the procedure described under IXb above, 6.2 g. (0.02 mole) of 3,6-bis(dimethylamino)-9-(methylmercapto)acridine and 3.5 g. (0.02 mole) of 2,2′-(3-aminopropylimino)diethanol afforded 6.1 g. (54%) of orange crystals from ethanol-acetone, m.p. 154° dec.

Anal. Calcd. for $C_{24}H_{35}N_5O_2 \cdot 3HCl \cdot 2H_2O$: C, 50.48; H, 7.42; N, 12.27; Cl^-, 18.63; H_2O, 6.31. Found: C, 50.63; H, 7.29; N, 12.19; Cl^-, 18.27; H_2O (Karl Fischer), 6.05.

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The Mesylation of Kojic Acid and Other 3-(or 5)-Hydroxy-4H-pyran-4-ones. Displacement of a Mesyloxy Group under Acidic Conditions[1,2]

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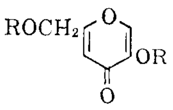
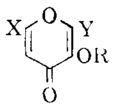
With methanesulfonyl chloride in pyridine in a short term reaction, kojic acid gave the dimethanesulfonate. A long term reaction led to an oily product, which with hydrochloric acid yielded 2-chloromethyl-5-mesyloxy-1,4-pyrone. Pyridinium salts from kojic acid dimethanesulfonate and several 2-halomethyl-1,4-pyrone derivatives are described. The mesyloxy group of kojic acid dimethanesulfonate is displaced in hydrobromic and hydrochloric acids to afford the 2-halomethyl derivative.

Kojic acid (I), available from the action of a variety of microörganisms on several carbohydrates, is potentially an important synthetic precursor of many 1,4-pyrone (4H-pyran-4-one) derivatives.[3] The present paper describes the preparation of kojic acid dimethanesulfonate from I and excess methanesulfonyl chloride, as well as mesyl derivatives of related 3-(or 5)-hydroxy-1,4-pyrones.[4] The initial aim of the present study, to block selectively the enolic hydroxyl group of I by interaction of I with one mole of methanesulfonyl chloride, did not prove feasible. There is reported the isolation of 2-chloromethyl-5-mesyloxy-1,4-pyrone from the action of hydrochloric acid on an unidentified long-term mesylation product of I. The reaction of kojic acid dimethanesulfonate with hydrohalogen acids is included, as well as certain interconversions of 2-halomethyl-1,4-pyrone derivatives.

Reaction of kojic acid (I) with methanesulfonyl chloride in pyridine, over a relatively long term of forty-eight hours, did not lead to a water-insoluble product. By extraction procedures, an oily product was obtained, which upon treatment with hydrochloric acid gave 2-chloromethyl-5-mesyloxy-1,4-pyrone (II) in low yield. The identity of II was confirmed by its independent preparation through mesylation of chlorokojic acid (III), and by reduction of II to give allomaltol methanesulfonate (V). Independent synthesis of V was achieved by direct mesylation of allomaltol (IV), which was prepared from III by a modification (sequel) of Yabuta's reduction procedure.[5] These reactions are summarized in Chart I.

In view of the well known tendency of reactive sulfonic esters to undergo quaternization in pyridine,[6] a short term mesylation of I was investigated to avoid this potential side reaction. The colorless, crystalline, water-insoluble kojic acid dimethanesulfonate (VI) was obtained in yields up to 70% with a large excess of mesyl chloride in pyridine at 0° by carefully controlling the reaction period. From Fig. 1, it is evident that satisfactory yields of VI can be obtained only in a narrow time interval in the vicinity of fifteen minutes. With mesyl chloride in pyridine, the 3-(or 5)-hydroxy-1,4-pyrones allomaltol (IV), maltol (VII), and pyromeconic acid (VIII) gave the methanesulfonic esters V, IX, and X, respectively. The duration of the reaction appeared less critical in the mesylation of IV, VII, and VIII.





I. R = H
VI. R = CH_3SO_2
VII. X = R = H; Y = CH_3
VIII. X = Y = R = H
IX. X = H; R = CH_3SO_2; Y = CH_3
X. X = Y = H; R = CH_3SO_2

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[1] This investigation was supported in part by a research grant (E-1703) from the National Institute of Allergic and Infectious Diseases, Public Health Service, and in part by a grant from the University of Nebraska Research Council.

[2] A preliminary account of this work was presented before the Organic Chemistry Division, 125th National Meeting of the American Chemical Society, Kansas City, March, 1954, Abstracts, p. 9-N.

[3] A review of the extensive literature on kojic acid is given by A. Beelik, "Advances in Carbohydrate Chemistry," Vol. 11, M. L. Wolfrom, ed., Academic Press, New York, N. Y., 1956, pp. 145–183.

[4] Properties, but not experimental procedures for preparation, of several of these derivatives are included in ref. 3.

[5] T. Yabuta, *J. Chem. Soc.*, **125**, 575 (1924).

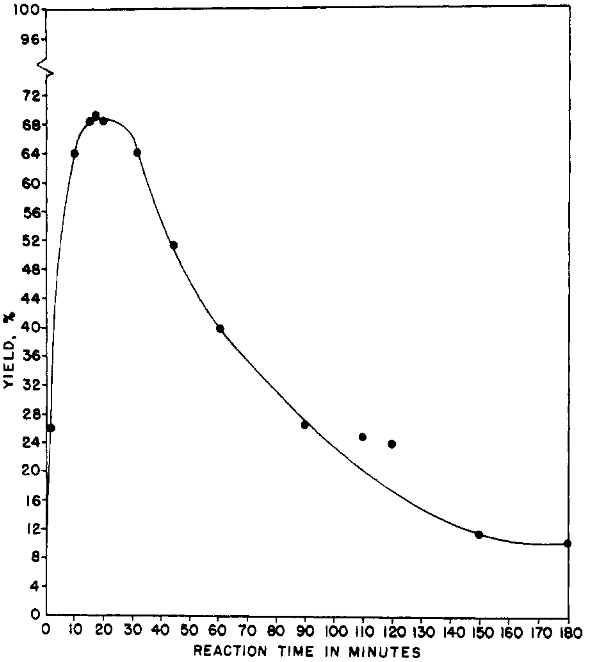
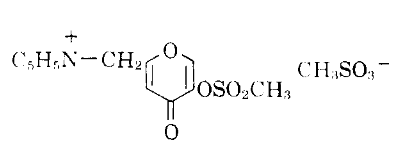


Fig. 1.—Yield of (VI) *vs.* reaction time: total yield of crude (VI) from mesylation of a 5% pyridine solution of (I) at 0° with 135% excess mesyl chloride.

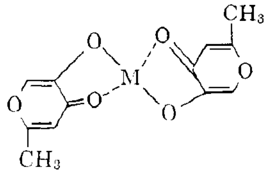
Kojic acid dimethanesulfonate (VI) formed a pyridinium salt with dry pyridine. In Table I are listed melting points and analytical data for pyridinium salts of certain 2-halomethyl derivatives of 1,4-pyrones. The quaternization of chlorokojic acid was regarded as satisfactory evidence that 2-halomethyl groups in 1,4-pyrones react with pyridine. Because of the well known chemical similarity between mesyloxy groups and halogen, structure XI appeared reasonable for the pyridine quaternization product of VI. Also, since allomaltol methanesulfonate (V) did not react with pyridine, it is evident that 3(or 5)-mesyloxy groups do not undergo quaternization Pyridine quaternization affords a method for the solubilization of water-insoluble 2-halo(and mesyloxy)-methyl-1,4-pyrones. The melting point of the pyridine quaternization product of 2-chloro-5-acetoxy-1,4-pyrone is remarkably low. However, this quaternization product has properties expected for a pyridinium salt (complete water solubility and instantaneous precipitation of silver chloride with aqueous silver nitrate).



XI

A rough study of the rate of quaternization of pure VI indicated a rather slow reaction: 74% recovery of VI from pyridine after four hours. Yet from Fig. 1 it is evident that after three hours virtually no water-insoluble product was present in the pyridine mesylation mixture. Either the quaternization of VI in the mesylation mixture is subject to a marked catalysis, or the pyridinium salt is subject to further reaction(s) of undetermined nature. The known reaction of pyridinium chloride with sulfonic esters,[7] in this case with VI to give II, followed by quaternization of II, is unlikely (excluding possible catalysis), since II also reacts slowly with pyridine: 75% recovery of II from pyridine after four hours. It appears likely, therefore, that the rather rapid formation of water-soluble by-products (Fig. 1) in the mesylation of I involves reactions more complex than simple quaternization of VI or II.

In characterizing II, allomaltol (IV) was prepared by the general method of Yabuta.[5] In our hands, the first product isolated was a high-melting solid, which left an ash on ignition. We were able to obtain IV only after further treatment of the high-melting solid with sulfuric acid. Even then, the product allomaltol had a melting point appreciably different from that previously reported: 148.5–150.5° instead of 166°.[5, 8] Combustion analyses for VI, m.p. 148.5–150.5°, are in good agreement with theory. The high-melting solid obtained initially in the reduction procedure may be a zinc chelate. On the basis of formally similar chelates of kojic acid studied by workers in other laboratories,[9] an obvious possible structure is XII.



XII: M = Zn

In a study of the stability of VI in concentrated hydrochloric acid, a reaction was observed in which the mesyloxy group of the 2-mesyloxymethyl unit was displaced by halogen to give the previously characterized II in virtually quantitative yield. Interaction of VI with concentrated hydrobromic acid resulted in 2-bromomethyl-5-mesyloxy-1,4-pyrone (XIII) in excellent yield if rather long reaction periods were employed. Only a 15% yield was obtained after one day. The derivative XIII formed a crystalline pyridinium salt (Table I). Hydriodic acid with VI gave allomaltol methanesulfonate (V), instead of the iodo derivative. Zinc in acetic acid also reduced VI to V. The 2-bromomethyl and 2-chloromethyl derivatives (XIII and II, respectively) are readily inter-

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(6)(a) J. H. Looker, *J. Org. Chem.*, **17**, 510 (1952); (b) R. S. Tipson, "Advances in Carbohydrate Chemistry," Vol. 8, C. S. Hudson and M. L. Wolfrom, ed., Academic Press, New York, N. Y., 1953, p. 118.

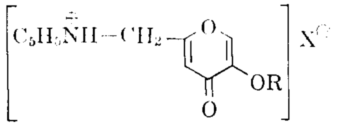
(7) K. Hess and H. Stenzel, *Ber.*, **68**, 981 (1935).

(8) A value of 150–151° has been reported for allomaltol by A. Beelik and C. B. Purves, *Can. J. Chem.*, **33**, 1361 (1955).

(9) Ref. 3, p. 165.

Table I

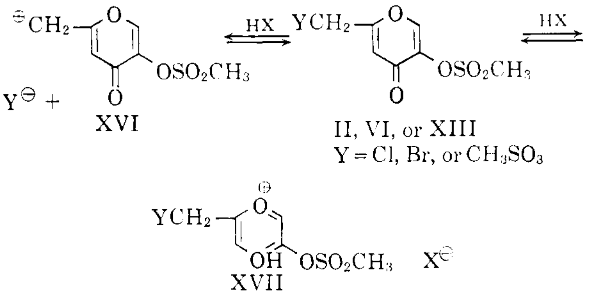
Melting Points and Analyses for Pyridinium Salts from 2-Halomethyl-1,4-pyrones



R	X	M.p., °C.	Calcd. N	Calcd. Cl	Found N	Found Cl
CH_3SO_2	Cl	191–192	4.41	11.13	4.45	11.17
H	Cl	188–188.5	5.85	14.79	5.87	14.60
CH_3CO	Cl	95–97	4.94	...	4.95	...
CH_3SO_2	Br	194–195	3.87[a]	...	4.05 3.88	...

[a] Calcd. for $C_{12}H_{12}BrNO_5S$: C, 39.79; H, 3.34. Found: C, 39.80, 39.82; H, 3.29, 3.33.

convertible in good yields. We also have observed conversion of 2-chloromethyl-5-methoxy-1,4-pyrone (XIV) to 2-bromomethyl-5-methoxy-1,4-pyrone (XV) by hydrobromic acid. These various reactions are summarized in Chart I. It is to be stressed that the displacements observed were induced under conditions quite different from those used in treating active alkylsulfonyloxy- and arylsulfonyloxy- groups with metal halides in alcohol or acetone to give halomethyl derivatives.[10]



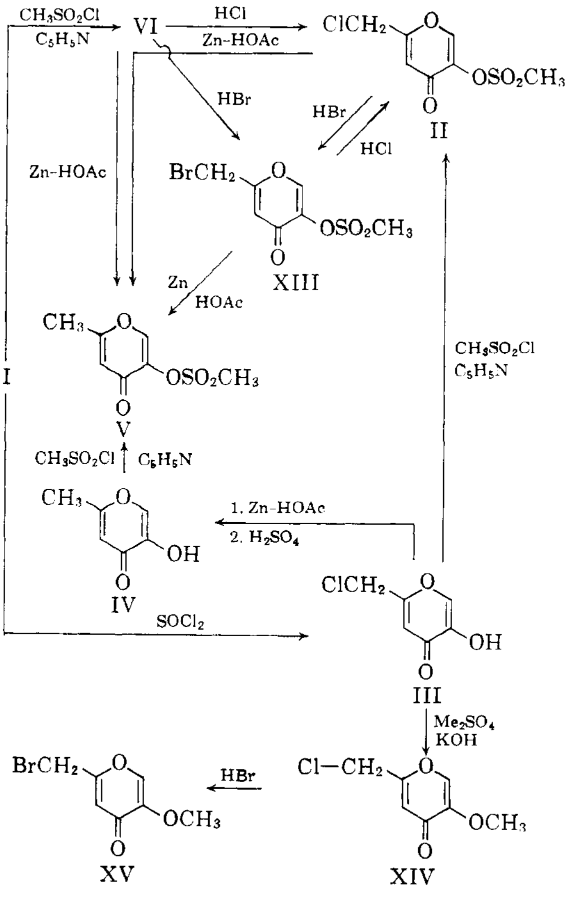


Chart I

The slow displacements of mesyloxy by halogen, and especially the interconvertibility of II and XIII, suggest strongly that a common intermediate is present in the displacement reactions. Possibly an incipient ionization to give the carbonium ion XVI is competitive with the commonly formulated ionization[11] to the pyroxonium salt XVII.

Experimental

Melting points are uncorrected. Reagent grade pyridine contained 0.09% water. Dry pyridine indicates that the reagent grade solvent was dried over potassium hydroxide pellets for several days prior to use.

Chlorokojic Acid (2-Chloromethyl-5-hydroxy-4H-pyran-4-one) (III).—This substance was prepared by the procedure of Yabuta; m.p. and lit.,[5] m.p. 166–167°.

2-Chloromethyl-5-mesyloxy-1,4-pyrone (2-Chloromethyl-5-methanesulfonyloxy-4H-pyran-4-one). (II). A. From Kojic Acid.—To 2.84 g. of kojic acid in 56 ml. of reagent pyridine at 0–5° was added 9.20 g. of methanesulfonyl chloride in 6 ml. of pyridine. The temperature was maintained at 5–10°. After 48 hr., the reaction mixture was poured into approximately 150 ml. water. Concentrated hydrochloric acid was added portionwise until the pyridine odor virtually disappeared. The resulting mixture was permitted to stand in a refrigerator for 48 hr. No crystalline material separated, however. The mixture was extracted with two 300-ml. portions of ethyl acetate, and the combined extracts were dried over Drierite. Solvent removal left a residual oil, to which were added a few milliliters of concentrated hydrochloric acid, and then a few milliliters of water. After standing overnight, crystals were present, which were collected and dried; m.p. 83–85°, unchanged after recrystallization from chloroform. Qualitative analysis indicated sulfur and halogen.

Anal. Calcd. for $C_7H_7ClSO_5$: C, 35.23; H, 2.96. Found: C, 35.07; H, 2.86.

B. From Chlorokojic Acid.—To 10 g. of chlorokojic acid in 10 ml. pyridine at −5° was added, dropwise, 10 ml. of methanesulfonyl chloride with stirring. After addition was complete, *ca.* 30 min., the reaction mixture was poured over 50 ml. of ice–water mixture to give a crystalline product. The crystals were collected by filtration and recrystallized from 95% ethanol; yield of colorless product, 11.75 g. (79.2%), m.p. 83.5–85°, no depression upon admixture with product prepared in (A).

2-Chloromethyl-5-mesyloxy-1,4-pyrone (171 mg.) was dissolved in 2.0 ml. of dry pyridine at 0° and permitted to stand for varying periods of time. At the end of the reaction period, the reaction mixture was poured onto 20 g. of ice–water, to which 2 ml. of concentrated hydrochloric acid previously had been added. The total unchanged 1,4-pyrone was determined by collecting, drying, and weighing the precipitated starting material, and then extracting the filtrate with ethyl acetate. Solvent removal gave additional starting material as crystalline residue, the weight of which was determined. Total yields of recovered 2-chloromethyl-5-mesyloxy-1,4-pyrone after 14-, 140-, and 240-min. reaction periods were 145, 142, and 128 mg., respectively.

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(10) Ref. 6b, p. 180.

(11) J. Fried, "Heterocyclic Compounds," Vol. 1, R. C. Elderfield, ed., J. Wiley & Sons, New York, N. Y., 1950, p. 374.

Allomaltol (2-Methyl-5-hydroxy-4H-pyran-4-one) (IV).—Chlorokojic acid (10 g.) was heated under reflux 4 hr. with stirring in 100 ml. of glacial acetic acid containing 6 g. of zinc dust, which previously had been washed with dilute sulfuric acid and then with water. A dense, cream-colored precipitate formed, which was collected and dried; yield, 9.2 g., m.p. above 300°. This substance was dissolved with warming in 50 ml. of 3 *N* sulfuric acid, and the solution was diluted with 70 ml. of water. Extraction with chloroform, followed by solvent removal and recrystallization from 95% ethanol gave 2.5 g. of white crystals of allomaltol, m.p. 148.5–150.5°; mixture m.p. with maltol, 126–145°.

Anal. Calcd. for $C_6H_6O_3$: C, 57.14; H, 4.80. Found: C, 56.98, 56.94; H, 4.93, 4.82.

Allomaltol Methanesulfonate (2-Methyl-5-methanesulfonyloxy-4H-pyran-4-one) (V). A. From 2-Chloromethyl-5-mesyloxy-1,4-pyrone.—2-Chloromethyl-5-mesyloxy-1,4-pyrone (4 g.) was dissolved in 16 ml. of glacial acetic acid containing 2.0 g. of zinc dust (previously washed with dilute sulfuric acid and then with water). The reaction mixture was heated on a steam bath for 8 hr., and then was neutralized with sodium carbonate. The mixture was extracted with chloroform. Solvent removal gave a residue which was recrystallized from 95% ethanol to give 2.21 g. (65%) of colorless allomaltol methanesulfonate, m.p. 99.5–101°.

Anal. Calcd. for $C_7H_8O_5S$: C, 41.17; H, 3.95. Found: C, 41.50; H, 4.26.

B. From Allomaltol.—To 0.42 g. of allomaltol in 1 ml. of dry pyridine at 0° was added, dropwise, 0.2 ml. methanesulfonyl chloride. After 5 min., 20 ml. of ice–water mixture was added. The crystalline product was recrystallized from 95% ethanol to give 0.52 g. (76%) allomaltol methanesulfonate, m.p. 99.5–101°, no depression upon admixture with substance prepared in procedure A.

Kojic Acid Dimethanesulfonate (2-Methanesulfonyloxymethyl-5-methanesulfonyloxy-4H-pyran-4-one) (VI).—To 2 g. of pure, dry kojic acid in 40 ml. of reagent grade pyridine at 0° was added 5 ml. of methanesulfonyl chloride. The reaction mixture stood at 0° for exactly 15 min., and then was poured onto 400 ml. of ice–water mixture to which 40 ml. of concentrated hydrochloric acid previously had been added. The precipitated crude product was collected by filtration and washed thoroughly with cold water; yield, 2.88 g. (69%) m.p. 103–108°. Recrystallization from 95% ethanol gave analytically pure kojic acid dimethanesulfonate (82% efficiency), m.p. 109–110°.

Anal. Calcd. for $C_8H_{10}O_8S_2$: C, 32.21; H, 3.38. Found: C, 32.47; H, 3.51.

Reaction under identical conditions, but at reaction times of 10 and 20 min., respectively, gave yields of 64 and 68% respectively. Application of the above general procedure to 12 g. of kojic acid in 95 ml. of pyridine, with 45 ml. of methanesulfonyl chloride and a 15-min. reaction period, gave 15.2 g. (60.3%) of kojic acid dimethanesulfonate, m.p. 103–105°, raised to 109–110° by recrystallization from ethanol. Attempts to mesylate larger quantities resulted in lower yields.

Kojic acid dimethanesulfonate (214 mg.) was dissolved as much as possible in 2.0 ml. of dry pyridine at 5°, and the resulting mixture permitted to stand for 60 min. Then the mixture was poured onto 20 ml. of ice–water mixture containing 2.0 ml. of concentrated hydrochloric acid; yield of recovered kojic acid dimethanesulfonate, 175 mg. Repetition of the experiment with a 240-min. reaction period led to recovery of 159 mg. of kojic acid dimethanesulfonate.

Kojic acid dimethanesulfonate (0.25 g.) was dissolved in 10 ml. of concentrated hydrochloric acid and permitted to stand 1 week. Crystals appeared during the fourth day. Thirty milliliters of water was added, and the crystalline product collected; yield, 0.20 g. (100%). This substance, 2-chloromethyl-5-mesyloxy-1,4-pyrone, was recrystallized from 95% ethanol; m.p. and mixture m.p., 83.5–85°.

Kojic acid dimethanesulfonate (1.00 g.) was dissolved in 40 ml. of hydriodic acid (sp. gr. 1.50, hypophosphorous acid present as preservative). There was an apparent initial evolution of iodine, followed by slow disappearance of the iodine color. The mixture stood for 39 days, and then was diluted with an equal volume of water, neutralized with 5% sodium bicarbonate, and extracted with ethyl acetate. Evaporation of the dried extract gave 450 mg. of crystalline residue (65.5%), m.p. 97–101°. Recrystallization from benzene–isoöctane gave allomaltol methanesulfonate, m.p. 100.4–102.5°, no depression upon admixture with authentic material.

To 3 g. of kojic acid dimethanesulfonate was added 30 ml. of glacial acetic acid, and then 3 g. of zinc dust (previously washed with dilute sulfuric acid) over a 5-min. period. The reaction mixture stood on a steam bath for 5 hr., was filtered, and the filtrate neutralized with sodium carbonate. The neutral solution was extracted exhaustively with chloroform; solvent removal gave 1.5 g. (73%) of allomaltol methanesulfonate, m.p. 99–100°. Recrystallization from ethanol gave the pure substance, m.p. and mixture m.p. 100–101°.

Pyromeconic Acid (3-Hydroxy-4H-pyran-4-one) (VIII).—This substance was prepared by the decarboxylation of comenic acid.[12]

Maltol Methanesulfonate (2-Methyl-3-methanesulfonyloxy-4H-pyran-4-one) (IX).—A solution of 50 g. of dry maltol in 205 ml. of dry pyridine was placed in a 500-ml. three-necked flask, equipped with mercury-sealed stirrer and two dropping funnels. Methanesulfonyl chloride (33 ml.) was placed in the two dropping funnels and the flask immersed in a Dry Ice–acetone bath. Methanesulfonyl chloride was added dropwise to the stirred mixture simultaneously from the two dropping funnels. After sulfonyl chloride addition was complete, *ca.* 50 ml. of water was added and the mixture permitted to stand 30 min. Reaction mixture was poured onto 500 ml. of ice–water mixture containing 25 ml. of concentrated hydrochloric acid, and the resulting mixture extracted with ethyl acetate. Solvent removal from the dried extract gave a brownish colored oily residue, which was dissolved in hot carbon tetrachloride and permitted to stand 1 hr. After standing in a refrigerator overnight, brown crystalline material separated from solution; yields ranged from 35 to 51 g. (44–64%). Repeated crystallization from carbon tetrachloride gave colorless, analytically pure maltol methanesulfonate, m.p. 62–63°.

Anal. Calcd. for $C_7H_8O_5S$: C, 41.18; H, 3.92; S, 15.69. Found: C, 41.23, 41.02; H, 3.97, 3.87; S, 15.50, 15.35.

Pyromeconic Acid Methanesulfonate (3-Methanesulfonyloxy-4H-pyran-4-one) (X).—To 150 mg. of pyromeconic acid in 1 ml. of dry pyridine, previously cooled to −5°, was added 0.2 ml. of methanesulfonyl chloride. The resulting mixture was maintained at −5° for 25 min. and was poured into 15 ml. of ice water. After standing overnight, the mixture was extracted with ethyl acetate, which then was removed under an air jet. Concentrated hydrochloric acid was added to the oily residue, the mixture permitted to stand in air for a few hours, and then *in vacuo* over phosphorus pentachloride and potassium hydroxide pellets; a residual oil resulted. After repeated rubbing with isoöctane, crystalline material resulted. Recrystallization from benzene-isoöctane, with collection of several crops, gave a total yield of 140 mg. (55%), m.p. 60–67°. Recrystallization from benzene–isoöctane, followed by drying *in vacuo* for 2 weeks, gave analytically pure pyromeconic acid methanesulfonate, m.p. 65–67°.

Anal. Calcd. for $C_6H_6O_5S$: C, 37.89; H, 3.18; S, 16.86. Found: C, 37.97; H, 3.35; S, 16.62.

(5-Methanesulfonyloxy-4H-pyran-4-on-2-yl)methyl Pyridinium Methanesulfonate (XI).—Dry pyridine (10 ml.), pre-cooled to 0°, was added to 0.5 g. of kojic acid dimethanesulfonate. The resulting solution was permitted to stand

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[12] H. Ost, *J. prakt. Chem.*, **19**, 183 (1879).

at −2° for 24 hr. The crystalline material present in the reddish brown reaction mixture was collected by filtration, and while still moist with solvent was dissolved in absolute ethanol and precipitated with ether. Minute traces of pyridine caused the product to have a slight brown color. Analytically pure pyridinium salt was obtained by crystallization from hot absolute ethanol; yield 0.25 g. (40%), m.p. 189.5–190.5.

Anal. Calcd. for $C_{13}H_{15}NO_8S_2$: C, 41.37; H, 4.01; N, 3.71; S, 16.99. Found: C, 41.93; H, 4.26; N, 3.60; S, 17.20.

Reaction products from other pyridine quaternization reactions with 2-chloromethyl- and 2-bromomethyl-4H-pyran-4-ones are listed, with melting points and analytical data, in Table I. Procedure for their preparation is as immediately above, except that in some cases products were transferred to a vacuum desiccator immediately upon isolation, dried over concentrated sulfuric acid, and then recrystallized from absolute ethanol or absolute ethanol-benzene.

2-Bromomethyl-5-mesyloxy-1,4-pyrone (2-Bromomethyl-5-methanesulfonyloxy-4H-pyran-4-one) (XIII). A. From Kojic Acid Dimethanesulfonate.—To 4 g. of kojic acid dimethanesulfonate was added 160 ml. of 48% hydrobromic acid. The reaction mixture was allowed to stand at room temperature undisturbed for 1 month, and then was neutralized with solid sodium bicarbonate. The mixture was extracted exhaustively with chloroform and solvent removed from the dried combined extracts to give a light brown residue, m.p. 102–103°; yield, 3.5 g. (92.5%). Mixture melting point with starting material, m.p. 110°, gave a depression to 86°. Recrystallization of 2-bromomethyl-5-mesyloxy-1,4-pyrone from 95% ethanol gave 2.9 g. of colorless, crystalline compound, m.p. 102–103°.

Anal. Calcd. for $C_7H_7BrO_5S$: C, 29.70; H, 2.49; Br, 28.23; S, 11.32. Found: C, 29.68; H, 2.37; Br, 27.79; S, 11.17.

B. From 2-Chloromethyl-5-mesyloxy-1,4-pyrone.—To 2 g. of 2-chloromethyl-5-mesyloxy-1,4-pyrone was added 80 ml. of 48% hydrobromic acid. The reaction mixture was permitted to stand at room temperature for 10 days, and then was neutralized with solid sodium bicarbonate. The mixture was extracted exhaustively with chloroform. Solvent removal from the dried combined extracts gave 2.1 g. (86%) of product, m.p. 101–102.5°. Recrystallization from 95% ethanol gave 1.7 g. of colorless 2-bromomethyl-4-mesyloxy-1,4-pyrone, m.p. and mixture m.p. 102–103°. Mixture melting point with starting material was 78°.

When 1 g. of 2-bromomethyl-5-mesyloxy-1,4-pyrone reacted with 50 ml. of concentrated hydrochloric acid for 5 days, and the product was isolated as immediately above, 0.8 g. (97%) of 2-chloromethyl-5-mesyloxy-1,4-pyrone, m.p. and mixture m.p. 82–83°, was obtained.

To 1 g. of 2-bromomethyl-5-mesyloxy-1,4-pyrone was added 10 ml. of glacial acetic acid. One gram of zinc dust, previously treated with dilute sulfuric acid and washed with water, was added slowly and the mixture allowed to stand on the steam bath 7 hr. The mixture was filtered and the filtrate neutralized with solid sodium bicarbonate. Extraction with chloroform and solvent removal gave 0.37 g. (51.4%) of colorless tablets, m.p. 99.5–100.5°. Mixture melting point with starting material, m.p. 102–103°, was 77–78°. Recrystallization from chloroform gave colorless tablets of allomaltol methanesulfonate, m.p. and mixture m.p. 100–101°.

2-Chloromethyl-5-methoxy-4H-pyran-4-one (XIV).—This substance was prepared by the method of Yabuta.[5]

2-Bromomethyl-5-methoxy-4H-pyran-4-one (XV).—2-Chloromethyl-5-methoxy-4H-pyran-4-one (17.5 g.) was dissolved in 275 ml. of 48% hydrobromic acid. The solution stood for 10 days at room temperature, and then was carefully neutralized with solid sodium bicarbonate. After the resulting mixture stood in a refrigerator overnight, the white solid present was collected by filtration, washed with cold water, and air-dried; yield, 19 g. (85%). Recrystallization was effected with hot water to give cream-colored crystals of 2-bromomethyl-5-methoxy-4H-pyran-4-one, m.p. 135–136°.

Anal. Calcd. for $C_7H_7BrO_3$: C, 38.53; H, 3.21; Br, 36.24. Found: C, 38.46; H, 3.37; Br, 36.67.

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Sulfenic Acids and Their Derivatives. XLI. Sulfenyl Nitrates and Sulfinyl Radicals[1]

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Sulfenyl nitrates, $RSONO_2$, represent a novel class of sulfenyl compounds. The preparation of the first examples is described and some of their properties are recorded. The near-quantitative conversion of sulfenyl nitrates to thiolsulfonate esters ($2RSONO_2 \rightarrow RSO_2SR + 2NO_2$) is demonstrated and interpreted as a dimerization reaction of sulfinyl radicals.

In seeking routes to substances capable of generating sulfinyl radicals, $RSO\cdot$, a series of sulfenyl nitrates, $RSONO_2$, a new class of sulfenyl derivatives of both theoretical and practical interest has been prepared. It was reasoned that the loss of NO_2 radicals from the sulfenyl nitrates could provide an advantageous source of the little known sulfinyl radicals, and that the chemistry of these radicals and of the sulfenyl nitrates would offer a new field of study.

For small-scale synthesis, the preparation of sulfenyl nitrates by reactions of equivalent quantities of the sulfenyl chlorides and silver nitrate in

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