The properties of the precursor II are being further investigated.

THE RESEARCH LABORATORIES
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Unsaturated Fatty Acid Benzylidene Glycerols[1]

BY B. F. DAUBERT

In our studies on the properties of synthetic glycerides, particularly those containing unsaturated fatty acids, it became necessary to prepare the oleyl and elaidyl esters of 1,3-benzylidene glycerol. Since the compounds are new and are not directly related to our present investigations, it was considered desirable to report their analytical constants at this time.

Experimental

1,3-Benzylidene Glycerol.—This acetal was prepared according to the method of Hibbert and Carter,[2] but with the changes suggested by Stimmel and King.[3] The acetal was also prepared from U. S. P. benzaldehyde and U. S. P. glycerol directly, to determine whether it was necessary to dry the reagents in advance. It was found that the condensation reaction required only an additional five minutes beyond the time necessary with dry reagents, and the yields were of the same magnitude as those obtained by Stimmel and King (m. p. 84.0°).

Acid Chlorides.—Oleyl and elaidyl chlorides were prepared from the corresponding highly purified fatty acids and oxalyl chloride by the method described previously.[4]

2-Elaidyl-1,3-benzylidene Glycerol.—Esterification of the 1,3-benzylidene glycerol with acid chloride was carried out essentially by the method of Bergmann and Carter.[5] The method is given in detail for 2-elaidyl-1,3-benzylidene glycerol.

1,3-Benzylidene glycerol (5 g.) was dissolved in 20 ml. of dry pyridine and the solution cooled to 5° in an ice-bath. Elaidyl chloride (8.4 g.) was added dropwise to the pyridine solution of the acetal, the temperature being maintained at 5° until the complete addition of the acid chloride. The mixture was allowed to stand at room temperature for twenty-four hours. After the addition of 200 ml. of ice water, the esterified acetal separated first as an oily liquid which later solidified on repeated washing with ice water. The solidified product was suction filtered and washed with ice water until the odor of pyridine was no longer perceptible. The product, after drying in a vacuum desiccator for several days, was dissolved in petroleum ether (b. p. 35–60°) and the resulting solution cooled to 5° for twenty-four hours. The crystalline mass was suction filtered and then recrystallized several times from a 1:1 mixture of petroleum ether and ethyl alcohol and finally from ethyl alcohol. The colorless, prismatic crystals melted at 43.5–44.0°; yield, 10 g. (82%); iodine value (Wijs), 56.6 (calcd. 57.1); mol. wt., 441 (calcd. 444).

Anal. Calcd. for $C_{28}H_{44}O_4$: C, 75.63; H, 9.97. Found: C, 75.58, 75.61; H, 9.88, 9.92.

Constants for the 2-oleyl-1,3-benzylidene glycerol prepared in an analogous manner are as follows: m. p., 4.0–5.0°; iodine value (Wijs), 56.7 (calcd. 57.1); mol. wt., 440 (calcd. 444).

Anal. Calcd. for $C_{28}H_{44}O_4$: C, 75.63; H, 9.97. Found: C, 75.55, 75.51; H, 9.85, 9.87.

Hydrogenation of the Esterified Acetals.—Reduction with hydrogen of both 2-elaidyl- and 2-oleyl-1,3-benzylidene glycerol in ethyl alcohol solution with palladium black as the catalyst[5] resulted in the isolation of 2-monostearin (m. p. 74.5°). Mixed melting points of the 2-monoesters obtained by the separate reduction of the two esterified acetals showed no melting point depression.

Although other conditions of hydrogenation with many different catalysts have been used, the fully saturated 2-monoester was always obtained. It is planned to study further the conditions of hydrogenation and hydrogenolysis which will lead to the removal of the benzylidene group without at the same time affecting the double bond of the unsaturated fatty acid.

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[1] The generous aid of the Buhl Foundation is gratefully acknowledged.

[2] Hibbert and Carter, THIS JOURNAL, **51**, 1601 (1929).

[3] Stimmel and King, *ibid.*, **56**, 1724 (1934).

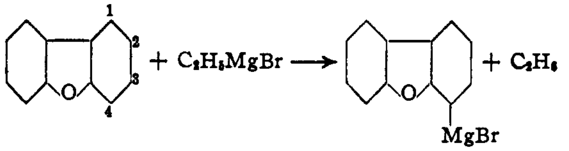
[4] Wood, Jackson, Baldwin and Longenecker, *ibid.*, **66**, 287–289 (1944).

[5] Bergmann and Carter, *Z. physiol. Chem.*, **191**, 211 (1930).

Interconversion Reactions with Some Aluminum Compounds[1]

BY HENRY GILMAN AND A. H. HAUBEIN

Dibenzofuran has been metalated in the 4-position irrespective of the metalating agent: organometallic compounds, inorganic salts or metals. The rate and extent of metalation is markedly influenced by the reactivity of the organometallic compound: that is, the more highly active organoalkali compounds effect metalation most rapidly and can give di-metalation.[2] Organoaluminum compounds are relatively low in reactivity, and we have observed that triethylaluminum does not metalate dibenzofuran. However, the moderately reactive Grignard reagent does effect metalation in the 4-position.



The metalation of an aromatic ether under forced conditions by means of Grignard reagents was to have been expected in view of earlier studies by Challenger and Miller[3] with anisole and phenetole.

Inasmuch as "mixed" organoaluminum compounds appear to be more reactive in some reactions than the simple compounds which contain no halogen, dibenzofuran was treated under forced conditions with ethylaluminum iodides [$(C_2H_5)_2AlI + C_2H_5AlI_2$]. Metalation did occur, but the product isolated subsequent to carbonation and hydrolysis was 2-dibenzofurancarboxylic acid. This anomalous behavior suggested that one of the active agents might have been aluminum iodide, present in the mixture

$$(C_2H_5)_2AlI + C_2H_5AlI_2 \rightleftarrows (C_2H_5)_3Al + AlI_3$$

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[1] Paper LXI in the series: "The relative reactivities of organometallic compounds"; the preceding paper with Brown is in THIS JOURNAL, **67**, 824 (1945).

[2] Gilman and Young, *ibid.*, **57**, 1121 (1935), and *J. Org. Chem.*, **1**, 315 (1936). See, also, pp. 533–538 of Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1943.

[3] Challenger and Miller, *J. Chem. Soc.*, 894 (1938).

Accordingly, an experiment was carried out with aluminum iodide under conditions like those used with the ethylaluminum iodides, and again 2-dibenzofurancarboxylic acid was isolated. This finding is not without some interest in connection with Friedel–Crafts reactions which also involve the 2-position of dibenzofuran, and in connection with mercuration in the 4-position by mercuric acetate.[4a]

The ethylaluminum iodides do effect a halogen-metal interconversion reaction with 4-iododibenzofuran to give, on carbonation, 4-dibenzofurancarboxylic acid

$$IC_{12}H_7O + C_2H_5AlI_2 \xrightarrow[\text{[}H_2O\text{]}]{\text{[}CO_2\text{]}} (HOOC)C_{12}H_7O$$

However, they do not give a corresponding reaction with *o*-bromophenol, which does undergo a halogen–metal interconversion with the more reactive ethylmagnesium bromide.

Experimental

Triethylaluminum and Dibenzofuran.—A benzene solution of 25 g. (0.15 mole) of dibenzofuran was added to triethylaluminum prepared in 35% yield by heating a mixture of 10 g. (0.039 mole) of diethylmercury and 3.78 g. (0.14 g. atom) of aluminum chips at 150°. for six hours. After removal of the benzene by distillation, the mixture was heated for 24 hours at 145–150°. Benzene was then added to the cooled residue and carbon dioxide was passed in to a negative color test.[4b] The yield of recovered dibenzofuran was 89.5%.

Ethylaluminum Iodides, and Aluminum Iodide, with Dibenzofuran.—A mixture of 0.3 mole of ethylaluminum iodides[5] and 16.8 g. (0.1 mole) of dibenzofuran was heated in a sealed tube (dry nitrogen atmosphere) at 210° for seventy-two hours. To the cooled mixture was added 50 cc. of benzene, and after carbonation at reflux temperature with carbon dioxide, there was isolated 0.25 g. (1.1% yield) of 2-dibenzofurancarboxylic acid. The identity of the product was established both by comparison with an authentic specimen of the 2-acid, and by conversion to the known methyl 2-dibenzofurancarboxylate by diazomethane.

From a corresponding reaction in which anhydrous aluminum iodide was used in place of the ethylaluminum iodides, the yield of 2-dibenzofurancarboxylic acid was 1.4%, and 15.5 g. or 92% of the dibenzofuran was recovered.

Ethylmagnesium Bromide and Dibenzofuran.—To a filtered ether solution of ethylmagnesium bromide (prepared from 0.4 mole of ethyl bromide) was added 16.8 g. (0.1 mole) of dibenzofuran in 50 cc. of ether. Subsequent to removal of the ether, by distillation, the mixture was heated for six hours at 165°. The cooled reaction product was dissolved in 300 cc. of ether, and then carbonated in a customary manner by Dry Ice. The yield of 4-dibenzofurancarboxylic acid was 1.05 g. (5%). Identification was completed by conversion to the methyl ester by means of diazomethane.

Ethylaluminum Iodides and 4-Iododibenzofuran.—After removal of benzene from a solution of 0.3 mole of ethylaluminum iodides and 29.2 g. (0.1 mole) of 4-iododibenzofuran, the mixture was heated for twenty-four hours at 145°. Benzene was added to the cooled residue, and carbonation was effected by passing carbon dioxide into the hot solution. The yield of crude 4-dibenzofurancarboxylic acid was 3.19 g. (15%), and identification was completed in the usual way. No experiment was made to determine whether heating for an extended period at a more elevated temperature might induce any rearrangement of the C–Al grouping from the 4-position to the 2-position.

Ethylaluminum Iodides and Ethylmagnesium Bromide with *o*-Bromophenol.—Subsequent to the removal of benzene from a mixture of 0.2 mole of ethylaluminum iodides and 8.3 g. (0.05 mole) of *o*-bromophenol, the residue was heated for five hours at 120°. Then carbon dioxide was added to a hot benzene solution of the reaction mixture until a negative color test was obtained. The recovery of *o*-bromophenol was 88%, and no dibenzofurancarboxylic acid was isolated.

To an ether solution of ethylmagnesium bromide (prepared from 0.2 mole of ethyl bromide) was added 7.5 g. (0.043 mole) of *o*-bromophenol in 50 cc. of ether. Subsequent to removal of the ether by distillation, the mixture was heated for two hours at 120°. The cooled mixture was taken up in ether, and this solution was carbonated by Dry Ice to yield 2.7 g. (45%) of salicylic acid and 3.8 g. (51%) of crude *o*-bromophenol. It is to be noted that in this experiment some residual ether was probably contained in the mixture, whereas in the corresponding experiment with the ethylaluminum iodides no ether was present. However, halogen–metal interconversion was effected in the ether-free mixture of ethylaluminum iodides and 4-iododibenzofuran.

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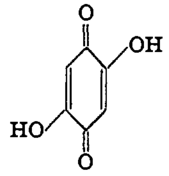
[4] (a) Gilman and Young, THIS JOURNAL, **56**, 1415 (1934); (b) Gilman and Schulze, *ibid.*, **47**, 2002 (1925).

[5] Grignard and Jenkins, *Bull. soc. chim.*, [4] **37**, 1376 (1925).

The Preparation of 2,5-Dihydroxyquinone

BY REUBEN G. JONES AND H. A. SHONLE

The synthesis of a series of compounds required 2,5-dihydroxyquinone (I) as an intermediate.



(I)

This quinone has generally been prepared by the hydrolysis of a 2,5-diaminoquinone,[1] diiminoresorcinol,[2] 2-hydroxy-5-anilinoquinone and related compounds.[3] Unfortunately, however, diiminoresorcinol and the 2,5-diaminoquinones must be obtained by tedious syntheses.

Recently Brecht and Rogers[4] have reported the formation of 2,5-dihydroxyquinone by the oxidation of salicylic acid in 25% sodium hydroxide solution by the addition of hydrogen peroxide in small portions at three-day intervals. While the oxidation of sodium salicylate required as long as fifty-four days, high yields of 2,5-dihydroxyquinone were obtained. These authors also stated that 2,5-dihydroxyquinone was obtained by the hydrogen peroxide oxidation of

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[1] (a) Mylius, *Ber.*, **18**, 463 (1885); (b) Kehrmann, *ibid.*, **23**, 897, 1264 (1890); (c) Kehrmann and Prager, *ibid.*, **40**, 1234 (1907).

[2] Nietzki and Schmidt, *ibid.*, **21**, 2374 (1888).

[3] Kehrman and Bahatrian, *ibid.*, **31**, 2399 (1898).

[4] Brecht and Rogers, *J. Am. Pharm. Assoc.*, **29**, 178 (1940).