Isomeric Phenylstearic Acids and Related Compounds: Composition and Partial Separation[1]

F. D. SMITH, A. J. STIRTON and C. J. DOOLEY
Eastern Regional Research Laboratory,[2] Philadelphia, Pennsylvania 19118

Abstract

Reaction of benzene with oleic acid, methyl oleate, oleyl alcohol and oleonitrile, catalyzed by $AlCl_3$, yielded the expected phenylstearic acid or the related ester, alcohol or nitrile as a viscous oil which failed to crystallize.

Gas liquid chromatography of the ketone fraction obtained by CrO_3 oxidation showed 12 position isomers, with the phenyl group at C atoms 6–17, for phenylstearic acid, methyl phenylstearate and phenylstearonitrile. Oxidation of phenyloctadecanol revealed one more isomer, (5-phenyloctadecanol). Distribution of isomers was quite similar for the acid, ester, alcohol and nitrile. Repeated low temperature crystallization from acetone and other solvents separated the 17-, 16- and 15-phenyl isomers in a pure state. Initial crystallization gave the 17-phenyl isomer, except for phenylstearic acid. In this case, contrary to our previous report, the product from initial crystallization was 16-phenylstearic acid.

Introduction

A COMPARISON OF oleic acid, methyl oleate, oleyl alcohol and oleonitrile in the Friedel-Crafts reaction with benzene showed that in each case the product was a viscous oil. Failure to crystallize even at low temperatures is caused by their composition as a mixture of several isomers, as has been demonstrated for the acid and alcohol (5,7).

Gas liquid chromatography of ketones obtained by CrO_3 oxidation showed 12 position isomers, with substitution at C atoms 6–17, for the acid, ester and nitrile. A small amount of one more isomer, 5-phenyloctadecanol, was found in the case of the alcohol. Distribution of isomers was quite similar.

Gas-liquid chromatography of distilled methyl phenylstearate showed a partial separation (Fig. 1) which led us to believe that it would be possible to isolate the more external isomers of the acid, ester, alcohol and nitrile by fractional crystallization.

Low temperature crystallization of the oily, viscous reaction product from acetone separated the higher melting and least soluble 17-phenyl isomer in a crystalline state, in the case of methyl phenylstearate, phenyloctadecanol, and phenylstearonitrile. Repeated low temperature crystallization from the mother liquor gave the 16-phenyl isomer.

Initial low temperature crystallization of phenylstearic acid from acetone gave the highest melting isomer which in this case and contrary to our previous report (5) we have now found to be 16-phenylstearic acid. The crystalline arylstearic acids from o- and p-xylene and o- and p-chlorotoluene have been correctly reported (5) as the 17-aryl isomer.

Experimental Procedures

Optimum conditions including the order of addition of reactants and $AlCl_3$ ratio are described for the acid, ester, alcohol and nitrile.

Phenylstearic Acid

Anhydrous $AlCl_3$, 448 g, 3.36 moles, 1.1 mole ratio, was added in portions in 35 min to a stirred solution of 862 g, 3.05 moles, of purified oleic acid (97%) in 1,360 ml of benzene, the temperature rising from 27 C to 44 C. The stirred mixture was heated 30 min at 80 C, cooled, and hydrolyzed in iced HCl. The benzene layer was separated, washed and distilled to give phenylstearic acid, $b_{0.2}$ 217–231 C, n_D^{25} 1.4867, N.E. 359.1 (theo. 360.5), yield 57%, purity by GLC of the methyl ester 98%.

Methyl Phenylstearate

Methyl oleate, 84 g, 0.283 moles, purity 99.4%, was added dropwise in 30 min to a stirred suspension of 41.5 g $AlCl_3$, 1.1 mole ratio, in 126 ml of benzene, the temperature rising from 28 C to 57 C. The mixture was stirred 3 hr while cooling to room temperature, and poured on ice. The benzene layer was separated, washed and distilled to give methyl phenylstearate, $b_{0.3}$ 191–211 C, n_D^{25} 1.4807, S.E. 375.2 (theo. 374.6), yield 61%. GLC analysis showed the absence of methyl palmitate or stearate.

Phenyloctadecanol

Oleyl alcohol 260 g, 0.97 moles, purity 99% was added dropwise in 40 min to a stirred suspension of 142 g $AlCl_3$, 1.1 mole ratio, in 516 ml of benzene, the temperature rising from 27 C to 59 C. The mixture was stirred 2 hr while cooling to room temperature, then poured on ice. The benzene layer was separated, washed, and distilled to give phenyloctadecanol, $b_{0.2}$ 176–190 C, n_D^{25} 1.4889, %OH 4.86 (theo. 4.91), yield 81%.

A portion was converted to phenyloctadecyl acetate n_D^{25} 1.4805, S.E. 388.9, (theo. 388.6), purity 99.9%, by heating 2 hr at reflux with a 2 molar ratio of acetic anhydride, in the presence of sodium acetate.

Phenylstearonitrile

Distillation of commercial oleonitrile, purity 82%, through a packed column gave a fraction $b_{0.3}$ 139–

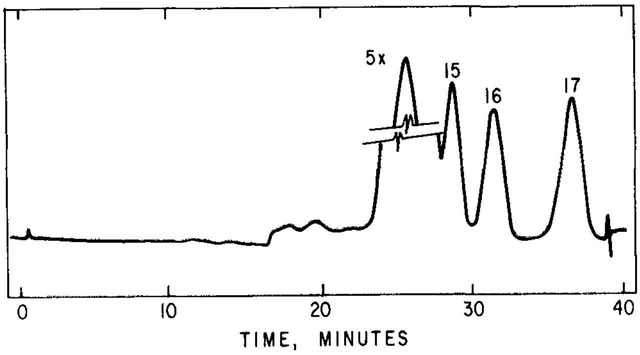

FIG. 1. Gas liquid chromatography showing partial separation of methyl phenylstearate.

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[2] E. Utiliz. Res. Dev. Div., ARS, USDA.

TABLE I
Distribution of Isomers

Position isomer	Phenylstearic acid[a]	Methyl phenylstearate[b]	Phenyloctadecanol[a]	Phenylstearonitrile[b,c]	Phenylstearonitrile[b]
17	11.6	12.4	9.9	9.1	16.8
16	2.9	3.6	3.3	2.8	3.8
15	4.8	5.6	5.2	4.8	6.2
14	7.3	8.0	6.9	7.8	8.2
13	8.8	9.0	7.8	9.6	9.4
12	10.2	10.4	9.4	11.8	10.4
11	12.0	12.3	10.6	14.0	11.4
10	15.3	15.1	13.5	15.8	13.2
9	12.9	12.8	12.9	13.6	10.7
8	8.4	6.9	9.6	7.0	6.8
7	4.5	3.1	6.7	3.6	2.8
6	1.5	1.0	3.6	trace	0.2
5	......	......	0.7	......	......

[a] $AlCl_3$ added in portions to reactants.
[b] Olefin added dropwise to suspension of $AlCl_3$.
[c] 0.3 Molar ratio of $AlCl_3$. All others, 1.1 molar ratio.

141.5 C. Crystallization from acetone at −70 C removed polyunsaturated material in the filtrate. Subsequent crystallization at −50 C removed saturated material. Redistillation gave oleonitrile, $b_{0.3}$ 158.5–159.5 C, I.V. 95.9 (theo. 96.4), purity by GLC 99.1%.

Oleonitrile 288.4 g, 1.094 moles, was added dropwise in 25 min to a stirred suspension of 43.8 g $AlCl_3$, 0.3 mole ratio, in 584 ml of benzene, the temperature rising from 28 C to 46 C. The mixture was heated to 60 C and stirred 2 hr while cooling to room temperature, then poured on iced HCl. The benzene layer was separated, washed and distilled to give phenylstearonitrile, $b_{0.6}$ 197–203 C, n_D^{25} 1.4872, % N 3.98 (theo. 4.10), purity by GLC 99.1%, yield 81%. Lower yields were obtained with higher $AlCl_3$ ratios (4).

Chromic Acid Oxidation

Chromic acid oxidation was carried out as described previously (5,7) with a ratio of 2 g of the viscous oil to 3 g of CrO_3, increased to 4 g in the case of phenyloctadecanol to allow for oxidation of the primary alcohol group. Methyl phenylstearate and phenylstearonitrile were hydrolyzed to phenylstearic acid prior to oxidation. Direct oxidation of phenylstearonitrile was also feasible to give a neutral ketone fraction containing both alkyl aryl ketones $CH_3(CH_2)_xCOC_6H_5$ and ω-benzoyl fatty acid nitriles $C_6H_5CO(CH_2)_yCN$, the presence of which did not interfere with the recognition of the acetophenone homologs. Gas-liquid chromatography gave the same product distribution with or without prior hydrolysis of the nitrile.

Gas-Liquid Chromatography

The instrument was an F&M Model 810 dual column chromatograph fitted with a commercial 8 ft. 20% SE-30 silicone gum rubber column. It was connected to a digital integrator, Model CRS-11 HSB (Infotronics) and printer (Victor Digit-matic). Relative amounts of products were based on area count or per cent area. The alkyl aryl ketones were recognized by comparison with reference acetophenone homologs. Product distribution for the acid, ester and alcohol, and for phenylstearonitrile at different $AlCl_3$ ratios is shown in Table I.

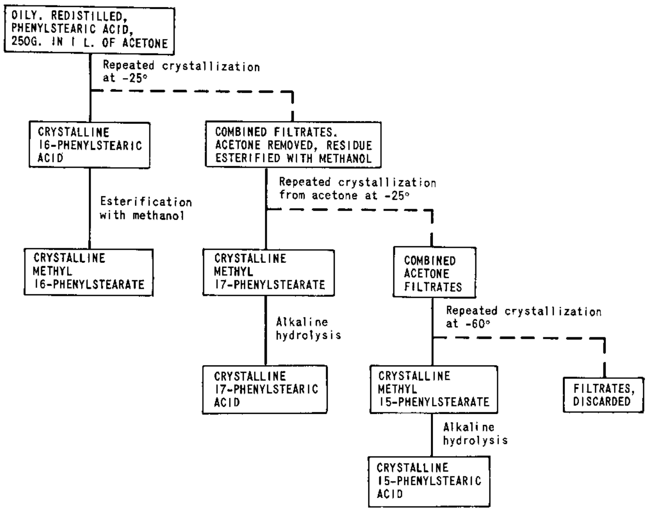

FIG. 2. Fractional crystallization of phenylstearic acid and methyl phenylstearate.

Separation of Crystalline Isomers

The scheme for the isolation of crystalline 15-, 16- and 17-phenylstearic acid and the corresponding methyl esters by low temperature crystallization from acetone is shown in Fig. 2. Contrary to our previous report (5,7) the first isomer obtained, the least soluble and the highest melting, is the 16-phenylstearic acid mp 66–67 C. This has been confirmed by oxidation to propiophenone and comparison with an authentic sample, superimposition of the methyl ester upon the curve of Fig. 1, interconversion with methyl 16-phenylstearate and 16-phenylstearonitrile and by mass spectra. The 17- and 15-phenyl isomers were obtained by esterification of the residue from selected mother liquors, fractional crystallization of the methyl ester from acetone and hydrolysis of the isolated methyl 17-phenylstearate and methyl 15-phenylstearate. Throughout the many recrystallizations GLC was a guide to the selection of fractions rich in the desired isomer.

Low temperature crystallization of phenyloctadecanol from acetone gave 17- and 16-phenyloctadecanol in a similar manner. Low temperature crystallization of phenyloctadecyl acetate from acetone gave 17-phenyloctadecyl acetate. The residue from selected mother liquors, crystallized from 95% ethanol gave 16-phenyloctadecyl acetate.

Phenylstearonitrile was crystallized from acetone to give 17-phenylstearonitrile. The residue from the mother liquor, crystallized from 95% ethanol, gave a 40:60 mixture of the 17- and 16-phenyl isomers. Crystallization of the mixture from hexane gave 16-phenylstearonitrile.

Hydrolysis of Phenylstearonitrile

A mixture of 12.8 g phenylstearonitrile, 15 g KOH pellets, 20 ml water and 100 ml of 95% ethanol was refluxed 40 hr and poured into a separatory funnel containing 1 l. of 6 N HCl and 250 ml of ether. The ether layer, separated, washed, evaporated

TABLE II
Melting Points of Isolated Crystalline Isomers

Position isomer	Phenylstearic acid C	Methyl phenylstearate C	Phenyloctadecanol C	Phenyloctadecyl acetate C	Phenylstearonitrile C
17-phenyl	48.5–49.5	42.2–42.9	44.1–45	34.9–35.5	35–36
16-phenyl	66–67	30.8–31.5	45.4–46.2	31.3–31.9	30.7–31.5
15-phenyl	49.6–50.5	43.6–44.5	....	....	....

in a rotary evaporator at 100 C and 0.2 mm gave phenylstearic acid, N. E. 360.4 (theo. 360.6), yield 98%.

Mass Spectra

Mass spectrometric analyses on the isolated crystaline esters and nitriles of Table II were made using a Consolidated Electrodynamics Corporation Model 21–103 C mass spectrometer equipped with an all-glass heated inlet system. The inlet and source temperatures were about 250 C. The expected mass spectrometric patterns were obtained.

The fragmentation patterns of the isomeric methyl phenylstearates and phenylstearonitriles showed fragmentation taking place at the bonds between CH and R_1 or R_2 (Fig. 3), like that proposed by Grubb and Meyerson (1) for alkylbenzenes.

In each case the peak at P–R_2 was very intense and was used to identify the isomer. The peak at P–R_1 was less intense but gives further proof of structure.

The structures of methyl 17-, 16- and 15-phenylstearate, and of 17- and 16-phenylstearonitrile were confirmed in this manner.

The structure of the crystalline arylstearic acid from p-xylene (5,8) could not be established by CrO_3 oxidation; apparently it is too susceptible to oxidation to give a neutral ketone fraction. Similar application of mass spectrometric analysis, however, showed it to be 17-(2′,5′-dimethyl)phenylstearic acid.

Discussion

In carrying out the Friedel-Crafts reaction better results were obtained by adding the $AlCl_3$ in portions to the other reactants, in the case of the arylstearic acids (8). The reverse order of addition, adding the olefin dropwise to an $AlCl_3$ suspension, was more convenient and gave higher yields of methyl phenylstearate, phenyloctadecanol and phenylstearonitrile. A 1.1 molar ratio of $AlCl_3$ to olefin was necessary except for phenylstearonitrile which required only a 0.3 molar ratio.

Distribution of products as determined by CrO_3 oxidation was quite similar for the acid, ester, alcohol and nitrile (Table I). The stoichiometrical ratio of $AlCl_3$ gave, in the case of phenylstearonitrile, higher yields of the 17- and less of the 9-, 10-, 11- and 12-phenyl isomers.

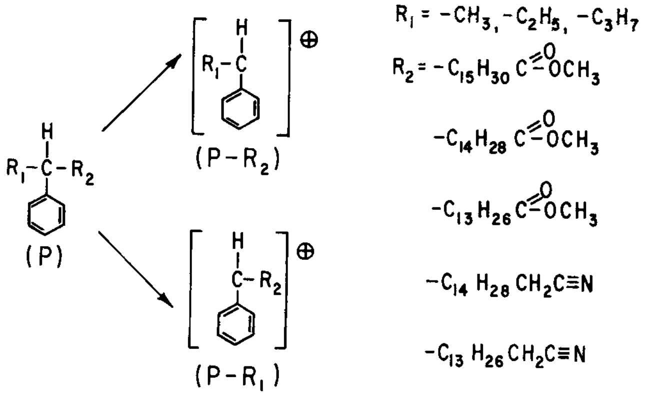

FIG. 3. Fragmentation patterns of isomeric methyl phenylstearates and phenylstearonitriles.

It is evident from an investigation of the phenylalkanes (6) and also from Fig. 1, which shows resolution of the 17- and 16- and partial resolution of the 15-phenyl isomers, that the distribution as given by CrO_3 oxidation needs correction to reduce somewhat the 17-phenyl and increase the amount of the 16-phenyl isomer. From area integration of Fig. 1 and similar curves for phenyloctadecanol and phenylstearonitrile the ratio of isomers, 17:16, was found to be in the range 1.5–1.8 for the compounds of Table I, compared to 3.0–4.4 as shown by CrO_3 oxidation.

The melting points of the crystalline isomers are shown in Table I. For comparison, the melting points of the 9- and 10-phenylstearic acids, synthesized from benzaldehyde by the Grignard reaction and the malonic ester synthesis (2), were 36.5–38 C and 40–41.5 C, respectively. It is likely that the internal isomers will all have very similar physical properties and be difficult to separate.

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