the relative intensities of diffraction lines of the three substances showed no differences. The three bromopalmitamides are therefore identical. The sulfonation of palmitic acid with sulfur trioxide appears to be as specific as the Hell–Volhard–Zelinskiĭ reaction. Only monosubstitution seems to occur and only at the α-carbon atom.

Experimental[16]

α-Bromopalmitic Acid and Amide.—α-Bromopalmitoyl bromide was prepared as described by Hell and Jordanoff.[17] Bromine was added to a mixture of palmitic acid (neut. equiv. 257.7, m.p. 61.0–61.3°) and red phosphorus over a period of one hour. The mixture was heated from 40 to 95° for five hours.

α-Bromopalmitoyl bromide was hydrolyzed with ice to give α-bromopalmitic acid. After purification by two crystallizations from acetone and three crystallizations from petroleum ether, the yield was 85%, m.p. 49.4–49.8°.

Anal. Calcd. for $C_{16}H_{31}O_2Br$: neut. equiv., 335.3. Found: neut. equiv., 336.4.

α-Bromopalmitamide was prepared by pouring α-bromopalmitoyl bromide into an excess of aqueous ammonia and ice. It was purified by three crystallizations from alcohol and one crystallization from petroleum ether to give a 50% yield. Table I, Column A, lists the chemical analyses and melting points.

α-Mercaptopalmitic Acid.—The method of Nicolet and Bate[18] was followed in preparing α-mercaptopalmitic acid from α-bromopalmitic acid without purification of the tetradecyl pseudothiohydantoin. Three crystallizations from 95% ethanol gave the required α-mercaptopalmitic acid in a 47% yield based on α-bromopalmitic acid, m.p. 71.6–71.8°.

Anal. Calcd. for $C_{16}H_{32}O_2S$: neut. equiv., 288.5. Found: neut. equiv., 289.3.

TABLE II

DIFFRACTION PATTERNS OF BROMOPALMITAMIDES

A Hell–Volhard–Zelinskiĭ reaction		B Sulfonated palmitic acid + PBr_5 + NH_3		C Oxidation of Na α-mercaptopalmitate + PBr_5 + NH_3	
I, obsd.	*d*, Å.	*I*, obsd.	*d*, Å.	*I*, obsd.	*d*, Å.
M	15.5	M	15.7	M	15.6
W^{++}	10.30	W^{++}	10.35	W^{++}	10.32
M^-	7.71	M^-	7.73	M^-	7.74
W^{+++}	6.18	W^{+++}	6.21	W^{+++}	6.20
W^-	5.73	W^-	5.73	W^-	5.73
M	5.13	M	5.16	M	5.17
W^-	4.58	W^-	4.60	W^-	4.58
W^{++}	4.41	W^{++}	4.43	W^{++}	4.42
S^-	4.16	S^-	4.17	S^-	4.17
W	4.03	W	4.03	W	4.02
M^{++}	3.77	M^{++}	3.78	M^{++}	3.79
W^{++}	3.67	W^{++}	3.67	W^{++}	3.68
W	3.44	W	3.44	W	3.44
W^+	3.35	W^+	3.35	W^+	3.35
W^{+++}	3.15	W^{+++}	3.16	W^{+++}	3.16
W	3.07	W	3.06	W	3.07
W^+	2.90	W^+	2.91	W^+	2.90
W^-	2.82	W^-	2.83	W^-	2.82
W^+	2.67	W^+	2.67	W^+	2.67
W	2.60	W	2.61	W	2.60
W	2.48	W	2.49	W	2.49
W	2.43	W	2.43	W	2.43
W^{+++}	2.26	W^{+++}	2.26	W^{+++}	2.26

Sodium α-Sulfopalmitic Acid from Sodium α-Mercaptopalmitate.—The oxidation was a modification of the method of Levene, Mori and Mikeska.[19] Sodium α-mercaptopalmitate was treated with sodium hypobromite in an aqueous solution buffered with excess sodium carbonate. After being acidified to form the monosodium salt, it was purified by two crystallizations from water and one extraction with hot acetone; the yield was 43%.

Anal. Calcd. for $C_{16}H_{31}O_5SNa$: S, 8.95; neut. equiv., 358.5. Found: S, 8.98; neut. equiv., 358.1.

Direct Sulfonation of Palmitic Acid.—A 60% excess of sulfur trioxide was added slowly to palmitic acid in tetrachloroethylene.[9] The product was neutralized to form the monosodium salt, twice extracted with hot acetone and crystallized from water four times, giving a 61% yield. Yields of 80–90% of the monosodium salt of monosulfonated palmitic or stearic acid can be obtained with less rigorous purification.

Anal. Calcd. for $C_{16}H_{31}O_5SNa$: S, 8.95; neut. equiv., 358.5. Found: S, 8.92; neut. equiv., 358.9.

Bromopalmitamide from Sodium Sulfopalmitic Acid.—Phosphorus pentabromide, 0.10 mole, freshly prepared from phosphorus tribromide and bromine,[20] was intimately mixed with 0.04 mole of sodium sulfopalmitic acid and warmed on the steam-bath for two hours. The resultant viscous liquid was stirred into 60 ml. of 29% aqueous ammonia and 200 g. of cracked ice. The crude product was purified by two crystallizations from 95% ethanol and one crystallization from petroleum ether. The yield of purified product was 40%. Table I lists the chemical analyses and the melting points of bromopalmitamides made by the reaction of phosphorus pentabromide and ammonia with sulfonated palmitic acid (B), and from the mercaptan oxidation product (C).

X-Ray Technique.—The X-ray diffraction patterns were recorded with a powder camera of 14.32 cm. diameter; CuKα radiation, λ = 1.5405 Å. was used. Specimens were prepared for the camera by passing a finely ground sample on a glass slide and cutting from it a narrow section 0.3 mm. thick. Table II reports interplanar spacings and relative diffraction intensities for α-bromopalmitamide prepared by the three methods.

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[16] All melting points corrected.

[17] C. Hell and C. Jordanoff, *Ber.*, **24**, 936 (1891).

[18] B. H. Nicolet and L. F. Bate, THIS JOURNAL, **49**, 2064 (1927).

[19] P. A. Levene, T. Mori and L. A. Mikeska, *J. Biol. Chem.*, **75**, 337 (1927).

[20] H. S. Booth and C. G. Seegmiller, "Inorganic Syntheses," Vol. II, 1st ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 151.

Studies on the Mucohalic Acids. III. The Chlorobromo Acids. Mechanism of Formation of the Mucohalic Acids

BY HARRY H. WASSERMAN, FRANK M. PRECOPIO AND TIEN-CHUAN LIU

RECEIVED JANUARY 8, 1953

In the course of investigations on halogenated furoic acids, Hill and Jackson[1] reported that a mucohalic acid, $C_4H_2BrClO_3$ (I), containing both bromine and chlorine atoms could be formed by the action of excess aqueous bromine on what was considered to be 3-chloro-2-furoic acid. Vander Wal[2] later showed that Hill's chlorofuroic acid was actually the 4-chloro-isomer but the "mucochlorobromic" acid derivable therefrom was never completely characterized. Our interest in replacement reactions involving the halogens of the mucohalic acids and esters has led us to study this product.

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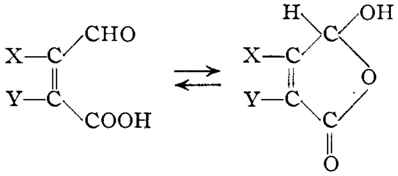
[1] H. B. Hill and O. R. Jackson, *Am. Chem. J.*, **12**, 37 (1890).

[2] R. J. Vander Wal, *Iowa State Coll., J. Sci.*, **11**, 128 (1936).

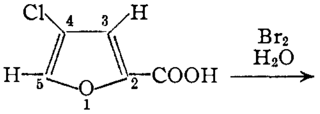
We have prepared "mucochlorobromic" acid following Hill's detailed procedure[1] as modified by Vander Wal,[3] and have shown, as outlined below, that it is α-bromo-β-chloro-β-formylacrylic acid (I, X = Cl, Y = Br).

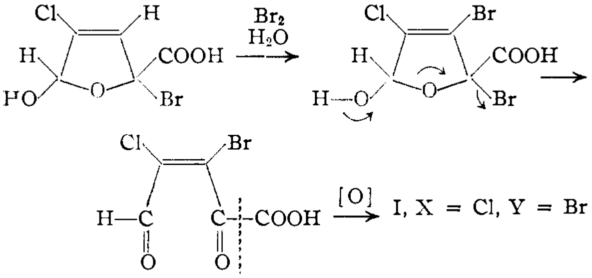


I

Treatment of Hill's "mucochlorobromic" acid with aqueous potassium phenylate yielded mucophenoxychloric acid (I, X = Cl, Y = OC_6H_5) identical with the product derived by the action of phenol and alkali on mucochloric acid (I, X = Y = Cl). That the halogen *α to the carboxyl group* was replaced by a phenoxy group in this reaction as originally postulated by Hill and Stevens[4] was verified by conversion of mucophenoxychloric acid to the known mucoxychloric acid system (I, X = Cl, Y = OH) through mild barium hydroxide hydrolysis. The barium salt isolated from this reaction was identical with known barium mucoxychlorate[8] $BaC_4HO_4Cl \cdot H_2O$, as shown by comparison of the infrared spectra of the two salts, and by conversion of each to the same monoanilino derivative,[5] $C_{10}H_8O_3NCl$. The above replacement reactions clearly establish the structure of Hill's "mucochlorobromic" acid as I, X = Cl, Y = Br, and are in accord with the recent findings of E. Kuh who has prepared an isomeric α,β-dihalo-β-formylacrylic acid to which he has assigned the structure I, X = Br, Y = Cl.[6] In agreement with this assignment we have found that Kuh's chlorobromo acid was transformed, by the action of aqueous potassium phenylate, into mucophenoxybromic acid (I, X = Br, Y = OC_6H_5) identical with the product similarly derived from mucobromic acid (I, X = Y = Br). In both of the latter conversions the halogen undergoing replacement must have been α to the carboxyl group.

The formation of α-bromo-β-chloro-β-formylacrylic acid by the bromination of 4-chloro-2-furoic acid, is good evidence for the fact that in the reaction of 2-furoic acids with aqueous halogens whereby the mucohalic acids are produced, the newly formed aldehyde group must have originated at C-5. The above conversion may have taken place by a process such as that depicted below, involving in successive steps, 1,4-addition of HOBr to the furan ring, replacement of hydrogen, ring opening, and then oxidative cleavage of the α-keto acid.





Experimental

Hydrolysis of Chlorobromo Acids.—The hydrolysis of the chlorobromo acids with aqueous potassium phenylate was accomplished according to the general procedure outlined by Hill and Stevens[4] as later modified by Sawyer.[7]

Barium Mucoxychlorate from Mucophenoxychloric Acid.—A stirred suspension of mucophenoxychloric acid, 7.0 g. (0.031 mole), in 300 ml. of water, was cooled in ice to 0°, and 9.75 g. of powdered $Ba(OH)_2 \cdot 8H_2O$ was added over a period of 1.5 hours while the temperature was maintained between 0 and 5°. The cloudy yellow solution was filtered while cold and an equal volume of 95% ethyl alcohol was added to the clear solution. After cooling in an ice–salt mixture for a short time, barium mucoxychlorate precipitated in its characteristic microcrystalline form[8]; yield 2.5 g. Infrared absorption spectra of this barium salt and of the authentic barium mucoxychlorate were almost identical. The action of aniline hydrochloride on this barium salt yielded an anil which was found to be identical in every respect with mucoxychloric acid anil.

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[3] R. J. Vander Wal, doctoral dissertation, Iowa State College (1936).

[4] H. B. Hill and E. K. Stevens, *Am. Chem. J.*, **6**, 187 (1884).

[5] H. B. Hill and A. W. Palmer, *ibid.*, **9**, 147 (1887).

[6] E. Kuh, private communication, U. S. Patent 2,588,852. We are indebted to Dr. Kuh of American Cyanamid Co. for a sample of his chlorobromo acid.

[7] H. E. Sawyer, *Proc. Am. Acad. Arts Sci.*, **29**, 242 (1894).

[8] H. H. Wasserman and F. M. Precopio, THIS JOURNAL, **74**, 326 (1952).

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t-Butyl Sulfone

BY J. ELIOT WOODBRIDGE

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A sulfone in which all alpha hydrogen atoms have been replaced by alkyl groups has been prepared. This compound has not been reported previously. Attempts to isolate it may have been unsuccessful as it sublimes readily above 80° and decomposes at temperatures somewhat above 120°.

The method of preparation was as follows: 10 ml. of 30% hydrogen peroxide was added slowly with stirring to 8.15 g. (0.046 mole) of *t*-butyl sulfide[1] and 10 ml. of glacial acetic acid, the temperature being kept between 70 and 80° by means of an ice-bath. The sulfide was oxidized by the first equivalent of the hydrogen peroxide rapidly and by the second slowly. After 45 minutes, the solution was cooled and sufficient 5 *N* sodium hydroxide was added to neutralize the mixture. Sodium bisulfite, 5 g., was added to destroy any remaining peroxide, and the solution was cooled to room temperature and extracted four times with 50-ml. portions of ethyl ether. The ether was evaporated until crude colorless crystals appeared, after which the mixture was dissolved in 60 ml. of 50% ethanol, washed with 5.0 ml. of pentane, and allowed to crystallize in an ice-bath. The yield was 3.75 g., m.p. 127–128°.[2] The mother liquor was evaporated to 24 ml., and cooled to obtain 1.78 g. of additional material. The total yield was 5.53 g. or 55.8%.

Anal. Calcd. for $C_8H_{18}O_2S$: C, 53.9; H, 10.2; O, 18.0; S, 18.0; mol. wt., 178.28. Found: C, 54.2; H, 10.3; O, 17.6; S, 17.5; mol. wt. (mass spectrometer), 178.

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[1] Prepared by procedure of Edward A. Fehnel and Marvin Carmack, THIS JOURNAL, **71**, 84 (1949).

[2] Sufficient material should be used, and the temperature should be raised fairly rapidly to avoid complete sublimation. There appears to be a transition point at 100 to 105°.