N-dimethylamino-10(9)-hydroxystearic acid is attributed to the higher basic strength of the dimethylamino moiety, which would enhance salt formation and, consequently, solubility in water. The surface-active properties of the compounds are to be expected in view of their salt formation and structural relationship to amine salts of long-chain fatty acids in which properly balanced hydrophilic and hydrophobic groups are present. Sinking time measurements on canvas disks immersed in aqueous solutions of these substances show that the canvas is penetrated rapidly but not nearly so rapidly as in aqueous solutions of the sodium salt of dioctyl sulfosuccinate of the same concentration.

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Further Aspects of the Schmidt Reaction

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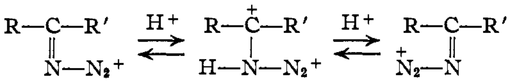
The Schmidt reaction of *p*-methylbenzophenone has been studied both by Smith and Horwitz[1] and Sherk, *et al.*[2] Smith and Horwitz, using trichloroacetic acid as the solvent and only a relatively small amount of sulfuric acid as the catalyst, obtained benz-*p*-toluidide and *p*-toluanilide in a ratio of 54:46. Sherk, *et al.*, by passing hydrogen azide slowly through a mixture of the ketone in an excess of sulfuric acid, with benzene as the solvent, obtained benz-*p*-toluidide in a yield of 82%. The divergent results suggested that product ratios might be very sensitive to the experimental conditions in this reaction.

Inasmuch as the Schmidt reaction of aldehydes gives rise to different product ratios as the sulfuric acid concentration is altered,[3] it seemed reasonable to suppose that the same might hold true for the Schmidt reaction of ketones. Specifically, it was thought that the geometrically isomeric cations, I and III, first proposed by Smith[4] as product controlling intermediates (*trans* rearrangement) in the Schmidt reaction of ketones, might undergo an acid-catalyzed interconversion, possibly *via* the conjugate acid, II. As Smith and Horwitz[1] have suggested, it is possible for "migration aptitudes"[5] to influence the product ratio, if the rate of interconversion of the *syn* and *anti* forms of the intermediate compares in magnitude with the rate of migration of either R (phenyl) or R′ (*p*-tolyl). In this connection, it has been established[6,7] that in the Schmidt reaction of 1-phenyl-1-*p*-tolylethylene, the *p*-tolyl group migrates about five times as fast as the phenyl group.



I II III

The Schmidt reaction of *p*-methylbenzophenone has been repeated under two different sets of conditions in order to determine any possible change in product ratio with increase in the sulfuric acid concentration. By use of an 8:1 molar ratio of sulfuric acid to the ketone, there was obtained a product ratio of 51% benz-*p*-toluidide to 49% *p*-toluanilide. The conditions of Sherk, *et al.*,[2] were employed in a second run. Here also there was obtained a ratio of benz-*p*-toluidide to *p*-toluanilide of 53:47. Since our method of analysis (see the experimental section) is probably accurate to not more than ± 5%, these results are in agreement with that of Smith and Horwitz,[1] who used a different method of analysis of the products.

Since the *p*-anisyl group migrates at a faster rate than the *p*-tolyl group in the Schmidt reaction of 1,1-diarylethylenes,[6,7] and since the methoxyl group is a stronger base strengthening substituent than the methyl group, both effects should enhance the possibility of a change in product ratio with change in sulfuric acid concentration in the Schmidt reaction of *p*-methoxybenzophenone. Even in this case, however, in the presence of a large excess of sulfuric acid, there was obtained a ratio of benz-*p*-anisidide to anisanilide of 66:34, in substantial agreement with the ratio of 61:39 reported by Smith and Horwitz.[1,8] Hence we conclude that a change in sulfuric acid concentration does not affect product ratios in the Schmidt reaction of *p*-substituted benzophenones.

Prior to the publication of Boyer's[9] work on conjugate addition reactions of hydrazoic acid, we had investigated the Schmidt reaction of 2-vinylpyridine. The rearrangement usually exhibited by arylethylenes was not detected, and only 1-α-pyridyl-2-azidoethane was isolated, the product obtained by Boyer in the absence of sulfuric acid.

Experimental[10]

Azeotropic Esterification of a Known Mixture of *p*-Toluic Acid and Benzoic Acid.—To a solution of 6.80 g. (0.05 mole) of *p*-toluic acid and 6.10 g. (0.05 mole) of benzoic acid in 75 cc. of absolute ethanol and 75 cc. of benzene was added 1 cc. of concentrated sulfuric acid. The mixture was slowly distilled through an 18″ electrically heated Vigreux column, to which an azeotropic head was attached. When the temperature of the overhead vapor reached 72°, the distillation was stopped and the remaining alcohol and benzene removed *in vacuo*.

A small amount of water was added to the residual mixture, which was then neutralized with powdered sodium carbonate. The mixture was extracted with ether, dried over anhydrous sodium sulfate, filtered and the ether evaporated. Distillation of the residue through a Todd column

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[1] P. A. S. Smith and J. P. Horwitz, THIS JOURNAL, **72**, 3718 (1950).

[2] J. K. Sanford, F. T. Blair, J. Arroya and K. W. Sherk, *ibid.*, **67**, 1941 (1945).

[3] W. E. McEwen, W. E. Conrad and C. A. VanderWerf, *ibid.*, **74**, 1168 (1952).

[4] P. A. S. Smith, *ibid.*, **70**, 320 (1948).

[5] There is growing evidence that the term "migratory aptitude" has little meaning. A superior interpretation is based on the concept of a driving force due to the participation of the migrating group in the attainment of the transition state. See S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber and J. Corse, *ibid.*, **74**, 1113 (1952), and other recent papers by Winstein, *et al.*, for the elaboration of this theory.

[6] W. E. McEwen, M. Gilliland and B. I. Sparr, *ibid.*, **72**, 3212 (1950).

[7] W. E. McEwen and N. B. Mehta, *ibid.*, **74**, 526 (1952).

[8] *Cf.* P. A. S. Smith and B. Ashby, *ibid.*, **72**, 2503 (1950).

[9] J. H. Boyer, *ibid.*, **73**, 5284 (1951).

[10] Analyses by Oakwold Laboratories, Alexandria, Va. All m.ps. are corrected.

afforded 6.70 g. (89%) of ethyl benzoate, b.p. 95–96° (15 mm.), $n^{20}D$ 1.5048; reported b.p. 87° (10 mm.),[11] $n^{20}D$ 1.5057.[12] A second fraction consisted of 7.40 g. (90%) of ethyl *p*-toluate, b.p. 107° (11 mm.), $n^{20}D$ 1.5082; reported b.p. 110°(12 mm.),[13] $n^{18}D$ 1.5089.[13] Acenaphthene was used as a "chaser."

Reaction of Hydrazoic Acid with *p*-Methylbenzophenone. A.—To a mixture of 51.5 cc. (0.92 mole) of concentrated sulfuric acid, 19.6 g. (0.1 mole) of *p*-methylbenzophenone and 200 cc. of benzene was added 7.8 g. (0.12 mole) of sodium azide, in small portions, during two hours, at room temperature. The mixture was then warmed to 45–55° until the theoretical volume of nitrogen had evolved (8 hours). The reaction mixture was poured on crushed ice, partially neutralized with 10% sodium hydroxide solution, then made basic with saturated sodium carbonate solution. The mixture was extracted with ether, and the ether solution washed with dilute hydrochloric acid and 10% sodium carbonate solution. The ether solution was dried over anhydrous magnesium sulfate, filtered and the ether evaporated. There remained 18.7 g. of solid material, which was hydrolyzed by refluxing for five days with a mixture of 400 cc. of glacial acetic acid and 100 cc. of 40% hydrobromic acid. The mixture was diluted and extracted with ether. The ether solution was washed with water, dried over anhydrous sodium sulfate, filtered and the ether evaporated. There remained 12.8 g. of mixed solids containing benzoic and *p*-toluic acids.

The acids were esterified and fractionated as described above for the known mixture. There was obtained 4.00 g. (31%) of ethyl benzoate, b.p. 96–97° (17 mm.), $n^{20}D$ 1.5066 and 4.25 g. (33%) of ethyl *p*-toluate, b.p. 115–116° (17 mm.), $n^{20}D$ 1.5090.

B.—The procedure of Sherk, *et al.*,[2] was employed on 19.6 g. (0.1 mole) of *p*-methylbenzophenone. The reaction mixture was handled as in A. There was obtained 6.2 g. (41.3%) of ethyl benzoate, b.p. 96–98° (18 mm.), $n^{20}D$ 1.5048 and 6.0 g. (36.6%) of ethyl *p*-toluate, b.p. 118–119° (19 mm.), $n^{20}D$ 1.5083.

Schmidt Reaction of *p*-Methoxybenzophenone.—*p*-Methoxybenzophenone, 22.7 g. (0.1 mole), was reacted in the same manner as that described for *p*-methylbenzophenone, part A, except that the temperature was maintained at 25–30° throughout the reaction, and a benzene solution of hydrazoic acid was used instead of sodium azide. There was a large amount of tar formed, which was ether insoluble. From the ether solution there was obtained 18.7 g. of mixed neutral solids. On digestion with a small amount of ether, 8.0 g. of *p*-methoxybenzophenone was recovered from the ether solution. The remaining 10.7 g. of neutral solids was refluxed for five days in a solution of 90 g. of potassium hydroxide in 500 cc. of ethanol. The ethanol was distilled *in vacuo*, the residual solid dissolved in water and extracted with ether. Addition of hydrochloric acid to the aqueous layer precipitated the carboxylic acids, which were taken up in ether and dried over anhydrous sodium sulfate. Evaporation of the ether afforded 3.3 g. of mixed acids.

Anal. Found: methoxyl, 6.83, 7.04.

The analytical results indicate the presence of about 34% of *p*-anisic acid and 66% of benzoic acid.

1-α-Pyridyl-2-azidoethane.—Under the same conditions as employed in the Schmidt reaction of unsymmetrical diarylethylenes,[6] there was obtained a 17% yield of 1-α-pyridyl-2-azidoethane, b.p. 91° (8.5 mm.), 84–85° (4.5 mm.), 58° (0.6 mm.). The same substance was obtained in 97% yield by use of Boyer's procedure.[9]

Mercuric Chloride Addition Product.—Crystallized from 95% ethanol, the colorless addition product melted at 117°.

Anal. Calcd. for $C_7H_8N_4HgCl_2$: C, 20.13; H, 1.45; N, 13.41. Found: C, 19.91, 19.64; H, 1.60, 1.75; N, 13.14.

Catalytic Reduction of 1-α-Pyridyl-2-azidoethane.—A solution of 8.90 g. (0.06 mole) of 1-α-pyridyl-2-azidoethane in 30 cc. of absolute ethanol was hydrogenated at three atmospheres in a Parr apparatus for 24 hours over 0.10 g. of platinum oxide catalyst. The solution smelled of ammonia. Distillation afforded 3.1 g. (35%) of β-2-pyridylethylamine, b.p. 76–78° (4 mm.), reported[14] b.p. 92–93° (12 mm.).

Picrate.—Yellow needles were obtained from ethanol, m.p. 213–215°; reported[14] 215–216°.

Dihydrochloride.—Colorless crystals were obtained, m.p. 186–189°; reported m.p. 185–186°,[15] 189°.[16]

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[11] I. M. Heilbron and H. M. Bunbury, "Dictionary of Organic Compounds," Vol. II, Oxford University Press, New York, N. Y., 1936, p. 20.

[12] J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publishing Co., Inc., New York, N. Y., 1950, p. 484.

[13] Reference 11, Vol. III, p. 777.

[14] K. Loffler, *Ber.*, **37**, 161 (1904).

[15] L. A. Walter, W. H. Hunt and R. J. Fosbinder, THIS JOURNAL, **63**, 2771 (1941).

[16] F. K. Kirchner, J. R. McCormick, C. J. Cavallito and L. C. Miller, *J. Org. Chem.*, **14**, 388 (1949).

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Molecular Refractions of the SO_3 and SO_2Cl Groups in *p*-Ethylbenzenesulfonyl Chloride and the Methyl, Ethyl and *n*-Butyl Esters of *p*-Ethylbenzenesulfonic Acid

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During a study of *p*-ethylbenzenesulfonyl chloride and its derivatives we have prepared three new esters derived from the sulfonyl chloride and obtained previously unrecorded constants for the compounds. The density and refractive index data gave molecular refraction values for the SO_3 and SO_2Cl groups showing deviations from the rather narrow range of values previously recorded for these groups in other compounds. We wish to record at this time the results of these observations.

p-Ethylbenzenesulfonyl chloride was prepared by the action of phosphorus pentachloride on the crude sulfonic acid.[2] The sulfonic acid was prepared by reaction of excess ethylbenzene with concd. sulfuric acid under conditions which permitted removal of the water formed during the reaction as the ethylbenzene–water azeotrope. The reaction was continued until the theoretical amount of water was collected. The sulfonyl chloride was obtained in 47% yield based on the amount of sulfuric acid used. It was characterized as the previously described[2b,2d,3] amide, m.p. 108°.

The fact that the amide prepared from this sulfonyl chloride consists chiefly of the isomer which melts at 108° is considered good evidence that the material is substantially pure *p*-ethylbenzenesulfonyl chloride. Also, it is known that mixtures of ortho and para isomers are obtained from low temperature (0°) sulfonations[3b] and that the ortho isomer rearranges to the para isomer at 100°.[2d] The pure amide of the ortho isomer melts at 126°.[3b] The sulfonation was run at 115° in our experiments. The crude amide, m.p. 97–106°, was obtained in 95% yield from the sulfonyl chloride.

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[2] (a) P. Chruschtschow, *Ber.*, **7**, 1164 (1874); (b) L. Semptowski, *ibid.*, **22**, 2673 (1889); (c) A. Tohl and O. Eberhard, *ibid.*, **26**, 2940 (1893); (d) G. T. Moody, *ibid.*, **29R**, 663 (1896).

[3] (a) J. Moschner, *ibid.*, **34**, 1257 (1901); (b) R. Fricke and G. Spilker, *ibid.*, **58**, 1589 (1925).