added and the salt which separated was filtered; yield, 173 g. The hydrobromide, upon recrystallization from alcohol, melts at 177–178°.

Anal. Subs., 0.1170: 9.18 cc. of 0.0502 *N* $AgNO_3$. Calcd. for $C_{12}H_{18}NBr$: Br, 31.21. Found: 31.47.

The free amine boils at 134–135°, at 6 mm. The picrate melts at 164–165°.

Condensation of Cyclohexyl Bromide with Cyclohexylaniline and Dicyclohexylamine.—It was hoped that by the condensation of cyclohexyl bromide with cyclohexylaniline in molecular quantities in the presence of absolute alcohol, it might be possible to prepare dicyclohexylphenylamine. The results were entirely negative, however, resulting products consisting of cyclohexylaniline hydrobromide and cyclohexene.

A similar reaction took place between dicyclohexylamine and cyclohexyl bromide. The salt which separated was dicyclohexylamine hydrobromide, which sublimes at 310–320°.

Anal. Subs., 0.1191: 9.08 cc. of 0.0502 *N* $AgNO_3$. Calcd. for $C_{12}H_{24}NBr$: Br, 30.60. Found: 30.57.

This reaction is apparently analogous to the first one, the cyclohexyl bromide being converted into hydrogen bromide and cyclohexene.

Summary

1. Upon catalytic reduction of diphenylamine hydrochloride with platinum-oxide platinum black, excellent yields of dicyclohexylamine were obtained.

2. Triphenylamine in the presence of a little hydrochloric acid was reduced to tricyclohexylamine with some by-products of cyclohexane and dicyclohexylamine.

3. Cyclohexylphenylamine was prepared from cyclohexyl bromide and aniline. Upon attempting the condensation of cyclohexylphenylamine with cyclohexyl bromide, there resulted merely the formation of cyclohexene and the hydrobromide of the original amine.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO]

A PHENYLSTEARIC ACID FROM OLEIC ACID

BY BEN H. NICOLET AND CLARA M. DEMILT[1]

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Ethylene and benzene react in the presence of aluminum chloride[2] to form ethylbenzene and further substitution products. To maintain the efficiency of the reaction, hydrogen chloride must occasionally be supplied to take the place of that lost during the run.

That this reaction is somewhat general for olefins is indicated by the

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[1] The material presented here was submitted by Clara M. deMilt in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Chicago, **1925**.

[2] Balsohn, *Bull. soc. chim.*, [2] **31**, 539 (1879). Milligan and Reid, THIS JOURNAL, **44**, 206 (1922).

work of Eykman,[3] who showed it to be possible to prepare phenyl-substituted saturated acids by a similar process from 11 of the simpler α,β- or β,γ-unsaturated fatty acids. The application of this reaction to oleic acid appeared of interest from a number of points of view, and was in fact under way[4] before we became acquainted with the results of Eykman.

In the experimental part of this paper, a method is described by which a phenylstearic acid can be obtained in about 35% yield from benzene, oleic acid and aluminum chloride. No proof of the position of the phenyl group can at present be offered, but it is considered very likely that it is 10-phenylstearic acid which is formed.

Perhaps the most suprising outcome of the work was that the acid proved to be a liquid, and that none of the numerous derivatives examined could be made to crystallize. The only solids obtained were certain of the salts of phenylstearic acid, and none of these were found suitable for recrystallization.

Oleic acid is by far the most complex olefin to which the reaction with benzene and aluminum chloride has been applied. The results obtained indicate that it reacts also with toluene and with naphthalene, but the products formed were not studied.

Experimental Part

Preparation of Phenylstearic Acid.—To 200 g. of oleic acid, dissolved in 400 g. of dry benzene, was added 100 g. (1.2 molecular proportions) of coarsely powdered aluminum chloride. There was an immediate, somewhat violent reaction, with evolution of hydrogen chloride. When this had moderated, the flask was heated gently (finally to 80°) with occasional shaking, until hydrogen chloride was no longer evolved (about six hours). The mixture was then poured into 600 cc. of 20% hydrochloric acid and the benzene removed by steam distillation. The brown, viscous oil recovered (equiv. wt., 335; I no., 14.0) weighed 240 g. It was fractionated thrice under about 4 mm. pressure. Table I gives the results of the third fractionation.

TABLE I

THIRD FRACTIONATION OF ACID AT 4 MM.

Fraction	B. p. range, °C.	Weight, g.	Equiv. wt.	n_D
1. Low-melting solid[a]	140–220	33	293	
2. Yellow oil	220–240	25	344	1.4790
3. Yellow oil	240–250	27	361	1.4885
4. Yellow oil	250	34.5	362	1.4905

[a] The solid portion of this fraction was apparently saturated fatty acids which had originally been present in the oleic acid used.

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[3] Eykman, *Chem. Weekblad*, **1**, 421 (1904); **2**, 229 (1905); **4**, 727 (1907); **5**, 655 (1908); see Eijkman, *Chem. Centr.*, **75** [I], 1416 (1904); **76** [I], 1388 (1905); *Chem. Zentr.*, **78** [II], 2045 (1907); **79** [II], 1100 (1908).

[4] Acknowledgment is here made of some preliminary work by H. W. Kline [*Master's Dissertation*, University of Chicago, March, 1925], which made it probable that the reaction took place, although no products were isolated.

Most of the material not accounted for remained behind as a viscous, red residue[5] in the various distillations. Assuming that Fractions 3 and 4, and 75% of Fraction 2, are the desired material, the yield is about 35%. Other trials showed that the introduction of dry hydrogen chloride during the reaction did not improve the yield, and that both larger and smaller proportions of aluminum chloride gave poorer results.

The purest phenylstearic acid obtained was a yellowish oil, b. p. 250° at 4 mm., which did not solidify at —15°; n^{20} (Abbé), 1.4905.

Anal. Calcd. for $C_{24}H_{40}O_2$: C, 80.0; H, 11.2; equiv. wt., 360. Found: C, 80.07, 79.97; H, 11.47, 11.50; equiv. wt., 362.

It is very resistant to oxidation by hot alkaline permanganate; benzoic acid was the only product isolated.

Salts and Esters of Phenylstearic Acid.—The sodium and potassium salts behave like typical soaps. The silver salt, precipitated from a solution of the sodium salt, is a white, curdy solid, insoluble in alcohol or ether, and darkened by heating or exposure to light.

Anal.[6] (Ignition) Calcd. for $C_{24}H_{39}O_2Ag$: Ag, 23.13. Found: 22.96, 22.95.

The LEAD SALT, a white, waxy solid melting somewhat indefinitely at 86°, dissolves in ether, ligroin or chloroform, but could not be made to crystallize from such solutions.

METHYL PHENYLSTEARATE is a pale yellow oil; b. p., 228°, at 4 mm.; n^{20}, 1.4840.

Anal. Calcd. for $C_{25}H_{42}O_2$: C, 80.2; H, 11.3; equiv. wt., 374. Found: C, 79.81, 79.66; H, 11.37, 11.90; equiv. wt., 373.6.

The *p*-nitrobenzyl ester[7] would not solidify, and was not analyzed.

Amides of Phenylstearic Acid.—The acid chloride was prepared both with thionyl chloride and with phosphorus pentachloride. Its reaction with ammonium carbonate gave phenylstearamide. Evaporation of the well-washed ether extract left a light brown, viscous liquid.

Anal. (Kjeldahl) Calcd. for $C_{24}H_{41}ON$: N, 3.8. Found: 3.4.

Reaction of the crude chloride with aniline gave a poor yield of phenylstearanilide which, after fractional distillation, was obtained as a faintly yellow liquid of the consistency of glycerol; b. p., 282°, at 4 mm.

Anal. (Dumas) Calcd. for $C_{30}H_{45}ON$: N, 3.20; Found: 3.42, 3.47.

Attempts to prepare the *p*-tolyl- and α-naphthylamides were apparently successful, but no solid product was formed.

Nitration of Phenylstearic Acid.—The acid was added gradually to a mixture of concd. nitric and sulfuric acids, and the mixture was warmed to 60° for an hour. The product, a clear red viscous mass from which no crystals were obtained, was essentially a dinitro derivative.

Anal. (Kjeldahl)[8] Calcd. for $C_{24}H_{38}O_6N_2$: N, 6.22. Found: 6.43.

Nitration with fuming nitric acid in acetic acid gave similar results. Procedures which should have yielded diamino, diacetylamino, dibenzoylamino and tribromodiamino derivatives of phenylstearic acid gave products which ranged from brown oils to red-brown resins. As the chief aim in their preparation was to secure a suitable derivative for characterization, these were not further studied.

Reaction of Other Aromatic Hydrocarbons With Oleic Acid.—Under conditions

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[5] This material was still soluble in ether. It gave unexpectedly high saponification numbers. As it decomposed before distillation at 4 mm., it was not examined further.

[6] Two different preparations.

[7] Reid, THIS JOURNAL, **39**, 1727 (1917).

[8] Modified method; compare "Methods of Analysis," *Assoc. Official Agr. Chem.*, Washington, D. C., **1919**, p. 7.

analogous to those used in the preparation of phenylstearic acid, oleic acid also reacts with toluene and with naphthalene. In the latter case, carbon disulfide was used as solvent. The nature of the reaction appears to be the same in all these cases, but the products were not further studied.

Summary

1. Phenylstearic acid has been prepared from benzene and oleic acid. Its derivatives show a rather surprising reluctance to crystallize.

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[Contribution from the Havemeyer Chemical Laboratory of New York University]

STUDIES ON UNSATURATED 1,4-DIKETONES. III. THE MODE OF ADDITION OF HALOGEN TO DIBENZOYLETHYLENE

By Robert E. Lutz

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Two stereo-isomers of dibenzoylethylene, $C_6H_5COCH{=}CHCOC_6H_5$, are known[1] and each adds halogen readily and quantitatively in acetic acid as the solvent to give almost exclusively the same (high-melting) dihalide, $C_6H_5COCHXCHXCOC_6H_5$. Two such dihalides are possible and as I have shown in the first paper[2] of this series, the lower-melting stereo-isomers are formed simultaneously but only in small amounts. When halogen adds to certain other unsaturated 1,4-diketones, in each case a similar pair of stereo-isomeric dihalides is obtained, the relative yields of which more nearly approach equality when the reactions proceed in chloroform at ordinary or somewhat elevated temperatures. On the basis of consistent physical relationships, these stereo-isomers may be classified as lower-melting or alpha, and higher-melting or beta, but there has been available practically no evidence to indicate which of these isomers corresponds to the *dl* and which to the *meso* forms.[3]

It is known that at —20° in chloroform, chlorine adds to the stereo-isomers of dibenzoylethylene to give almost exclusively in each case a different dichloride, the colorless *cis* modification yielding the alpha dichloride and the yellow *trans* isomer yielding the beta dichloride.[1c] In this research I have added bromine to the two isomers of dibenzoylethylene at —12° in chloroform and in each case, also, I have obtained almost exclusively a different dibromide; the colorless *cis* isomer yields (as with chlorine) the alpha dihalide, and the yellow *trans* isomer the beta dihalide.

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[1] (a) Paal and Schulze, *Ber.*, **33**, 3800 (1900); (b) **35**, 168 (1902). (c) Conant and Lutz, This Journal, **47**, 881 (1925).

[2] Lutz, *ibid.*, **48**, 2905 (1926).

[3] Dibenzoyldibromo-ethane(β), $C_6H_5COCHBrCHBrCOC_6H_5$, was prepared, however, from *meso*dibromosuccinyl dichloride by Meyer and Marx [*Ber.*, **41**, 2469 (1908)]. A question has been raised concerning the identity of the acid chloride used [Ing and Perkin, *J. Chem. Soc.*, **125**, 1814 (1924)].