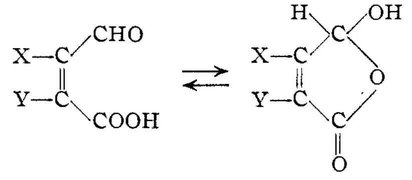
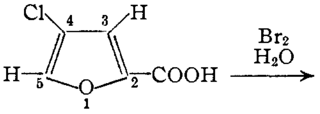
We have prepared "mucochlorobromic" acid following Hill's detailed procedure[1] as modified by Vander Wal,[3] and have shown, as outlined below, that it is α-bromo-β-chloro-β-formylacrylic acid (I, X = Cl, Y = Br).

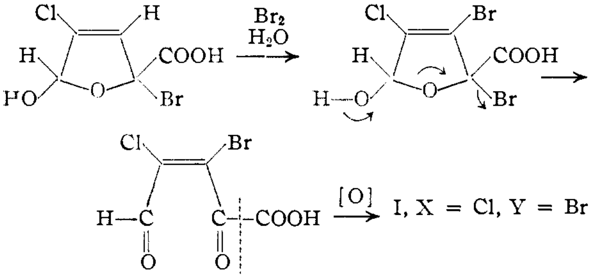


I

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).

DEPT. OF CHEMISTRY, STERLING CHEMISTRY LABORATORY
YALE UNIVERSITY
NEW HAVEN, CONN.

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t-Butyl Sulfone

BY J. ELIOT WOODBRIDGE

RECEIVED NOVEMBER 10, 1952

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°.

The presence of sulfone and *t*-butyl groups was indicated by infrared. The compound decomposed on heating to give sulfur dioxide and isobutylene.[3]

SOLUBILITIES

Solvent	Temp., °C.	Solubility, g./100 ml.
Water	20, 50, 80	1.08, 1.54, 3.18
0.1 *N* HCl	20	1.03
0.1 *N* NaOH	20	0.95
n-Pentane	20	0.82
Diethyl ether	20	5.61
Ethanol	20	16.1

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(3) The compound decomposes or builds up vapor pressure suddenly on heating in the combustion tubes, and mixtures with oxygen were several times obtained which ignited and ruined the analysis. The oxygen analysis was made by the Unterzaucher method.

RESEARCH AND DEVELOPMENT DEPARTMENT
CHEMICAL PRODUCTS DIVISION
THE ATLANTIC REFINING CO.
PHILADELPHIA, PA.

A Rapid Method for Fractionating Crude Rare Earth Ores into Mixtures Greatly Enriched with Regard to Particular Rare Earths

BY E. J. WHEELWRIGHT AND F. H. SPEDDING

RECEIVED FEBRUARY 6, 1953

It has been found in this Laboratory that efficiency of producing very pure rare earth oxides by ion-exchange methods can be greatly increased if the crude rare earth mixtures, as leached from the ores, can be first rapidly fractionated into several fractions, enriched in specific rare earths. Normally, the rare earth oxide, as obtained from the ore, consists of from 10 to 14 individual rare earths and rare earth-like elements. Some of these are present in very small amounts and some such as cerium, lanthanum, neodymium and yttrium may represent up to 50% of the total mixture, depending upon the ore involved. When the rare earth mixture is dissolved and adsorbed on the ion-exchange columns, these elements then occupy the major part of the resin band and require considerable time to elute. If the bulk of these less desirable elements can be removed by a preliminary, rapid fractionation, the efficiency of production of the pure heavy rare earths by ion-exchange methods can be increased many fold.

The older type fractionations are usually very slow and laborious. However, Schwarzenbach and Freitag,[1] Marsh,[2] Beck,[3] Vickery[4] and others, have pointed out that the rare earths do form very tight complexes with chelating agents such as Versene (ethylenediaminetetraacetic acid) and Marsh[2] and Vickery[4] have shown that fractionations using these complexes are more rapid than the older methods. However, their methods are still laborious and give smaller enrichments than might be desired. Recent determinations of the equilibrium constants of the rare earth–Versene complexes by Vickery[4] and by Wheelwright, Spedding and Schwarzenbach[5] show that the apparent equilibrium constants, determined at fixed ionic strength, differ by a factor of 10^5 across the rare earth series. It should therefore be possible to take advantage of this fact in effecting a rapid fractionation of the mixed rare earths. The purpose of this note is to indicate one of the ways in which this can be accomplished.

Most of the methods for separating the rare earths by ion-exchange columns, for example, the citrate elution as developed by this Laboratory,[6] depend upon an adsorption of a band of rare earths on the resin and the subsequent elution of this band down the column in a manner roughly analogous to chromotography. However, a much more rapid process could be effected if the ion-exchange columns were used—in a manner analogous to water-softening—to differentially adsorb one rare earth or group of rare earths and allow the others to pass through without being appreciably adsorbed. This technique has been tried by Fitch and Russell,[7] using other chelating agents, but the enrichments obtained have not been great enough to be entirely satisfactory for a preliminary separation to precede the citrate separation to obtain pure rare earths.

Our present process consists essentially of complexing part of the rare earths in a mixture with Versene, then separating the complexed rare earth ions from the uncomplexed ions by passing the solution through an ion-exchange column. The complexed ions pass through the column while the uncomplexed ions are adsorbed on the resin. Care must be taken that the capacity of the resin is such that it is capable of adsorbing all of the uncomplexed rare earths. The rare earth–Versene stability constants range from $10^{14.72}$ for La to $10^{19.65}$ for Lu, with Y appearing in the series between Tb and Dy. Since the rare earth mixture we used in this experiment contained about 60% Y, 15% heavy rare earths and 25% light rare earths, it was decided to complex the heavy rare earths Lu to Dy, make the initial separation with an ion-exchange column, and then remove the Y and the lighter rare earths from the column by passing successive solutions, containing a predetermined amount of Versene, through the column. While this experiment was performed with the resin in a column, it might be more desirable to place the resin in a tank, adsorb the rare earth mixture on the resin, and then intimately mix it with successive fixed amounts of Versene. The complexed rare earths could be removed by draining or filtering, and of course an equilibration period of about 24 hours should be allowed for each solution. We are continuing this work and it is obvious that the conditions can be greatly improved. However, the preliminary experiments were so promising and efficient that we felt that they should be reported at this time. This can best be illustrated by giving the procedure and data for one of our runs.

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(1) G. Schwarzenbach and E. Freitag, *Helv. Chim. Acta*, **34**, 1503 (1951).

(2) J. K. Marsh, *J. Chem. Soc.*, 1819 (1950); 3057 (1951).

(3) G. Beck, *Helv. Chim. Acta*, **29**, 357 (1946); *Mikrochemie ver. Mikrochim. Acta*, **33**, 344 (1948).

(4) R. C. Vickery, *J. Chem. Soc.*, 1101 (1950); 2058 (1950); 1817 (1951).

(5) E. J. Wheelwright, F. H. Spedding and G. Schwarzenbach, in press.

(6) F. H. Spedding, E. I. Fulmer, J. E. Powell and T. A. Butler, THIS JOURNAL, **72**, 2354 (1950); F. H. Spedding, E. I. Fulmer, J. E. Powell, T. A. Butler and I. S. Yaffe, *ibid.*, **73**, 4840 (1951). Also see earlier papers.

(7) F. T. Fitch and D. S. Russell, *Can. J. Chem.*, **29**, 363 (1951); *Anal. Chem.*, **23**, 1469 (1951).