and 9.6 g. (0.16 mole) of acetic acid. Distillation under reduced pressure yielded a low-boiling fraction, and a higher fraction distilling at 148–150° (11 mm.). The low-boiling fraction was refluxed for six hours with 75.5 g. (0.75 mole) of acetic anhydride and the mixture, after standing for several days, was distilled in a vacuum as before. The total yield of diacetate distilling at 128–130° (5–6 mm.) and melting at 51–52° was 60 g. or 87%. Hydrolysis with normal sulfuric acid gave 5-bromofurfural.

Anal. Calcd. for $C_9H_9O_5Br$: Br, 28.88. Found: Br, 29.02, 29.00.

Summary

The first bromofurfural, 5-bromofurfural, has been prepared by the direct bromination of furfural diacetate and characterized by a few appropriate derivatives.

AMES, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF BIOLOGICAL CHEMISTRY OF THE UNIVERSITY OF MARYLAND SCHOOL OF MEDICINE]

THE PHENYLATION OF OLEIC ACID

BY E. G. SCHMIDT

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As a preliminary step in the study of the metabolism of certain fatty acids the introduction of various aromatic groups into the double bond of oleic acid has been investigated. Eijkman[1] as well as Marcusson[2] have studied the reaction between unsaturated fatty acids, benzene and anhydrous aluminum chloride with the production of phenyl-substituted saturated acids; however, if the double bond was in the α-position to the carboxyl group, phenylation did not take place. Marcusson drew attention to the fact that Poncio and Castaldi[3] found that these same acids had no iodine number and he pointed out the parallelism between unsaturated fatty acids which do not absorb iodine from Hubl's solution and non-reactivity with aromatic compounds in the presence of aluminum chloride. Nicolet and deMilt[4] noted that the derivatives of phenylstearic acid show little tendency to crystallize.

In the present work the reaction between benzene and oleic acid in the presence of anhydrous aluminum chloride has been studied with particular reference to the speed of the reaction and to the length of the reaction period as affecting the nature of the condensation products. The reaction proceeded with great speed and with a vigorous evolution of hydrogen chloride, and within less than five minutes it was practically completed, as determined by the drop in the iodine number and the neutralization equivalent. If the reaction was allowed to proceed for several hours, par-

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[1] Eijkman, *Chem. Centr.*, II, 1100 (1908).

[2] Marcusson, *Z. angew. Chem.*, **33**, 231 (1920).

[3] Poncio and Castaldi, *Chem. Centr.*, II, 1154 (1912).

[4] Nicolet and deMilt, THIS JOURNAL, **49**, 1103 (1927).

ticularly in the presence of an excess of aluminum chloride, a dark product with a neutralization equivalent much less than that required for phenylstearic acid was obtained. A similar effect was produced by the use of a considerable excess of aluminum chloride. The reaction went on best in the presence of approximately equimolecular quantities of oleic acid and aluminum chloride; with less than one-third of the equivalent quantity of aluminum chloride, very little condensation seemed to take place.

Experimental

Experiment 1.—The Phenylation of Oleic Acid.—In the first experiment 40 g. of oleic acid was dissolved in 225 cc. of benzene to which was added 28 g. of aluminum chloride during the course of about five minutes. Upon the introduction of the aluminum chloride there immediately resulted a vigorous evolution of heat and hydrogen chloride. After refluxing for about thirty minutes, the product was cooled, dissolved in 400 cc. of ether and gently mixed with 200 cc. of 20% hydrochloric acid. The aqueous layer was removed and the reaction product was shaken with water until free from hydrochloric acid. The solution was distilled from the water-bath and the final traces of solvents were removed from the oily residue by distillation from the water-bath, under reduced pressure. The final product was a light brown oil similar to oleic acid and was used without further attempts at purification. It had an iodine number of 10, a neutralization equivalent of 160.4 and the analysis of the silver salt gave the following data.

Anal. Subs., 0.6004: Ag, 0.1381. Calcd. for $C_{24}H_{39}O_2Ag$: Ag, 23.1. Found: Ag, 23.0.

Experiment 2.—In the next series of experiments the effect of varying the amount of aluminum chloride and the time the mixture was refluxed was studied. The data are given in Table I and indicate that the reaction would not proceed unless a considerable quantity of aluminum chloride was present but an excess produced compounds of lower neutralization equivalent, and a similar effect was produced if the reaction mixture was boiled too long. Complete saturation was never obtained.

TABLE I

THE EFFECT OF VARYING THE AMOUNT OF ALUMINUM CHLORIDE

Oleic acid, g.	Benzene, cc.	$AlCl_3$, g.	Refluxed, hrs.	Iodine, no.	Neut. equiv.[a]
40	225	0	0	91.0	197
40	225	7	1	89.7	193
40	225	7	3	88.7	193
40	225	14	1	33.3	176
40	225	14	3	32.4	173
40	225	21	1	14.6	158
40	225	21	3	11.1	157
40	225	28	1	10.0	159
40	225	28	3	7.1	158
40	225	40	3	15.0	122
40	225	65	1	12.0	129
40	225	65	3	11.1	105

[a] Calcd. for phenylstearic acid, 156.6.

Experiment 3.—In this experiment the speed with which phenylation took place and the effect of prolonged heating upon the final product were studied. Sixty grams of oleic acid was dissolved in 300 cc. of benzene and a 25-cc. aliquot was removed for analysis; 35 g. of aluminum chloride was added rapidly with shaking and after three minutes 25 cc. was removed, immediately dissolved in ether and treated with dilute hydrochloric acid to stop the reaction. In the meantime the reaction mixture was refluxed on the water-bath and at various intervals an aliquot was removed and worked up as outlined in the first experiment. The data are given in Table II and indicate that phenylation is extremely rapid—within three minutes the reaction had practically reached completion. If the mixture was allowed to boil too long, a product with a low neutralization equivalent was obtained.

Table II

The Effect of the Length of the Reaction Period

Refluxed, min.	0	3	7	11	30	60	120	180	240
Iodine number	90.8	9.7	11.0	12.1	10.0	13.0	11.5	9.0	13.6
Neut. equiv.[a]	197.0	161.4	160.5	161.0	160.6	159.3	156.0	140.3	133.0

[a] Calcd. for phenylstearic acid, 156.6.

Experiment 4.—The reaction of oleic acid with xylene was studied in a similar manner and was found to proceed with equal rapidity, yielding an oil similar in appearance and properties to phenylstearic acid. The product had an iodine number of 13 and a neutralization equivalent of 144; calcd. for xylylstearic acid, 144.1.

Anal. (silver salt). Subs., 0.5838; Ag, 0.1286. Calcd. for $C_{26}H_{43}O_2Ag$: Ag, 21.77. Found: Ag, 22.02.

Summary

Phenylation of oleic acid with the production of phenylstearic acid proceeded with great speed in the presence of approximately equimolecular quantities of aluminum chloride and oleic acid and an excess of benzene. A considerable excess of aluminum chloride or prolonged boiling of the reaction mixture produced compounds having lower neutralization equivalents than that of phenylstearic acid.

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[Contribution from the Chemical Laboratory of Harvard University]

STUDIES IN THE CYCLOPROPANE SERIES. XIII. A NEW TYPE OF CYCLOPROPENE DERIVATIVE

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In various papers of this series we have discussed the possibility that cyclopropene derivatives might serve as intermediates in the process by which bases convert nitro cyclopropanes into open-chained compounds. The open-chained products are unsaturated and they do not contain the nitro group; but since no cyclopropene derivatives were isolated in any of these cases, the loss of nitrous acid might have occurred either before or after the opening of the ring. We decided, therefore, to determine whether a cyclopropene can actually be formed by eliminating nitrous acid from a suitably constituted nitro cyclopropane.

The choice of suitable material was based on the following consideration.