacetyl-$\beta$-*d*-($\beta$-chloro-

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[1] Industrial Fellows, E. R. Squibb & Sons Industrial Fellowship, Mellon Institute.

[2] Research Laboratories, E. R. Squibb & Sons, Brooklyn, N. Y.

[3] Hill and Hibbert, THIS JOURNAL, **45**, 3108 (1923).

[4] Lange, U. S. Patent 1,714,565 (May 28, 1929).

[5] Schmidt and Meyer, U. S. Patent 1,922,459 (Aug. 15, 1933).

[6] Fischer and Fischer, *Ber.*, **43**, 2521 (1910).