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SYNTHESIS OF 2-FURYL THIOETHERS

R. A. Silverman, Rochester, N.Y., assignor to Eastman Kodak Company, Rochester, N.Y.

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ABSTRACT OF THE DISCLOSURE

A one step process of preparing a 2-furyl thioether which comprises reacting an aliphatic or aromatic mono or dithiol with a 2,5-diloweracyloxy-2,5-dihydrofuran; 2,5-dihydro - 2,5 - diloweralkoxyfuran; 2,5-dihydro - 2,5 - diloweralkoxy-2-methyl furan, or fumaric dialdehyde. Certain 2-furyl thioethers are novel compounds. Compounds prepared according to the described one step process are useful as silver complexing agents in photographic compositions.

This invention relates to a simplified synthesis of 2-furyl thioethers and certain novel 2-furyl thioethers. In one of its aspects it relates to a one-step method of preparing a 2-furyl thioether by reacting an aliphatic or aromatic mono or dithiol with certain dihydrofurans or fumaric dialdehyde. In another of its aspects it relates to certain novel 2-furyl thioethers which contain a carboxylalkylthio or carboxyarylthio group in the 2-position of a furan ring. The compounds prepared according to the invention are useful as silver complexing agents in photographic compositions.

Heretofore, several processes have been attempted for preparation of 2-furyl thioethers. For example, a few simple 2-furyl thioethers have been prepared by a route involving metalation of furan followed by sulfurization and reaction with an alkyl halide. This is described for example, in Y. L. Gol'dfarb, Y. L. Ganyushevskii, and M. A. Vinogradova, Dokl Akad. Nauk SSSR (Trans. Ed.), 151, 539 (1963). E. Niwa, H. Aoki, H. Tanaka, K. Munakata, and M. Namiki, Chem. Ber., 99, 3215 (1966). Another method employed for preparing 2-furyl thioethers involved reaction of 5-bromo-2-furoic acid or a corresponding ester with a mercaptide followed by decarboxyation. This method is described in the following references:

R. Adams and A. Ferretti, J. Am. Chem. Soc., 81, 4927 (1959)
D. G. Manly and E. D Amstutz, J. Org. Chem., 21, 516 (1956)

Also certain 2-carbonyl derivatives of 5-halofurans have been employed to prepare 2-acetyl-5-furyl-thioglycolic acid, 2-formyl-5-furyl-thioglycolic acid, and 2 - carboxy-5-furyl-thioglycolic acid. This is described, for example, in an article by Z. N. Nazarova and Yu. A. Babaev, Zhur. Obsh. Khim., (Trans. Ed.), 34, 4068 (1964). These prior art processes involve multistep methods of synthesis which are often complicated and involve expensive and often difficult to prepare starting materials.

There has accordingly been a need for a simplified process for preparing 2-furyl thioethers which eliminates the need of a multistep synthesis.

There has also been a need for compounds which form complexes with silver and photographic compositions, such as compounds which act as silver halide stabilizing agents or fixing agents as described for instance in the book The Theory of the Photographic Process, Mees and James, 3rd Edition, McMillan Co. (1966), 397–408.

There has also been a need for stable silver complexes which can be incorporated in gelatin photographic coatings as stable sources of silver for physical development. Certain compounds have been proposed, heretofore, such as silver complexes with para-toluene sulfonic acid as stable sources of silver for physical development. Coatings containing such silver complexes, however, have not been entirely satisfactory due to undersired keeping properties and light sensitivity. Certain 2-furyl thioethers prepared according to the invention have unexpectedly been found to provide silver complexes which are stable sources of silver for physical development, especially in photographic coatings employing a silver dye complex as a photosensitive component as described, for example, in U.S. application Ser. No. 764,330 of J. D. Bass, filed Oct. 1, 1968, concurrently, and French Pat. No. 1,453,635, issued Aug. 16, 1966.

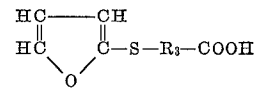
Accordingly, an object of the invention is to provide a simplified process for preparing 2-furyl thioethers.

Another object of the invention is to provide certain novel 2-furyl thioethers which are useful as silver complexing agents forming a stable silver complex useful as a stable source of silver for physical development.

According to the invention a simplified method of preparing a 2-furyl thioether is provided which comprises reacting in one step (A) an aliphatic or aromatic thiol, e.g., a mono- or dithiol with (B)

(1) 2,5-diloweracyloxy-2,5-hydrofuran,
(2) 2,5-dihydro-2,5-diloweralkoxyfuran,
(3) 2,5-dihydro-2,5-diloweralkoxy-2-methylfuran, or
(4) fumaric dialdehyde.

The invention also comprises a 2-furyl thioether represented by the formula:



wherein R_3 is a divalent hydrocarbon radical containing 1 to 20 carbon atoms, e.g., alkylene containing 1 to 20 carbon atoms, such as methylene, propylene, butylene and pentylene, preferably lower alkylene containing 1–4 carbon atoms; or arylene, containing up to 20 carbon atoms, such as, phenylene. These compounds are especially useful as silver complexing agents forming silver complexes which are stable sources of silver for physical development. This unexpected property of the described novel 2-furyl thioethers is illustrated in the following examples:

A wide range of aliphatic and aromatic thiols, e.g., mono or dithiol compounds, can be employed according to the method of the invention. These include any thiols, especially mono or dithiol compounds, which provide the desired condensation with the described furan or dialdehyde starting materials. Suitable aliphatic and aromatic mono thiol compounds include those represented by the formula:

R—SH

wherein R is a hydrocarbon radical, such as a hydrocarbon radical containing 1 to about 20 carbon atoms, e.g., alkyl, such as methyl, ethyl, propyl, butyl, eicosyl and the like, especially lower alkyl containing 1 to 5 carbon atoms, aryl such as phenyl, tolyl, xylyl and chlorophenyl; carboxyalkyl, e.g., containing 1 to 20 carbon atoms, such as carboxymethyl, carboxyethyl, carboxypropyl, carboxypentyl, carboxyoctyl, dicarboxyethyl, dicarboxypropyl, and the like; carboxyaryl, such as carboxyphenyl, carboxytolyl, containing up to 20 carbon atoms; acyl, such as acetyl, propionyl, butyryl and benzoyl; or hydroalkyl, such as containing 2 to about 20 carbon atoms, e.g., hydroxyethyl, hydroxypropyl, hydroxybutyl, hydroxydecyl,

etc.; and suitable dithiol compounds including those represented by the formula:

HS—R'—SH

wherein R' is a divalent hydrocarbon radical containing 1 to 20 carbon atoms, such as alkylene, e.g., methylene, ethylene, propylene, butylene, pentylene and decylene, especially lower alkylene containing 1–5 carbon atoms, arylene, such as phenylene, xylylene, tolylene and chlorophenylene; carboxyalkylene, such as carboxymethylene, carboxyethylene, carboxypropylene, carboxybutylene, dicarboxypropylene and dicarboxybutylene; hydroxyalkylene, such as hydroxyethylene, hydroxypropylene, hydroxybutylene and hydroxypentylene; and carboxyarylene, such as carboxyphenylene and carboxyxylylene.

Examples of suitable aliphatic and aromatic mono or dithiols as described include:

Methanethiol
Propanethiol
Hexanethiol
Dodecanethiol
1,2-ethanedithiol
1,4-butanedithiol
Mercaptoethanol
2,2-dichloroethanethiol
α-Toluenethiol
Benzenethiol
p-Chlorobenzenethiol
Methyl mercaptoacetate
Mercaptoacetic acid
Methyl α-mercaptopropionate
β-Mercaptopropionic acid
α-Mercaptopropionic acid
Mercaptosuccinic acid
o-Mercaptobenzoic acid
Thioacetic acid

A wide range of the described 2,5-dihydrofuran starting materials can also be employed. These include any 2,5-dihydrofurans, especially the 2,5-diloweracyloxy and 2,5-diloweralkoxy compounds which are compatible with the described aliphatic and aromatic mono or dithiol starting materials. Suitable compounds which can be employed as the furan starting moiety in the process of the invention are as follows:

(A) 2,5-diloweracyloxy-2,5-dihydrofurans:
2,5-diacetoxy-2,5-dihydrofuran
2,5-dihydro-2,5-dipropionoxyfuran
(B) 2,5-dihydro-2,5-diloweralkoxyfurans:
2,5-dihydro-2,5-dimethoxyfuran
2,5-diethoxy-2,5-dihydrofuran
(C) 2,5-dihydro-2,5-diloweralkoxy-2-methyl furan
2,5-dihydro-2,5-dimethoxy-2-methylfuran
2,5-diethoxy-2,5-dihydro-2-methylfuran

The described process of the invention is typically carried out in the presence of a solvent although the reaction can take place in the absence of a solvent medium. Any solvent which is compatible with the described reactants and which permits the reaction of the invention to take place is suitable. The following solvents have been found useful: acetonitrile, acetic acid and certain aromatic hydrocarbons, such as benzene and toluene. The choice of solvent has not been found to be critical except that lower alcohols such as methanol or ethanol can interfere with the mechanism of the reaction in an instance where alkoxy substituted furans are employed as starting materials. The concentration of solvent can vary over wide ranges and is usually sufficient to dissolve the reactants or provide suitable mobility for the reactants. A useful concentration is about 100 to about 400 percent by weight of solvent based on the weight of the described furan starting materials.

While the described process can take place in the absence of a catalyst, a catalyst has been found to be especially useful. The speed and yield of the reaction can be significantly improved by employing about 0.0001 to about 0.10 mole and typically about 0.001 to about 0.05 mole of catalyst per equivalent of the described furan starting material of an acid catalyst. Any acid catalyst is suitable which provides the desired improvement in reaction speed and yield. However, acid catalysts such as paratoluenesulfonic acid, sulfuric acid, maleic acid, acetic acid or oxalic acid have been found especially suitable. Oxygen and air can also catalyze the described reaction.

A wide range of reaction conditions can be employed. Suitable temperatures for the described reaction can be from about 20° C. to about 120° C. When a solvent reaction medium is employed the reaction is normally carried out at the reflux temperature of the solvent although in many cases it has been found useful to merely mix the described reactants in the solvent medium at room temperature such as at about 20° C. to about 30° C. until completion of the reaction.

The described reaction is usually carried out under normal atmospheric pressure, although increased pressure can be employed if desired. Since oxygen and air catalyze the reaction it is normally desirable to employ normal atmospheric conditions. The reaction, however, can be carried out in the absence of oxygen or air such as in a nitrogen atmosphere or other inert gas. In case oxygen or air is employed to aid in catalyzing the described reaction any suitable means and procedure can be employed for contacting the reaction mixture with air or oxygen such as by bubbling the catalyzing gas through the reaction mixture.

Suitable concentrations of the described reactants can vary over wide ranges but normally stoichiometric quantities are employed. Suitable concentration ratios of the described furan starting materials to the described thiol starting materials can be about 0.3 to about 3.0 equivalents of furan compound to thiol compound. A concentration range of about 0.5 to about 1.0 equivalents of described furan starting material is especially suitable. The desired concentration can be determined by those skilled in the art based on the particular starting materials and reaction conditions as well as solvent medium if one is employed.

The desired product can be recovered by methods commonly employed in organic chemistry such as by recrystallization from a suitable solvent such as ether, methylcyclohexane, ligroin and the like; distillation or extraction.

In some cases, however, it can be desirable not to recover the reaction product where the reaction mixture has no adverse effects on the desired use.

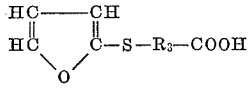
A typical method of the invention when employing 2,5-dihydro-2,5-dimethoxyfuran as a starting material comprises mixing in acetonitrile about 0.4 mole of 2,5-dihydro-2,5-dimethoxyfuran and about 0.4 to about 0.5 mole of the described thiol starting material. Usually about 200 milliliters of acetonitrile is sufficient. About 0.1 gram of acid catalyst, such as p-toluene-sulfonic acid monohydrate, is added to the reaction mixture and the solution stirred at about 25° C. until reaction completion. Except in the case where mercapto acids are employed as starting materials, the desired product can be recovered by diluting the reaction mixture with about an equal volume of water, neutralizing with an alkali metal bicarbonate such as sodium or potassium bicarbonate, extracting with a suitable solvent such as ether, drying over an agent such as magnesium sulfate, and distilling. In the case of mercapto acids employed as starting materials, the reaction mixture can be stripped of solvent employing normal procedures of organic chemistry and the residues extracted with alkali such as a dilute solution of sodium hydroxide and the desired product is precipitated from solution employing hydrochloric acid followed by recrystallization from a suitable solvent such as acetonitrile, dilute acetic acid, benzene or toluene.

A second typical method of the invention which has been found suitable comprises preparing a solution of

about 0.4 mole of 2,5-dihydro-2,5-dimethoxyfuran and about 0.4 to about 0.5 mole of the described thiol starting material. As described, acetonitrile is a suitable solvent for the reaction mixture. About 0.15 gram of acid catalyst, such as maleic acid, is added to the reaction mixture followed by heating under reflux in a nitrogen atmosphere until reaction completion. The desired product can be recovered as described.

Another typical method of the invention comprises carrying out the described reaction by preparing a solution of 2,5-dihydro-2,5-dimethoxyfuran with a described thiol starting material in acetonitrile followed by heating the resulting reaction mixture at reflux. During reflux air can be bubbled slowly through the reaction mixture. This can provide higher yields and minimize possibility of decomposition while speeding the reaction.

Compounds, as described herein, which can be prepared according to the process of the invention include novel 2-furyl thioethers represented by the formula:



wherein R_3 is a divalent hydrocarbon radical containing 1–20 carbon atoms, e.g., alkylene containing 1 to 20 carbon atoms, such as methylene, ethylene, propylene, butylene, pentylene and the like, preferably lower alkylene containing 1–5 carbon atoms. Examples of novel compounds which can be prepared according to the invention include:

(a) (2-furylthio) acetic acid
(b) (2-furylthio) propionic acid
(c) (2-furylthio) succinic acid, or
(d) (2-furylthio)-o-benzoic acid.

The described compounds of the invention are useful as silver complexing agents in photographic compositions, especially as stable sources of silver for physical development when complexed with silver. Suitable compositions and elements are described in copending application U.S. Ser. No. 764,330 of J. D. Bass, filed Oct. 1, 1968. Photographic compositions in which silver complexes of the described compounds of the invention can be employed include any of those wherein a stable source of silver is desirable for physical development. For example, a photographic element can be prepared containing a photosensitive coating containing a silver dye complex as a photosensitive moiety, and a silver complex of the described compounds of the invention. After exposure, the resulting latent image in the photographic element can be developed by contacting the photosensitive coating with a developer solution containing a silver halide developing agent in the presence of a development activator. The resulting developed image provides high resolution.

Various colloids can be used alone or in combination as vehicles or binding agents in photographic emulsions and elements employing compounds and silver complexes of compounds of the invention. Among such materials which are suitable are the natural and/or synthetic binding materials generally employed for this purpose including, for example, gelatin, colloidal albumin, water soluble vinyl polymers, mono and polysaccharides, cellulose derivatives, proteins, water soluble polyacrylamides, polyvinyl pyrrolidine and the like. In addition to the hydrophilic colloids, the vehicle or binding agents can contain dispersed polymerized vinyl compounds, particularly those which increase the dimensional stability of photographic materials. Suitable synthetic polymers of this type include water insoluble polymers of alkylacrylates and methacrylates, as well as polymers of acrylic acid, sulfoalkylacrylates or methacrylates and the like.

Various photosensitive salts can be employed in combination with the described silver complexes of the compounds of the invention. These include the various photosensitive silver salts employed in the photographic art as well as photosensitive nonsilver compounds. Suitable silver halides include any of the photographic silver halides as exemplified by silver bromide, silver iodide, silver chloride and mixed silver halide, such as silver chlorobromide, silver bromoiodide and the like. Silver halides used can be those which form latent images predominantly on the surface of the silver halides grains or those which form latent images inside the silver halide crystals as exemplified by U.S. Pat. 2,552,250, of Davy and Knott, issued Apr. 8, 1952, as well as direct positive emulsions such as those described in U.S. Pat. 2,541,472, of Kendall and Hill, issued Feb. 13, 1951.

The described compounds of the invention and silver complexes thereof can be employed in photographic layers coated on a wide variety of supports. These include any of those typically employed in the photographic art such as flexible supports including cellulose nitrate film, cellulose acetate film, poly (vinyl acetal) film, polystyrene film, poly (ethylene terephthalate) film, and related films or resinous materials, as well as glass, paper, metal and the like. Supports such as paper supports, which are partially acetylated or coated with baryta or an olefin polymer, particularly a polymer of an olefin containing 2–10 carbon atoms such as polyethylene, polypropylene, ethylene-butene copolymers and the like give good results.

The photographic emulsions and elements with which compounds of the invention, as well as silver complexes of compounds of the invention, can be employed can also contain additional addenda particularly those known to be beneficial in photographic materials of this nature. For example, they can contain stabilizers or antifoggants such as organic azoles, azaindenes, mercaptans, metal salts such as cadmium, lead, mercury, gold or other noble metal salts, spectral sensitizers such as the cyanines, merocyanines, complex (trinuclear) merocyanines, styryls, hemicyanines, speed increasing materials, such as polyalkylene glycols, onium salts and thioethers, plasticizers, coating aids such as anionic, nonionic and amphoteric surface active compounds and the like. The photographic silver salt emulsions employed herein can also be chemically sensitized with compounds of the sulfur group such as sulfur, selenium and tellurium sensitizers, noble metal salts such as gold, or reduction sensitized with reducing agents or combinations of such materials. The photographic elements can also contain fluorescent brighteners such as stilbenes, coumarins, benzothiazoles, benzoxazoles, imidazoles, etc.

As described, various photographic elements can be employed containing the compounds of the invention or silver complexes of the compounds of the invention. These can be nonspectrally sensitized emulsions such as X-ray type emulsions or they can be orthochromatic, panchromatic, infrared sensitive and the like emulsions containing spectral sensitizing dyes such as described in U.S. Pats. 2,526,-632 and 2,503,776.

The compounds of the invention and silver complexes of compounds of the invention can be used in photographic emulsions and/or receiver sheets intended for use in diffusion transfer processes which utilize undeveloped silver salts in the nonimage areas of the negative to form a positive by dissolving the undeveloped silver salts and precipitating them on a receiving layer in close proximity to the original silver salt emulsion layer. Such processes are described, for example, in U.S. Pat. 3,020,155 of Yackel et al., issued Feb. 6, 1962; U.S. Pats. 2,584,029 issued Jan. 29, 1952; 2,698,236 issued Dec. 28, 1954; and 2,543,181 issued Feb. 27, 1951 of E. H. Land and U.S. Pat. 2,352,014 of Rott, issued June 20, 1944. Compounds of the invention and silver complexes of compounds of the invention can be used also in color transfer processes which utilize the diffusion transfer of developer, coupler or dye from the light-sensitive layer to a second layer such as described in U.S. Pat. 2,559,643 of Land, issued July 10, 1951; U.S. Pat. 2,698,798 issued Jan. 4, 1955; U.S. Pat. 2,756,142 of Yutzy issued July 24, 1956; U.S.

Pat. 3,252,915 of Weyerts et al., issued May 31, 1966; and U.S. Pat. 3,227,550 of Whitman et al., issued Jan. 4, 1966.

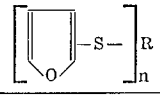
Compounds of the invention and silver complexes thereof can also be used in compositions and emulsions used in lithography, preparation of direct prints, or in colloid transfer processes as well as in elements used in monobath processing such as described in U.S. Pat. 2,875,048 of Haist et al., issued Feb. 24, 1959 and web-type processing or elements therefor, such as described in U.S. Pat. 3,179,517 of Tregillus et al., issued Apr. 20, 1965. They can also be used in so-called stabilization processing or elements therefor, such as processing an element containing an incorporated developer through an activator bath containing a thiocyanate stabilizer as described, for example, in British Pat. 1,061,892 issued Mar. 15, 1967 or in an article entitled "Stabilization Processing of Films and Papers" by H. D. Russell, E. C. Yackel and J. S. Bruce, PSA Journal, August 1950, pages 59–62.

The following examples are included for a further understanding of the invention.

EXAMPLE 1

In each of the following examples, 1 to 11, the following process is carried out: 0.4 mole of 2,5-dihydro-2,5-dimethoxy furan and 0.4–0.5 mole of the thiol compound corresponding to the radicals set out in Column A of Table I are mixed in 200 ml. of acetonitrile. 0.1 gram of p-toluenesulfonic acid monohydrate is added to the resulting mixture and the solution stirred at 25° C. until reaction is essentially complete, about 0.5 to 4 hours. Except for the products employing mercapto acids designated in Table I as starting materials the reaction mixture upon reaction completion is diluted with an equal volume of water, neutralized with sodium bicarbonate, extracted with ether, dried over magnesium sulfate and distilled to separate the desired product designated in Table I. Reaction products from mercapto acids designated in Table I are stripped of solvent and the residues extracted with a dilute sodium hydroxide solution with the product being precipitated from solution by hydrochloric acid and recrystallized from acetonitrile.

TABLE I
2-furyl thioethers

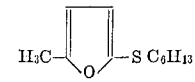


Example No.	Column A R	Column A n	Column B B.p., ° C. (mm. Hg. pressure)	Column C n_D^{25}
1	CH_3—	1	67 (75)	1.5191
2	—CH_2CH_2—	2	64 (0.12)	1.5805
3	Cl_2CHCH_2—	1	48–52 (0.04)	1.5455
4	p—ClC_6H_4—	1	86–88 (0.1)	1.6048
5	CH_3OCOCH_2—	1		
6	HOCOCH$_2$—	1	[1] 48–49	
7	$CH_3OCOCH(CH_3)$—	1	53 (0.25)	1.5054
8	HOCOCH(CH$_3$)—	1	[1] 64–65	
9	HOCO$(CH_2)_2$—	1	[1] 51.5–52.5	
10	HOCOCH$_2$CH(COOH)—	1	[1] 136–138	
11	CH_3CO—	1	70–73 (5.5)	1.5260

[1] Melting point.

EXAMPLE 12

The process set out in Example 1 is repeated with the exception that 2,5-dihydro-2,5-dimethoxy-2-methylfuran and hexane thiol are employed as starting materials. The reaction is carried to completion and the desired product:

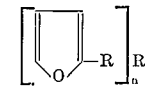


having a boiling point of 55–58° C. at 1.1 mm. Hg pressure, is recovered employing the procedure of Example 1.

EXAMPLE 13

0.4 mole of 2,5-dihydro-2,5-methoxy furan and 0.4–0.5 mole of the thiol compound corresponding to the radicals set out in Column A of Table II following are mixed in 200 ml. of acetonitrile containing 0.15 g. of maleic acid. The resulting solution is heated under reflux in a nitrogen atmosphere until reaction completion, about 4 to 6 hours. The resulting product is isolated as described in Examples 1–11. The desired product is set out in Table II.

TABLE II
2-furyl thioethers



Example No.	Column A R	Column A n	Column B B.p., ° C. (mm. Hg. pressure)	Column C $^5n_D^2$
13	$CH_3(CH_2)_2$	1	70 (15)	1.5028
14	$CH_3(CH_2)_5$	1	61–63 (0.1)	1.4919
15	$CH_3(CH_2)_{11}$	1	110–115 (0.01)	1.4835
16	—$(CH_2)_4$—	2	114–117 (0.015)	1.5621
17	$HOCH_2CH_2$	1	59–64 (0.08)	1.5379
18	$C_6H_5CH_2$	1	67–71 (0.07)	1.5845
19	CH_3OCOCH_2	1	60–63 (0.07)	1.5140

EXAMPLE 20

0.4 mole of 2,5-dihydro-2,5-dimethoxy furan and 0.4–0.5 mole of propanethiol are mixed in 200 ml. of acetonitrile. The resulting solution is refluxed and air is bubbled slowly through the mixture for about ½ hour. Refluxing is then continued until reaction completion. The desired product is isolated as described in Example 1 and is recovered in significantly higher yields than Example 1.

EXAMPLE 21

A mixture of 2 g. of fumaric dialdehyde (see reference by K. Alder, H. Betzing, and H. Heinbeck, Ann. vol. 638, page 187 (1960)) and 2.07 g. of propanethiol is dissloved in 9.5 g. of acetonitrile. The resulting mixture is stirred at 25° C. and 0.015 ml. of acetic acid is added. The mixture is heated under reflux until reaction completion. The desired product is isolated as described in Example 1.

EXAMPLE 22

A solution of 30.9 g. of mercaptoacetic acid and 0.12 g. of maleic acid is prepared in 350 ml. of benzene. The resulting solution is heated to reflux temperature and 43.7 g. of 2,5-dihydro-2,5-dimethoxyfuran in 30 ml. of benzene is added dropwise over a 2 hour period. A benzene methanol azeotrope results and is removed during reaction by fractional distillation. The reaction is continued until complete, about 9 hours, and the solvent evaporated. The residue is extracted with dilute aqueous sodium hydroxide. The desired product is precipitated with dilute hydrochloric acid and purified by recrystallization from methylcyclohexane to produce the desired (2-furylthio)acetic acid.

EXAMPLE 23

This example illustrates the process of the invention carried out in the absence of an acid catalyst.

The procedure set out in Example 22 is repeated with the exception that 2,5-diacetoxy-2,5-dihydrofuran is employed in place of 2,5-dihydro-2,5-dimethoxyfuran as a

starting material and no maleic acid is employed. The described reaction is carried out in acetonitrile in place of benzene. The desired product is recovered as set out in Example 22.

EXAMPLE 24

This illustrates preparation of the corresponding methyl ester of α-(2-furylthio)propionic acid.

The procedure set out in Example 1 is repeated with the exception that 61.4 g. (0.047 mole) of 2,5-dihydro-2,5-dimethoxyfuran and 50 g. (0.47 mole) of 2-mercaptopropionic acid are employed as starting materials. Analysis of the resulting product indicates a mixture of two products is obtained. Further analysis indicates that the mixture consists of α-(2-furylthio)propionic acid and its corresponding methyl ester, boiling point 52° C. (0.25 mm. mercury pressure). Recrystallization of the product from ligroin produces alpha-(2-furylthio)propionic acid, melting point 64–65° C.

EXAMPLE 25

Example 1 is repeated employing o-mercaptobenzoic acid as the described thio starting material. A 2-furyl thioether is produced as shown in Table I wherein *n* is 1 and R is o-$HOCOC_6H_4$— having a melting point of 170–171° C.

It is believed that maleic dialdehyde will also undergo the described reactions with thiols.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove, and as defined in the appended claims.

I claim:

1. A method of preparing a 2-furyl thioether which comprises reacting in one step (A) an aliphatic or aromatic thiol represented by the formula:

R—SH

wherein R is a hydrocarbon radical containing 1 to 20 carbon atoms; monocarboxyalkyl and dicarboxyalkyl containing up to 20 carbon atoms; monocarboxyaryl containing up to 20 carbon atoms; alkanoyl containing up to 6 carbon atoms; or monohydroxyalkyl containing 2 to 6 carbon atoms; and represented by the formula:

HS—R'—SH

wherein R' is a divalent hydrocarbon radical containing 1 to 20 carbon atoms; monocarboxyalkylene containing up to 5 carbon atoms, dicarboxyalkylene containing up to 5 carbon atoms, monohydroxyalkylene containing 2 to 7 carbon atoms, monocarboxyphenylene and monocarboxyxylyene, with (B)

(1) 2,5-diacetoxy-2,5-dihydrofuran, or 2,5-dihydro-2,5-dipropionoxyfuran,
(2) 2,5-dihydro-2,5-diloweralkoxyfuran,
(3) 2,5-dihydro-2,5-diloweralkoxy-2-methylfuran, or
(4) fumaric dialdehyde.

2. A method of preparing a 2-furyl thioether as in claim **1** which comprises reacting said aliphatic or aromatic thiol with 2,5-dihydro-2,5-dimethoxyfuran.

3. A method of preparing a 2-furyl thioether as in claim **1** wherein said reaction is carried out in the presence of an acid catalyst.

4. A method of preparing a 2-furyl thioether as in claim **1** wherein said reaction is carried out employing a concentration ratio of said compound (B) to said compound (A) of about 0.3 to about 3.0 equivalents.

5. A method as in claim **1** of preparing an α-(2-furylthio) lower alkyl carboxylic acid which comprises reacting a 2,5-dihydro-2,5-dimethoxyfuran with an α lower alkyl mercapto carboxylic acid.

6. A method as in claim **1** of preparing
(a) (2-furylthio) acetic acid,
(b) (2-furylthio) propionic acid,
(c) (2-furylthio) succinic acid, or
(d) (2-furylthio) o-benzoic acid
which comprises reacting 2,5-dihydro-2,5-dimethoxyfuran with, respectively,
(a) mercaptoacetic acid,
(b) mercaptopropionic acid,
(c) mercaptosuccinic acid, or
(d) o-mercaptobenzoic acid
in a solvent in the presence of an acid catalyst.

7. A method of preparing a 2-furyl thioether which comprises reacting in one step (A) an aliphatic or aromatice thiol of the formula:

R—SH

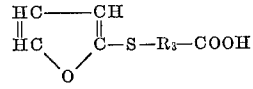
wherein R is alkyl containing 1 to 20 carbon atoms, phenyl, tolyl, xylyl, chlorophenyl, monocarboxyalkyl containing up to 20 carbon atoms, dicarboxyalkyl containing up to 20 carbon atoms, monocarboxyphenyl, monocarboxytolyl, alkanoyl containing 1 to 6 carbon atoms, benzoyl and monohydroxyalkyl containing 2 to 6 carbon atoms; and of the formula:

HS—R'—SH

wherein R' is alkylene containing 1 to 6 carbon atoms, phenylene, xylyene, tolylene, chlorophenylene, monocarboxyalkylene containing up to 5 carbon atoms, dicarboxyalkylene containing up to 5 carbon atoms, monohydroxyalkylene containing 2 to 7 carbon atoms, monocarboxyphenylene and monocarboxyxylylene, with (B)

(1) 2,5-diacetoxy-2,5-dihydrofuran,
(2) 2,5-dihydro-2,5-dipropionoxyfuran,
(3) 2,5-dihydro-2,5-diloweralkoxyfuran,
(4) 2,5-dihydro-2,5-diloweralkoxy-2-methylfuran, or
(5) fumaric dialdehyde.

8. A 2-furyl thioether represented by the formula:



wherein R_3 is alkylene containing 1 to 5 carbon atoms or phenylene.

9. A 2-furyl thioether as in claim **8** which is (2-furylthio)acetic acid.

10. A 2-furyl thioether as in claim **8** which is (2-furylthio) propionic acid.

11. A 2-furyl thioether which is (2-furylthio) succinic acid.

12. A 2-furyl thioether as in claim **8** which is (2-furylthio) o-benzoic acid.

References Cited

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ALEX MAZEL, Primary Examiner

B. I. DENTZ, Assistant Examiner

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96—66