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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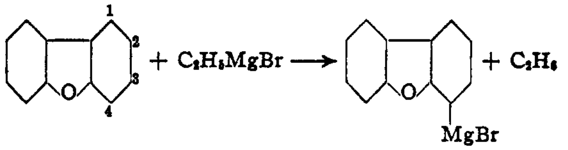
Interconversion Reactions with Some Aluminum Compounds[1]

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) 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).

(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).