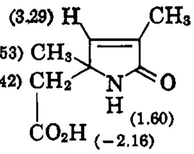

X

by a small chemical shift; in pyridine this band appears as a singlet with an area corresponding to one methylene group. The NH peak at τ 1.60 is rather broad, but its area is equal to that of the olefinic and of the acid proton peaks. In the infrared spectrum of this compound in potassium bromide pellet, bands characteristic of secondary cyclic amides, double bonds, and carboxyl groups (3358 and 1652, 2500 broad, 1708, 1406, and 1302 cm.$^{-1}$) appear.

The formation of X by alkaline hydrolysis of III and V (R = Me) followed by acidification is in fact an intramolecular Ritter reaction favored by the configuration. Should the configuration about the C-4–C-5 double bond be that shown in III and V, the formation of X appears to require isomerization about this bond. It seems probable that V forms X directly, while III must first be converted into V. Although such isomerizations are known to take place readily under the influence of hot alkali,[12] the readiness with which V cyclizes to X suggests that isomerization of V may not be required for the cyclization and that the C-5 methyl and cyano groups may have opposite configurations to those shown in the formulas III and V.

Experimental

N.m.r. spectra were measured with a Varian Associates HR-4302 high-resolution spectrometer with a 60-Mc. oscillator with super stabilizer and field homogeneity control. Samples were examined in 5–10% solution in deuteriochloroform, unless otherwise stated. Tetramethylsilane was used as internal standard and chemical shifts are reported as τ-values[6]; $\Delta\tau = \tau_{cis} - \tau_{trans}$, where the subscripts refer to the relative positions of the carboxyl group and of the olefinic or methyl protons, and not to the configuration of the acid.

Infrared spectra were determined in Nujol mulls and in potassium bromide wafers with a double-beam Jena UR-10 spectrophotometer. Ultraviolet absorption spectra were recorded with a CF-4 Optica Milano spectrophotometer in 96% ethanol.

Cyano acids were obtained[1] from 2,4,6-trimethylpyrylium and 2,6-dimethyl-4-ethylpyrylium perchlorates and aqueous sodium cyanide, followed by oxidation with sodium hypobromite. Samples of 4-carbethoxy-5-cyano-3-methylsorbic acids (VI and VII) were kindly supplied by Dr. G. Vogel.

3,5-Dimethyl-Δ^3-pyrrolin-2-one-5-acetic Acid (X).—Alkaline hydrolysis of 2-*cis*-5-cyano-3-methylsorbic acid (III) afforded[1] a 2,4-dimethylmuconic acid, m.p. 198°, and the acid X, m.p. 155°. The latter (X) is more soluble in water than the dimethylmuconic acid and was separated by fractional crystallization. It is the sole product from V.

Anal. Calcd. for $C_8H_{11}NO_3$: C, 56.79; H, 6.55; N, 8.28; neut. equiv., 169. Found: C, 57.27; H, 6.46; N, 8.38; neut. equiv., 165.

Acknowledgment.—We express our thanks to Dr. G. Vogel for discussions, for providing samples of compounds VI and VII, and for the determination of the mixture melting point of III (R = Me). We also thank Mrs. E. Romas and Mr. C. N. Rentea for recording the infrared spectra, Miss M. Mocanu for the ultraviolet spectra, and Mr. S. W. Thomas for the n.m.r. spectra. Final preparation of the manuscript was completed during the tenure of one of us (R. H. Wiley) as a visiting professor in the Graduate Division of the City University of New York.

The Effect of Structure on the Rate of Disproportionation of Aromatic Sulfinic Acids[1a]

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Received September 1, 1964

The rates of disproportionation of a series of aromatic sulfinic acids have been determined in acetic acid, containing small amounts of water and sulfuric acid. All of the disproportionations exhibit kinetics which are second order in sulfinic acid and show essentially the same dependence on water and sulfuric acid concentration previously found for *p*-toluenesulfinic acid. For *para*-substituted benzenesulfinic acids one finds that electron-withdrawing *para* substituents retard the disproportionation while electron-releasing ones accelerate it. This is exactly the opposite of the effect of the same substituents on the rate of decomposition of the corresponding sulfinyl sulfones I, eq. 2b, the reaction believed to be the rate-determining step in the disproportionation. This means that the observed effect of *para* substituents on disproportionation is entirely the result of their influence on the prior equilibrium between sulfinic acid and sulfinyl sulfone (eq. 2a). Evidence is also presented which indicates that the equilibrium between sulfinic acid and sulfinyl sulfone is not really too unfavorable thermodynamically to the sulfinyl sulfone, and that in favorable cases the equilibrium concentration of the sulfinyl sulfone may be as much as a few per cent of the stoichiometric concentration of the sulfinic acid.

On being heated in solution aromatic sulfinic acids undergo disproportionation to thiolsulfonate and sulfonic acid (eq. 1). An earlier detailed study[2] of the disproportionation of *p*-toluenesulfinic acid in acetic acid–water–sulfuric acid solution indicated a mechanism (eq. 2) for the reaction involving rate-determining decomposition of an intermediate sulfinyl sulfone I, eq. 2b. Subsequent study[3] of sulfinyl sulfones has confirmed that they undergo thermal decomposition in a manner entirely compatible with the kinetic and stoichiometric requirements of the disproportionation

$$3ArSO_2H \longrightarrow ArSO_2SAr + ArSO_3H + H_2O \qquad (1)$$

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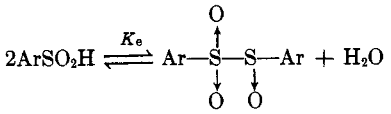
[1] (a) This research supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Grant AFOSR-106-63. (b) Participant in National Science Foundation Research Participation for College Teachers Program, Oregon State University, summer 1963.

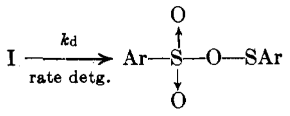
[2] J. L. Kice and K. W. Bowers, *J. Am. Chem. Soc.*, **84**, 605 (1962).

[3] (a) J. L. Kice and N. E. Pawlowski, *J. Org. Chem.*, **28**, 1162 (1963); (b) *J. Am. Chem. Soc.*, **86**, 4898 (1964).



$$2ArSO_2H \underset{}{\overset{K_e}{\rightleftharpoons}} Ar\text{—}\underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{S}}\text{—}\underset{\underset{O}{\downarrow}}{S}\text{—}Ar + H_2O \qquad (2a)$$

I



$$I \xrightarrow[\text{rate detg.}]{k_d} Ar\text{—}\underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{S}}\text{—}O\text{—}SAr \qquad (2b)$$

II

$$II \xrightarrow{ArSO_2H} ArSO_2SAr + ArSO_3H \qquad (2c)$$

and has thus provided strong support for the mechanism outlined in eq. 2.

Among the variables investigated[3b] in the studies of sulfinyl sulfone decomposition was the effect of changes in aryl group structure on the rate of decomposition of I. Certain statements in the literature[4] lead one to expect that there should be significant variations in the rate of disproportionation of aromatic sulfinic acids ($ArSO_2H$) with the nature of the aryl group, Ar. Accordingly, it seemed of interest to measure the rates of disproportionation of a series of aromatic sulfinic acids and to see how any variation of rate with structure correlated with the previously determined effects of structure on sulfinyl sulfone decomposition rate.

Results

Kinetics of Disproportionation.—The disproportionation of the various aromatic sulfinic acids has been studied in acetic acid solvent containing known amounts of water and sulfuric acid. In all cases except that of *p*-nitrobenzenesulfinic acid the rate of disappearance of the sulfinic acid could be followed by the same method used previously[2] to follow the disproportionation of *p*-toluenesulfinic acid. For the *p*-nitro compound an alternate procedure, described in the Experimental, was used.

In every case the disappearance of the sulfinic acid followed good second-order kinetics. In two cases, *p*-chlorobenzenesulfinic acid and benzenesulfinic acid, product studies were carried out to verify that the stoichiometry shown in eq. 1 was being obeyed. Table I summarizes the results of the various kinetic runs.

Dependence of Rate on Sulfuric Acid and Water Concentrations.—It was important to ensure that the variations of rate with Ar group were not the result of a pronounced difference in the response of the rate to sulfuric acid and water concentration in the different cases. For this reason the effect of these variables on the rates of disproportionation of *p*-chlorobenzenesulfinic and benzenesulfinic acids was determined and compared with similar data already obtained[2] for *p*-toluenesulfinic acid. The pertinent data are tabulated in Tables II and III. These data show clearly that the response of disproportionation rate to water and sulfuric acid concentration is essentially the same in all cases.

TABLE I

KINETICS OF THE DISPROPORTIONATION OF AROMATIC SULFINIC ACIDS IN ACETIC ACID

Ar, *M*	Temp., °C.	(H_2O),[a] *M*	(H_2SO_4), *M*	$k_2 \times 10^3$, M^{-1} sec.$^{-}$
C_6H_5, 0.10	80.3	0.56	0.00	0.65
			0.30	1.38
			0.60	1.91
			1.20	2.90
		1.12	0.60	0.83
		1.68	0.60	0.58
p-ClC_6H_4, 0.10	80.3	0.56	0.00	0.40
			0.30	0.80
			0.60	1.05
			1.20	1.63
		1.12	0.60	0.47
		1.67	0.60	0.29
p-BrC_6H_4, 0.10	80.3	0.56	0.60	1.01
p-$CH_3C_6H_4$, 0.10	59.6	0.56	0.60	0.43
	69.8			1.45
	80.3			4.50
	89.4			12.0
	69.8	0.56	0.30	1.03
	80.3			3.20
p-$CH_3OC_6H_4$, 0.10	80.3	0.56	0.60	10.3
p-$O_2NC_6H_4$, 0.10	80.3	0.56	0.60	0.36
β-Naphthyl, 0.10	80.3	0.56	0.60	6.95

[a] Stoichiometric concentration of water.

TABLE II

DEPENDENCE OF DISPROPORTIONATION RATE ON SULFURIC ACID CONCENTRATION

	H_2SO_4 concn.			
	0.0 *M*	0.3 *M*	0.6 *M*	1.2 *M*
Ar	$k_2/(k_2$ at 0.6 *M* $H_2SO_4)$ for $ArSO_2H$[a]			
C_6H_5	0.34	0.72	(1.0)	1.52
p-ClC_6H_4	0.38	0.76	(1.0)	1.55
p-$CH_3C_6H_4$[b]	0.37	0.73	(1.0)	1.61

[a] All data for acetic acid–0.56 *M* water. [b] Data of ref. 2.

TABLE III

DEPENDENCE OF DISPROPORTIONATION RATE ON WATER CONCENTRATION

	H_2O concn.		
	0.56 *M*	1.12 *M*	1.68 *M*
Ar	$k_2/(k_2$ at 0.56 *M* $H_2O)$ for $ArSO_2H$[a]		
C_6H_5	(1.0)	0.43	0.30
p-ClC_6H_4	(1.0)	0.45	0.28
p-$CH_3C_6H_4$[b]	(1.0)	0.39	0.22

[a] Data for $C_6H_5SO_2H$ and *p*-$ClC_6H_4SO_2H$ for acetic acid–0.6 *M* sulfuric acid. That for *p*-$CH_3C_6H_4SO_2H$ for acetic acid–1 *M* sulfuric acid. [b] Data of ref. 2.

Effect of Sulfinic Acid Structure on Disproportionation Rate.—The results in Tables II and III show that the relative rates of disproportionation of a series of aromatic sulfinic acids at a given water and sulfuric acid concentration will be essentially independent of the water and sulfuric acid concentrations chosen.

Accordingly, we elected to compare the rates for the various sulfinic acids at 0.6 *M* sulfuric acid and 0.56 *M* water at 80°, under which conditions the rates for all were conveniently measured experimentally. The pertinent results (Table I) are summarized in Table IV.

With the *para*-substituted benzenesulfinic acids it is clear that electron-donating groups accelerate the disproportionation while electron-withdrawing ones retard it. Plots of log k_2 against σ and σ_+ (Figure 1) show that the rates are much better correlated by σ_+ ($\rho = -1.1$), although even in this case the correlation is not outstandingly good.

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(4) Houben-Weyl, "Methoden der Organischen Chemie," Vol. 9, 4th Ed., Georg Thieme Verlag, Stuttgart, 1955, p. 332.

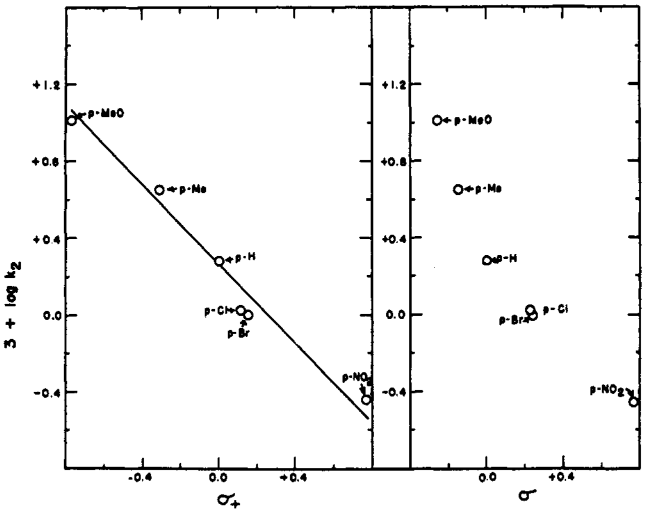


Figure 1.—Disproportionation rate of *para*-substituted benzenesulfinic acids in acetic acid–0.56 M water–0.6 M sulfuric acid at 80° *vs.* σ_+ and σ.

TABLE IV

EFFECT OF STRUCTURE ON RATE OF DISPROPORTIONATION OF AROMATIC SULFINIC ACIDS

Ar	$k_2^{ArSO_2H}/k_2^{PhSO_2H}$ [a]
p-$CH_3OC_6H_4$	5.4
p-$CH_3C_6H_4$	2.36
C_6H_5	(1.0)
p-ClC_6H_4	0.55
p-BrC_6H_4	0.53
p-$O_2NC_6H_4$	0.19
β-Naphthyl	3.64

[a] All data at 80° in acetic acid–0.6 M sulfuric acid–0.56 M water.

Discussion

We have just seen that electron-withdrawing groups retard and electron-donating groups accelerate the disproportionation of *para*-substituted benzenesulfinic acids. In more limited studies, exactly the reverse has been found for the decomposition of the corresponding sulfinyl sulfones (I).[3b] This is evident from comparison of the data in Table V with that in Table IV.

TABLE V

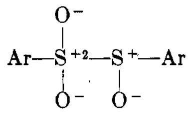
EFFECT OF STRUCTURE ON RATE OF DECOMPOSITION OF SULFINYL SULFONES

Ar	k_d^{Ar}/k_d^{Ph} [a]
p-$CH_3C_6H_4$	0.8
C_6H_5	(1.0)
p-ClC_6H_4	1.3
β-Naphthyl	1.3

[a] Data of ref. 3b; dioxane solvent at 50°.

Clearly then, in terms of the mechanism shown in eq. 2a–c, the observed effect of *para* substituents is the result of their influence on the initial equilibrium shown in eq. 2a and is exactly contrary to their effect on the rate of decomposition of the sulfinyl sulfone (eq. 2b). On the other hand, going from phenyl to β-naphthyl as the aryl group leads to an increase in both disproportionation rate and rate of decomposition of the sulfinyl sulfone.

That the various *para* substituents should have the influence they do on the first equilibrium is not surprising. In the sulfinyl sulfone one has a repulsion between two adjacent, somewhat electron-deficient sulfur atoms, which is not present in the corresponding sulfinic acid. Electron-releasing *para* substituents would therefore be expected to make formation of the sulfinyl sulfone more favorable, while electron-withdrawing substituents should make the initial equilibrium less favorable.



$$\mathrm{Ar{-}\overset{\overset{O^-}{|}}{\underset{\underset{O^-}{|}}{S}}{}^{+2}{-}\underset{\underset{O^-}{|}}{S}{}^{+}{-}Ar}$$

The data in Table I on the rate of disproportionation of p-toluenesulfinic acid at different temperatures permit one to calculate ΔH^* for the reaction. In acetic acid–0.56 M water–0.6 M sulfuric acid this turns out to be 26.4 kcal. Experiments at only two temperatures suggest it is essentially the same at 0.3 M sulfuric acid. In the study of sulfinyl sulfone decomposition[3b] the enthalpy of activation for the decomposition of p-toluenesulfinyl p-tolyl sulfone (I, Ar = p-$CH_3C_6H_4$) was measured in two solvents, dioxane and acetonitrile. It was found to be 24.8 kcal. in acetonitrile and 27.6 kcal. in dioxane. Although the variation of ΔH^* with solvent does not allow us to say unequivocally what ΔH^* is for decomposition of the sulfinyl sulfone in acetic acid, it certainly appears that almost all of the ΔH^* for the disproportionation must be due to ΔH^* for decomposition of the sulfinyl sulfone, and that the enthalpy change associated with the first equilibrium (eq. 2a) is quite small. Barring an unusually large negative entropy for reaction 2a, this means that the first equilibrium is not so unfavorable as one might have thought, and that, although the concentration of sulfinyl sulfone present at equilibrium is never large enough to cause the disproportionation to exhibit a detectable deviation from a second-order dependence on stoichiometric sulfinic acid concentration, it may under favorable circumstances amount to as much as a few per cent of the total sulfinic acid present.

This same conclusion can be reached in another way. From the mechanism shown in eq. 2a–c one can derive this expression governing the rate of disproportionation.

$$-\mathrm{d(ArSO_2H)/d}t = \frac{3k_\mathrm{d}K_\mathrm{e}(\mathrm{ArSO_2H})^2 f^2{}_{\mathrm{ArSO_2H}}}{a_{\mathrm{H_2O}} f_{*2\mathrm{b}}}$$

The measured rate constants for disproportionation, k_2, are therefore as shown in eq. 3. Independent measurement of the rate of decomposition of the sulfinyl sulfone[3b] yields a first-order rate constant, k_1, given by

$$k_2 = \frac{3k_\mathrm{d}K_\mathrm{e} f^2{}_{\mathrm{ArSO_2H}}}{a_{\mathrm{H_2O}} f_{*2\mathrm{b}}} \qquad (3)$$

$$k_1 = \frac{k_\mathrm{d} f_{\mathrm{ArSO_2SOAr}}}{f_{*2\mathrm{b}}}$$

Although ΔH^* for sulfinyl sulfone decomposition varies markedly with solvent, the rate constant k_1 apparently does not.[3b] The ratio k_2/k_1 is equal to

$$k_2/k_1 = \frac{3K_\mathrm{e} f^2{}_{\mathrm{ArSO_2H}}}{a_{\mathrm{H_2O}} f_{\mathrm{ArSO_2SOAr}}}$$

The equilibrium sulfinyl sulfone concentration can then be estimated from k_2/k_1 as follows.

$$(\mathrm{ArSO_2SOAr})_{\mathrm{equil}} = \frac{K_\mathrm{e} f^2{}_{\mathrm{ArSO_2H}}}{a_{\mathrm{H_2O}} f_{\mathrm{ArSO_2SOAr}}} (\mathrm{ArSO_2H})^2$$

$$(\mathrm{ArSO_2SOAr})_{\mathrm{equil}} = (k_2/3k_1)(\mathrm{ArSO_2H})^2 \qquad (4)$$

From the rate data for *p*-toluenesulfinyl *p*-tolyl sulfone in dioxane and acetonitrile[3b] one estimates that k_1 at 70° should be about 6×10^{-3} sec.$^{-1}$. At this temperature in acetic acid–0.56 M water–0.6 M sulfuric acid, k_2 for *p*-toluenesulfinic acid is 1.5×10^{-3} M^{-1} sec.$^{-1}$ (Table I). When inserted into eq. 4 these data lead to the conclusion that under these conditions the equilibrium concentration of sulfinyl sulfone in a solution 0.10 M in sulfinic acid will be about 8×10^{-4} M, or 8/1000ths the concentration of the sulfinic acid. This indication that the sulfinyl sulfone is not too thermodynamically disfavored in solvent systems such as the present one would seem to have significant implications for the chemistry of sulfinic acids.

Experimental

Preparation of Materials.—*p*-Toluenesulfinic,[2] *p*-chlorobenzenesulfinic,[5] *p*-bromobenzenesulfinic,[6] and *p*-methoxybenzenesulfinic[7] acids were all prepared by published procedures. β-Naphthalenesulfinic acid[8] and *p*-nitrobenzenesulfinic acid[9] were prepared from the corresponding sulfonyl chlorides by the same procedure[6] used for the *p*-bromo acid. Benzenesulfinic acid was liberated by acidification of sodium benzenesulfinate (Aldrich Chemical).

Once prepared, *p*-toluenesulfinic and *p*-methoxybenzenesulfinic acids were further purified by published procedures.[2,7] Benzenesulfinic acid was recrystallized from water, m.p. 85°. *p*-Chlorobenzenesulfinic acid was recrystallized from 1:1 ether–hexane, m.p. 94–96°. The *p*-bromo acid was purified in the same way, m.p. 112–114°. To purify β-naphthalenesulfinic acid, the crude acid obtained by acidification of an aqueous solution of the sodium salt was filtered off and dissolved in as little ether as possible. The ether solution was dried over anhydrous calcium sulfate and filtered. The acid was precipitated by addition of five times its volume of hexane to the filtrate. Another recrystallization from ether–hexane gave pure β-naphthalenesulfinic acid, m.p. 103–104.5°. A similar purification procedure, except that only three volumes of hexane were used per volume of ether, was employed for *p*-nitrobenzenesulfinic acid, m.p. 157–158°.

The purification of acetic acid and the preparation of the various stock solutions of sulfuric acid in acetic acid–water were carried out as previously described.[2,10]

Kinetic Studies.—The general procedure used for the kinetic runs was the one already described by Kice and Bowers.[2] In all cases except the *p*-nitro acid the progress of the reaction was followed by titrating the residual sulfinic acid with standard sodium nitrite solution in the manner previously described.[2]

For the *p*-nitro acid an alternate procedure involving the titration of the aliquot from the reaction with standard ceric sulfate, using a potentiometric end point,[11] was employed. The rate of oxidation of the sulfinic acid by ceric ion is enough faster than the oxidation by the same reagent of the thiolsulfonate from the disproportionation that a sufficiently sharp end point can be obtained.

Product Studies.—The stoichiometry of the disproportionation reaction was checked with both *p*-chlorobenzenesulfinic and benzenesulfinic acids. A solution of the sulfinic acid in acetic acid–water–sulfuric acid was made up and deaerated using the same procedure as in the kinetic runs. After being heated at 80° for a period of time sufficient to disproportionate most of the sulfinic acid, the solution was cooled, and an aliquot was removed and titrated for residual sulfinic acid. The remainder of the solution was then poured into ten times its volume of water, and the resulting mixture was extracted with ether. The ether extracts were washed first with aqueous sodium bicarbonate, then with water, and finally were dried over anhydrous sodium sulfate. The ether was removed and the infrared spectrum of the residue was determined. The infrared spectrum of the residue in each case was identical with the spectrum of the appropriate thiolsulfonate. In the case of the *p*-chloro compound the residue was also recrystallized from 95% ethanol to give a pure sample of *p*-chlorophenyl *p*-chlorobenzenethiolsulfonate, m.p. 137–139°, lit.[12] m.p. 136–138°. Disproportionation of 3.57 mmoles of *p*-chlorobenzenesulfinic acid gave 1.07 mmoles (90%) of crude *p*-chlorophenyl *p*-chlorobenzenethiolsulfonate, while disproportionation of 4.04 mmoles of benzenesulfinic acid gave 1.24 mmoles (92%) of crude phenyl benzenethiolsulfonate.

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Isomeric Arylstearic Acids

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Received July 27, 1964

The viscous oily arylstearic acid from oleic acid and an aromatic compound, with aluminum chloride as the condensing agent, was found by gas–liquid chromatography of alkyl aryl ketone oxidation products to be a mixture of 12 position isomers with substitution at C-6–17 in the fatty acid chain. Distribution of isomers depends in part on the relative reactivity of the particular aromatic compound. Substitution predominates at the C-17 atom and at positions near the middle of the chain. Crystalline arylstearic acids isolated in low yield from the viscous oil are the 17-aryl isomers. Phenylstearic and ethoxyphenylstearic acids formed with methanesulfonic acid as the condensing agent are also mixtures of 12 position isomers.

The Friedel-Crafts reaction of oleic acid with excess of aromatic hydrocarbon, with aluminum chloride as the condensing agent, gives an oily arylstearic acid as the main product. In the case of benzene, *o*- and *p*-xylene, and *o*- and *p*-chlorotoluene it had been possible to isolate a crystalline arylstearic acid from the main product by repeated crystallization from acetone at −20°, in yields of 1–7% for the crystals compared to 37–75% for the oil.[2] The oily arylstearic acid, in the case of benzene, has been variously considered as primarily a mixture of the 9- and 10-phenyl isomers,[3] of, if double-bond migration (hydride ion transfer) is extensive, as a mixture of several isomers[2] or a mixture in which the 17-phenyl isomer predominates.[4]

By gas–liquid chromatographic separation of alkyl aryl ketone oxidation products we have found that the oily arylstearic acid is a complex mixture of 12 position isomers, with the aromatic group attached at positions 6–17 on the C_{18} fatty acid chain. The crystalline

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