butane (V) from L(−)-*trans*-2,3-iminobutane and ethylamine, Fig. 5, was established as *erythro* by ethylation to *meso*-2,3-bis-(ethylamino)-butane (VI). Ditosylation of VI gave *meso*-2,3-bis-(N-ethyl-*p*-toluenesulfonamido)-butane (VII), m.p. 240.3–241.8°, mixed m.p. 240.6–242.0°, with *meso*-2,3-bis-(N-ethyl-*p*-toluenesulfonamido)-butane, m.p. 241.8–243.3°, from the tosylation of *meso*-2,3-bisethylaminobutane. Since a Walden inversion is proven by the *erythro*-configuration, the compound must belong to the D-family.

The (+)-3-ethylamino-2-butanol from D(+)-*trans*-2,3-epoxybutane and ethylamine is L(+)-*erythro*-3-ethylamino-2-butanol by relationship with L(+)-*erythro*-3-diethylamino-2-butanol of known configuration, $[\alpha]^{25}D$ +95.5°. The hydrochloride of this had m.p. 130.4–131.2°. The (+)-3-diethylamino-2-butanol from monoethylation of (+)-3-ethylamino-2-butanol had $[\alpha]^{25}D$ +91.8°. Its hydrochloride had m.p. 130.2–131.2°, mixed m.p. with authentic sample, 130.3–131.1°.

Derivatives.—Diacetyl and ditosyl derivatives are prepared as previously described[5] except that triethylamine usually replaces pyridine. Darkening is much less, and during tosylation triethylammonium chloride usually crystallizes out. With imines this prevents any replacement reaction by chloride ion. In the preparation of *p*-nitrobenzoyl derivatives, *p*-nitrobenzoic acid is removed with aqueous sodium carbonate. The hydrochlorides are prepared by the addition of 2 *M* hydrogen chloride in absolute ether to a cold solution of the base in absolute ether. The salt precipitates. The oxalates are prepared by mixing ether solutions of the base and of anhydrous oxalic acid in equivalent amounts. The salt separates immediately, essentially quantitatively and quite pure.[25]

Zinc Chloride Complex.—To a solution of 0.034 g. (0.00024 mole) of D(−)-*threo*-2,3-bis-(ethylamino)-butane in 2.0 ml. of 95% ethanol (α −1.63°) was added 0.10 ml. of 2.5 *M* zinc chloride (0.00025 mole) in 95% ethanol. Crystallization occurred almost immediately. The mixture stood overnight, the mother liquor (α −0.25°) was removed. The crystals were washed with two 0.5-ml. portions of 95% ethanol and dried; weight of product, 0.0426 g. (0.00015 mole) of colorless prisms, soluble in N,N-dimethylformamide and dilute nitric acid, essentially insoluble in water and most organic solvents.

(25) M. G. Ettlinger, THIS JOURNAL, **72**, 4792 (1950).

PASADENA 4, CALIF.

[CONTRIBUTION FROM AVERY LABORATORY, THE UNIVERSITY OF NEBRASKA]

Polycarboxylic Esters as Mesylation Products of Phenolic Acids[1,2]

BY J. H. LOOKER, CHARLES H. HAYES AND DONALD N. THATCHER

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Reaction of several hydroxybenzoic acids with methanesulfonyl chloride in pyridine has given complex products containing carboxylic esters, and in no instance was the methanesulfonic ester of the phenolic acid an isolable product. Trisalicylide was isolated as a crystalline mesylation product of salicylic acid.

The reaction of phenolic compounds with aromatic[3] and aliphatic[4] sulfonyl chlorides in pyridine to give sulfonic esters is well known. The nature of the products from phenolic acids in this reaction, however, has not been reported previously, although benzenesulfonic esters have been obtained in certain instances by reaction of benzenesulfonyl chloride with the phenolic acid in aqueous alkali.[5] The present paper demonstrates clearly that phenolic acids do not give simple sulfonic esters upon mesylation[6] in pyridine but instead complex products which contain polycarboxylic esters.

In Table I are given certain properties of the crude, water-insoluble mesylation products studied. The wide melting ranges are in distinct contrast to the sharp melting points usually observed for even crude mesylation products of simple phenols.[4] The slight solubility of all crude products in dilute sodium bicarbonate solution precludes the possibility that they are the simple mesyloxy acid, and this has been confirmed in the case of the monohydroxybenzoic acids by synthesis and characterization of the mesyloxy acid. Acidification of the bicarbonate extracts gave materials which melted over wide ranges. The infrared absorption spectra of all products show a prominent band in the region 1732–1755 cm.$^{-1}$, which is attributed to the presence of ester carbonyl groups.[7] A band in the vicinity of 1690 cm.$^{-1}$ is considered evidence for a carboxyl group in the mesylation products of *m*- and *p*-hydroxybenzoic and of 3,5-diiodo-4-hydroxybenzoic acids.[7] Definite bands in the latter

TABLE I

PROPERTIES OF CRUDE MESYLATION PRODUCTS

Phenolic acid reacted	Melting range, °C.	% soln., 5% $NaHCO_3$	Ester C=O, cm.$^{-1}$[a]	Sulfur, %
p-Hydroxybenzoic	175–250	8	1740	4.29[b]
m-Hydroxybenzoic	115–140	8	1732	3.90[b]
Salicylic	140–175	<1	1739	0.43[b]
3,5-Diiodo-4-hydroxybenzoic	>285	9	1743	0.78[c,d]
Gallic	110–250	2	1755	15.86[e,f]

[a] In Nujol mull. [b] Mesyloxybenzoic acids contain 14.83% S. [c] Mesyloxy acid contains 6.85% S. [d] 0.43% N present. [e] Trimesyloxy acid contains 23.78% S. [f] 1.66% N present.

(1) Taken in part from the M.S. Theses of Donald N. Thatcher, University of Nebraska, 1952, and Charles H. Hayes, University of Nebraska, 1955.

(2) Presented in part at the 16th Midwest Regional Meeting of the American Chemical Society, Omaha, Nebr., November 4, 1954; see Abstracts of Papers, p. 52.

(3) For leading references see (a) R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944); (b) R. S. Tipson, *Adv. in Carbohydrate Chem.*, **8**, 108 (1953); (c) D. D. Reynolds and W. O. Kenyon, THIS JOURNAL, **72**, 1597 (1950), and preceding papers.

(4) For leading references to mesyl esters, see J. H. Looker, *J. Org. Chem.*, **17**, 510 (1952).

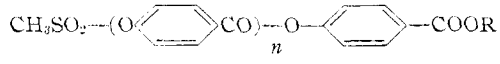
(5) The benzenesulfonic ester of salicylic acid has been prepared thus by M. Georgesco, *Bul. soc. Romane Stiinte*, **8**, 668 (1899–1900); *Chem. Zentr.*, **71**, I, 543 (1900). There is a report that mesyl chloride does not appear to react to any extent with salicylic acid in 1 *N* sodium hydroxide: B. C. Saunders, G. J. Stacey and I. G. E. Wilding, *Biochem. J.*, **36**, 374 (1942).

(6) Mesyl (methanesulfonyl or methylsulfonyl) denotes the CH_3SO_2– group, mesyloxy (methane- or methylsulfonoxy, or methane- or methylsulfonyloxy) the CH_3SO_3– group, and mesylation a reaction with mesyl (methanesulfonyl) chloride; see reference 3b, p. 109.

(7) F. A. Miller in "Organic Chemistry," Vol. III, edited by H. Gilman, John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 140–141, 143–150.

region are missing in the spectra of the corresponding products from salicylic and gallic acids. Attempts were made to isolate pure products from all mesylation mixtures, but only in the case of salicylic acid did a crystalline product prove isolable. More complete characterization has been restricted to the mesylation products of *p*-hydroxybenzoic and salicylic acids.

Since attempts to isolate crystalline material from the mesylation product of *p*-hydroxybenzoic acid were unsuccessful, the crude reaction product (I) was investigated. Although insoluble in sodium bicarbonate, compound I dissolved in dilute sodium hydroxide with decomposition to yield *p*-hydroxybenzoic acid as the sole isolable material. *p*-Mesyloxybenzoic acid would not be expected under these conditions because of its known lability in strong base[8] but has been obtained in low yield by treatment of I with 100% sulfuric acid. These chemical properties, combined with infrared spectral data and low sulfur content, indicated strongly the possibility that compound I was a mixture of depside-type compounds,[9] in which the phenolic hydroxyl was mesylated at some stage of the reaction with mesyl chloride. In addition, concurrently with the observations outlined, it was noted that a mixture of acetic acid and mesyl chloride in pyridine converted quercetin 3,3′,4′,7-tetramethyl ether to 5-acetoxy-3,3′,4′,7-tetramethoxyflavone, instead of the sulfonic ester.[10] Hence, it seemed reasonable to expect a mixture of *p*-hydroxybenzoic acid and mesyl chloride in pyridine to esterify phenolic hydroxyl groups of unreacted phenolic acid molecules to form depside derivatives.



Ia, R = H
II, R = H, n = 1
III, R = H, n = 2
IV, R = $CH_2C_6H_5$, n = 1
V, R = $CH_2C_6H_5$, n = 2

More complete characterization of I and Ia, an ethyl acetate-insoluble fraction obtained from I, has been effected by comparison of the infrared spectra with the corresponding spectra of the model depside derivatives *p*-(*p*′-mesyloxybenzoyloxy)-benzoic acid (II) and *p*-[*p*′-(*p*″-mesyloxybenzoyloxy)-benzoyloxy]-benzoic acid (III), prepared by a method outlined in the following paper. In Table II are shown positions of strong and medium bands in the region 1600-2000 cm.$^{-1}$ in the spectra of I, Ia, II and III, the benzyl esters of II and III (IV and V, respectively), *p*-mesyloxybenzoic acid (VI) and *p*-mesyloxybenzoic anhydride (VII, prepared as outlined in following paper). The data of Table II confirm the presence of carboxyl and carboxylic ester groups in I and Ia and indicate the absence of the carboxylic anhydride grouping. Comparison of complete infrared spectra of I and Ia with the spectrum of III (Experimental) reveals a marked similarity, although the spectrum of III contains more bands. The carboxyl band in the vicinity of 1685 cm.$^{-1}$ is quite characteristic in the spectra of Ia and III, showing at *ca.* 1700 cm.$^{-1}$ a prominent shoulder which does not appear in the spectra of II and VI. The combined chemical, analytical and spectral data presented for the mesylation product of *p*-hydroxybenzoic acid indicate it to be a mixture of depside derivatives of the type shown in Ia. The apparent value of n in Ia is 3, based on sulfur analysis, which constitutes a convenient end group assay.

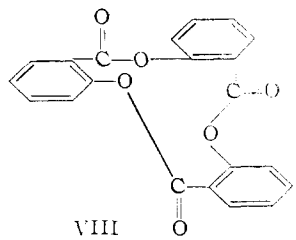
TABLE II

INFRARED SPECTRA[a] OF DEPSIDE DERIVATIVES

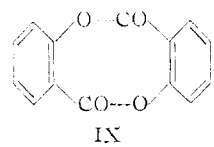
Compound	Absorption bands, cm.$^{-1}$ Anhyd. C=O	Ester C=O	Acid C=O	Subst. phenyl
I	..	1740	1692	1608
Ia	..	1732	1684	1598
II	..	1730–1740	1680	1603
III	..	1742	1690	1602
IV	..	1732(1720)[b]	..	1603
V	..	1732(1727)[b]	..	1601
VI	..	.....	1685	1606
VII	1786	.....	..	1601

[a] In Nujol mulls. [b] Denote weak band.

On the basis of low sulfur content, absence of the carboxyl band at *ca.* 1685 cm.$^{-1}$ in the infrared spectrum and slight solubility in dilute sodium hydroxide, the salicylic acid mesylation product appeared to consist of cyclic esters[11] or linear polymers of rather high molecular weight or a mixture of these types. A fractional crystallization procedure gave crystalline trisalicylide VIII[12] in approximately 1% yield as the only demonstrably homogeneous product isolable. Disalicylide IX may have been present but was not obtained in pure form. The major products were amorphous and upon attempted purification showed a tendency to form viscous oils which hardened to opaque glasses. Formation of VIII can be explained most simply by an initial reaction of mesyl chloride with the carboxyl group of salicylic acid to give a highly reactive mixed carboxylic-sulfonic anhydride. The latter could then react with phenolic hydroxyl groups directly, or indirectly, either *via* salicylic anhydride[13] by reaction with carboxyl groups of salicylic acid or *via* salicyloyl chloride by reaction with pyridinium chloride,[14] to give salicyloylsalicylic acid (Diplosal).



VIII



IX

(8) J. H. Looker and D. N. Thatcher, *J. Org. Chem.*, **19**, 784 (1954).

(9) For leading references to depside chemistry, see C. J. Cavallito and J. S. Buck, THIS JOURNAL, **65**, 2140 (1943).

(10) J. H. Looker and F. C. Ernest, *ibid.*, **76**, 294 (1954).

(11) Formation of salicylides (not further identified) as by-products in the reaction of sodium salicylate with tosyl chloride in benzene has been reported: German Patent 123,052; *Chem. Zentr.*, **72**, II, 518 (1901).

(12) In the earlier literature, this substance was called β-disalicylide. For molecular weight data supporting formulation as trisalicylide and leading references in the salicylide field, see W. Baker, W. D. Ollis and T. S. Zealley, *J. Chem. Soc.*, 201 (1951).

(13) This suggestion is based on the isolation of carboxylic anhydrides from reaction of benzene- and *p*-toluenesulfonyl chloride with salts of carboxylic acids; see reference 11.

(14) This speculation involves an expected similarity in the chemistry of mixed carboxylic-sulfonic anhydrides (*i.e.*, acyl or aroyl meth-

Salicyloylsalicylic acid would be expected to react by the same general scheme with additional salicylic acid to give disalicyloylsalicylic acid, which then could undergo ring closure under the influence of mesyl chloride–pyridine to give trisalicylide.

In general, formation of the mesylation products observed in the present study appears to involve always an intermediate mixed carboxylic–sulfonic anhydride, which acts as an aroylating agent in the presence of pyridine. A complex process of uncontrolled aroylation of phenolic hydroxyl groups then results to give polyesters. *o*-, *m*- and *p*-mesyloxybenzoic acids are stable in pyridine, thus precluding rearrangement as a source of reactive intermediates. *p*-Mesyloxybenzoic acid is stable in pyridine in the presence of *p*-hydroxybenzoic acid, indicating that mixed anhydrides, or other reactive intermediates, are not formed in this case by interaction of the mesyloxy acid with unreacted starting material. The size of the polymeric esters from *m*- and *p*-hydroxybenzoic acids is probably limited by the quantity (10% in excess of theoretical for mesylation of the phenolic hydroxyl) of mesyl chloride present and by formation of terminal mesyloxy groups. In the mesylation of salicylic acid, ring closure to give a mixture of salicylides is a possible additional factor controlling the size of the ester.

It is apparent that the mesyloxybenzoic acids cannot be prepared from the phenolic acid by the action of mesyl chloride in pyridine. *o*-Mesyloxybenzoic acid has been obtained by dichromate oxidation of the mesylation product of salicylaldehyde, presumably *o*-mesyloxybenzaldehyde. *m*-Mesyloxybenzoic acid has been obtained by the slow air-oxidation of the oily mesylation product of *m*-hydroxybenzaldehyde.

Acknowledgment.—The authors wish to express their gratitude to the Research Corporation for financial support of part of this investigation. J.H.L. is indebted to the du Pont Co. for a Faculty Summer Research Fellowship which made possible his participation in the experimental part of this work. Infrared absorption spectra were determined by Dr. W. Rook, Dr. W. C. Robison, Miss E. Shelton and Mr. E. Magnuson.

Experimental

Melting points are uncorrected, except where otherwise noted. The infrared absorption spectra of Nujol mulls were recorded with a Perkin-Elmer model 21 spectrophotometer using an NaCl prism. Elementary quantitative analyses are by Micro-Tech Laboratories, Skokie, Ill.

Mesylation of *p*- and *m*-Hydroxybenzoic Acids.—To a solution of 11.15 g. (0.081 mole) of *p*-hydroxybenzoic acid in 75 ml. of pyridine, previously cooled to 0°, was added a 10.1-g. (0.088 mole) quantity of mesyl chloride in 5–6 portions under ice-cooling. After standing 16 hr., the reaction mixture was poured into 750 ml. of water containing 75 ml. of concd. hydrochloric acid. The precipitated crude product was collected, washed well with water and air-dried, yield 10.0 g. The product then was washed with boiling water and dried in a vacuum desiccator to constant weight; yield 9.1 g. of I, melting 175–250°. Qualitative analysis showed the presence of sulfur and absence of nitrogen and halogen. Further purification of I was effected by repeated extraction with ethyl and butyl acetate, with retention of the insoluble fraction (Ia).

Anal. Calcd. for $C_{36}H_{24}O_{18}S$: S, 4.60. Found: S, 4.68.

Medium to strong infrared absorption bands were displayed by Ia at 1732, 1684, 1598, 1503, 1270, 1201, 1165, 1150, 1088, 1063, 1017, 971, 883, 788, 762 and 682 cm.$^{-1}$ and weak bands at 1416, 1100, 864, 836, 780, 757, 667 and 662 cm.$^{-1}$.

The crude mesylation product I showed medium to strong infrared absorption bands at 1740, 1692, 1608, 1512, 1265, 1205, 1160, 1153, 1060, 1016, 970, 877, 787, 760 and 685 cm.$^{-1}$ and weak bands at 1422, 1102, 887 and 663 cm.$^{-1}$.

The model depside III displayed medium to strong infrared absorption bands at 1742, 1690, 1603, 1510, 1275, 1206, 1170, 1160, 1088, 1075, 1020, 974, 883, 792, 763 and 680 cm.$^{-1}$ and weak bands at 1505, 1436, 1418, 1335, 1317, 1298, 1178, 1102, 860, 838, 833, 830, 814, 755 and 660 cm.$^{-1}$.

m-Hydroxybenzoic acid (11.15 g., 0.081 mole) was mesylated by the identical procedure to give 8.7 g. of product insoluble in boiling water and melting 115–140°. Qualitative analysis showed presence of sulfur and absence of nitrogen and halogen.

Gallic acid and 3,5-diiodo-4-hydroxybenzoic acid were mesylated using the general conditions outlined above except that the theoretical quantity (for three hydroxyl groups) of mesyl chloride reacted with gallic acid.

Isolation of Trisalicylide from the Mesylation Product of Salicylic Acid.—Salicylic acid (11.15 g., 0.081 mole) was mesylated by the procedure outlined above. Pyridine-insoluble material (fraction D) was removed by filtration, transferred to a vacuum desiccator and retained. The pyridine-soluble fraction was isolated in the usual manner by pouring the reaction mixture into dilute hydrochloric acid; yield 6.66 g., melting 140–175°. A preliminary fractionation of this material was effected as follows: Solution of the total crude product in chloroform at room temperature, with removal of two small amorphous fractions by filtration, followed by slow evaporation of the filtrate at room temperature gave crystalline fraction A, 0.66 g., melting 180–198°. Evaporation of the chloroform mother liquor to dryness gave a partly crystalline residue. The latter was extracted with 150 ml. of boiling glacial acetic acid; yield of insoluble material (fraction B), 2.56 g., melting 110–125°. Dilution of the acetic acid extract with 150 ml. of water gave 1.38 g., fraction C, melting 160–185°.

Slow evaporation of a chloroform solution of fraction A gave 180 mg. of crystalline material, m.p. 211–216° (in bath preheated to 195°), which is in fair agreement with previously reported values for the m.p. of *cis*-disalicylide, which range from 210–212°[15] and 213°[16,17] to 213–218°[18]; Baker, *et al.*, however, confirm[12] a value of 234°[19] for pure *cis*-disalicylide (also called salosalicylide and α-disalicylide). Apparently this fraction was not homogeneous, since on recrystallization from benzene a 76-mg. quantity of crystalline material melting instantly in a bath preheated to 200° was obtained.

Anal. Calcd. for $(C_7H_4O_2)_x$: C, 70.00; H, 3.36. Found: C, 69.98; H, 3.48.

Fraction B did not yield any appreciable quantity of crystalline material, even after repeated attempts at crystallization from chloroform and ethanol. Oils were obtained from chloroform, which were transformed to friable, opaque glasses in ethanol.

Fraction C was washed with 56 ml. of 2 *N* sodium hydroxide, and the insoluble fraction (0.90 g.) recrystallized from benzene to yield 300 mg. of material, m.p. 192–197°. Recrystallization from ethanol gave 120 mg. of trisalicylide, m.p. 201.5–203.5° (in bath preheated to 190°). Addition of isoöctane to the benzene mother liquor afforded an additional 24 mg. of trisalicylide.

By dividing the dried pyridine-insoluble fraction D (22.24 g.) equally, treating half with 500 ml. of water and weighing insoluble material, and the other half with 250 ml. of acetone and weighing insoluble material, fraction D was found to contain 1.32 g. of water-insoluble material melting 125–170°, and 12.14 g. of acetone-insoluble salt, m.p. 181–185°. The latter is very probably impure pyridinium methane-

anesulfonates) and the more reactive alkyl and aryl methanesulfonates. Authentic examples of the reaction of pyridinium chloride with tosyl esters to give chloro derivatives are presented by K. Hess and H. Stenzel, *Ber.*, **68**, 981 (1935). Additional data are given in reference 3.

(15) R. Anschütz and K. Riepenkröger, *Ann.*, **439**, 1 (1924).
(16) R. Anschütz, *Ber.*, **52**, 1875 (1919).
(17) L. Anschütz and R. Neher, *J. prakt. Chem.*, **159**, 264 (1941).
(18) L. Anschütz and R. Neher, *Ber.*, **77**, 634 (1944).
(19) G. Schroeter, *ibid.*, **52**, 2224 (1919).

sulfonate. (lit. m.p.[20] 185°). The total water-insoluble fraction was extracted successively with two 125-ml. portions of boiling ethanol. The first extract afforded 130 mg. of crystalline trisalicylide, m.p. 202–203.5°, unchanged upon further crystallization from ethanol with recovery of 110 mg.

The combined trisalicylide fractions (330 mg.) were recrystallized from 95% ethanol; yield 274 mg. (*ca.* 1%), m.p. 202–203.5° in bath preheated to 190° [lit. m.p.'s 200° (cor.),[12] 199–200°,[16,17] 200–201°,[21,22] 197–203°[23]]. In a preheated bath at 202.5°, the sample melted completely and instantly; in a bath preheated to 200°, the sample melted only partially at 202.5°. Further crystallization from benzene did not raise the m.p.

Anal. Calcd. for $(C_7H_4O_2)_x$: C, 70.00; H, 3.36. Found: C, 70.35; H, 3.42.

In Nujol mull, the substance showed a strong infrared absorption band due to the ester carbonyl at 1725 cm.$^{-1}$ and a weak band at 1738 cm.$^{-1}$. In carbon tetrachloride solution, the compound showed a strong band at 1744 cm.$^{-1}$. Corresponding literature values[24] for trisalicylide in Nujol mull are 1730 and 1743 cm.$^{-1}$ and in carbon tetrachloride 1749 cm.$^{-1}$. The literature values[24] for *cis*-disalicylide in Nujol are 1751 and 1764 cm.$^{-1}$ and in carbon tetrachloride 1773 cm.$^{-1}$.

Upon treating 150 mg. of trisalicylide in chloroform solution with aniline according to the general conditions of Anschütz and Riepenkröger,[15] there was recovered a 140-mg. quantity of trisalicylide, which after recrystallization from 95% ethanol and benzene gave m.p. and mixed m.p. 198.5–200.5° (cor.). Disalicylide under these conditions gives salicylolylsalicylanilide, m.p. 160°.[25] Heating 200 mg. of trisalicylide with aniline under reflux under the conditions of Anschütz and Riepenkröger[15] gave 290 mg. (82%) of salicylanilide, m.p. and mixed m.p. 136–138° (cor.) [lit. m.p.'s from 133°[15] to 136–137°[26]].

Addition of 33.45 g. of salicylic acid in 100 ml. of pyridine, precooled to 0°, in portions over 1 hr. to a solution of 21 ml. of mesyl chloride in 200 ml. of pyridine at 0°, permitting the mixture to stand 24 hr., and isolation of the crude product in the usual manner gave 29.7 g. of material melting 80–120°. The crude product was virtually insoluble in 5% sodium bicarbonate and 5% sodium carbonate and after washing with 5% sodium hydroxide gave 24.6 g. of alkali-insoluble product. The only crystalline material isolable was trisalicylide (*ca.* 450 mg.).

***o*-Mesyloxybenzoic Acid (*o*-Methanesulfonoxybenzoic or *o*-Methanesulfonyloxybenzoic Acid).**—To a solution of 26 g. of salicylaldehyde in 125 ml. of pyridine was added under ice-cooling a 29-g. quantity of mesyl chloride. After standing at 0° for 20 hr., the reaction mixture was poured into 1200 ml. of ice-water mixture, and concd. hydrochloric acid added until acid to congo red paper. The precipitated reaction product was collected, washed with water and air-dried, yield 32.2 g. (75%, calcd. as *o*-mesyloxybenzaldehyde), m.p. 45–49°. Upon recrystallization from ethyl acetate–hexane, the m.p. was raised to 47–51°. Upon attempted further purification from the same solvent system, the product (presumably the aldehyde) apparently underwent air oxidation, giving a substance, m.p. 116–122°, which gave analytical values in agreement with theory for the acid (C, 44.63; H, 3.89; S, 14.47).

The crude product, m.p. 45–49° (5 g.), was added all at once to a solution prepared by dissolving 2.5 g. of potassium dichromate in 39 ml. of 30% sulfuric acid. The resulting mixture was heated at 60–65° under constant stirring for 1 hr. and the crude product collected by filtration, washed with ice-water and extracted with several portions of water at 60–70° (total volume 80 ml.). The crude acid crystallized from the water extracts; yield 3.1 g. (57%), m.p. 116–121°. Recrystallization from benzene gave *o*-mesyloxybenzoic acid (2.20 g.), m.p. 124.5–126° (cor.), unchanged upon further crystallization from benzene.

Anal. Calcd. for $C_8H_8O_5S$: C, 44.44; H, 3.73; S, 14.83. Found: C, 44.39; H, 3.70; S, 14.65.

In acetone solution, the acid gave a negative test with alcoholic ferric chloride. *o*-Mesyloxybenzoic acid (0.4 g.) was obtained unchanged (m.p. and mixed m.p. 124–126°, recovery 90%) after standing in 2 ml. of pyridine for 26 hr. at 0°. An alternative purification of the acid involved solution in 5% $NaHCO_3$, followed by acidification to give *o*-mesyloxybenzoic acid.

***m*-Mesyloxybenzoic Acid (*m*-Methanesulfonoxybenzoic or *m*-Methanesulfonyloxybenzoic Acid).**—A 10-g. quantity of *m*-hydroxybenzaldehyde, m.p. 108–109°, was dissolved in 50 ml. of pyridine, cooled strongly in ice, and 8 ml. of mesyl chloride added. The reaction mixture was permitted to stand at *ca.* 5° for 40 hr. and then was poured into 500 ml. of ice-water mixture, containing 50 ml. of concd. hydrochloric acid. The water layer was separated by decantation from the oily reaction product, which was washed with 5% sodium bicarbonate, concd. hydrochloric acid and water. It did not prove possible to crystallize this product under a variety of conditions employed. The oily reaction product was dissolved in ethyl acetate and washed successively with water, 3% sodium bicarbonate, water, 6 *N* hydrochloric acid and water, after which the ethyl acetate was dried over anhyd. sodium sulfate. After standing for 14 months, solvent removal gave a residual solid melting indistinctly at *ca.* 140–152°. Solution in 5% sodium bicarbonate, with removal of insoluble material, followed by acidification with concd. hydrochloric acid, gave 3.70 g. of crude *m*-mesyloxybenzoic acid, m.p. approximately 155–160°. Recrystallization from methanol-water (1:1 vol.), followed by two additional crystallizations from the minimal volume of methanol, gave analytically pure material.

Anal. Calcd. for $C_8H_8O_5S$: C, 44.44; H, 3.73; S, 14.83. Found: C, 44.46; H, 3.76; S, 14.64.

The actual m.p. of this acid appears to be 153–155° (cor.), obtained in a bath preheated to 150°. When taken in the usual manner from room temperature, and also in a bath preheated to 145°, a value of 163–168° was obtained. *m*-Mesyloxybenzoic acid (1.0 g.) was obtained unchanged (m.p. and mixed m.p. 153–155° (cor.), recovery 94%) after standing in 5 ml. of pyridine for 24 hr. at 0°.

***p*-Mesyloxybenzoic Acid (*p*-Methanesulfonoxybenzoic or *p*-Methanesulfonyloxybenzoic Acid).**—This acid was prepared by a previously described procedure.[8] *p*-Mesyloxybenzoic acid (1.0 g.) was obtained unchanged (m.p. and mixed m.p. 224° (cor.), recovery 99%) after standing in 5 ml. of pyridine for 26 hr. A solution of 1 g. of *p*-mesyloxybenzoic acid and 1 g. of *p*-hydroxybenzoic acid in 7 ml. of pyridine, permitted to stand at 5° for 24 hr., then poured into dilute hydrochloric acid, gave 0.89 g. of material insoluble in boiling water, shown to be recovered *p*-mesyloxybenzoic acid by m.p., mixed m.p. and infrared absorption spectrum. *p*-Hydroxybenzoic acid (0.92 g.) was recovered by ethyl acetate extraction and identified by m.p. and mixed m.p.

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