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SULFONAMIDE COMPOUNDS

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6 Claims. (Cl. 260-556)

The present invention relates to novel chemical compounds and more particularly to novel sulfonamide compounds and to processes for preparing these compounds. The present invention further relates to novel compounds which accelerate or promote the release of oxygen from oxygen releasing compounds in aqueous media and which are useful in bleaching and washing operations. The term "oxygen releasing compound" as used herein is intended to include hydrogen peroxide and all compounds which, when placed in water, form hydrogen peroxide.

Sulfonamide compounds are compounds whose molecules contain an SO₂ group in which the sulfur atom is linked to a nitrogen atom. A number of these compounds, specifically the so-called sulfa drugs, including sulfadiazine, sulfa-guanidine, sulfamerazine, sulfanilamide, sulfapyridine, sulfathiazole and the like are well known and have been widely used as drugs in combating bacterial infections. These and other sulfonamides of the prior art have occasionally been employed in the manufacture of dyes and/or dye intermediates.

The novel sulfonamide compounds of the present invention have a novel, unrelated and unexpected utility, namely the acceleration and/or promotion of the bleaching activity of oxygen releasing compounds not possessed by the above mentioned sulfonamides.

Detergent compositions containing an oxygen releasing compound, for example, an inorganic per-salt, such as an alkali metal perborate or percarbonate, or a peroxide such as urea peroxide have been disclosed heretofore as useful for washing and bleaching purposes. Although such compositions provide a satisfactory bleaching action when they are used in water at or near the boiling point (e.g., 95° C.-100° C.), the bleaching activity is unsatisfactory when the water is at lower temperature, that is temperatures below 75° C. Detergent and/or bleaching compositions containing oxygen-releasing compounds thus have the disadvantage of being unsatisfactory for many uses such as the washing and/or bleaching of textiles and fabrics which cannot withstand higher temperatures, that is, temperatures above about 70° C. or when it is desired to use washing media at lower temperatures.

Such disadvantages have been recognized and the prior art indicates that attempts have been made to find compounds which would promote or accelerate the release of oxygen-releasing compounds in water at low temperature (e.g., 50° C.-70° C.) with the goal of providing more effective bleaching activity and washing activity of such oxygen releasing compounds.

Examples of such prior art compounds are those disclosed in the following: U.S. Patent 2,898,181, issued August 4, 1959, discloses the use of certain carboxylic acid amides, such as acetamide or acrylamide to accelerate or promote the release of oxygen from aqueous solutions containing inorganic per-salts; U.S. Patent 2,955,905, issued October 11, 1960, discloses the addition of esters such as the benzoyl esters of alkali metal phenol sulfonates and glucose penta-acetate as oxygen-releasing promoters to washing compositions containing inorganic per-salts; German Patent 1,081,181, published July 8, 1955, discloses the addition of certain compounds such as malonitrile or ethylene dicyanide in compositions containing inorganic pre-salts; and German Patent 1,038,693, published November 22, 1956, discloses cer-

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tain carboxylic anhydrides such as benzoic anhydride and phthalic anhydride in compositions containing sodium perborate to promote or accelerate the release of oxygen therefrom.

However, the promoter compounds of the above-mentioned patents have certain disadvantages in that, when incorporated in compositions containing oxygen-releasing compounds, the compositions either do not bleach efficiently in water at temperatures of between 50° C. or 75° C. or the oxygen-releasing compound in the composition tends to decompose, resulting in a loss of available oxygen therefrom, when the compositions are stored under normal storage conditions for periods of from one week to several months.

It has presently been found that the novel sulfonamide compounds of the instant invention are, surprisingly, highly effective in accelerating or promoting the bleaching properties and the release of oxygen from oxygen-releasing compounds in water at temperatures as low as 40° C. Additionally these novel compounds overcome the disadvantages of instability, above-referred-to, of the prior art compounds heretofore described for use with oxygen-releasing compounds.

It is one object of this invention to provide novel sulfonamide compounds.

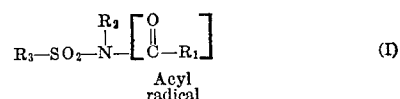
It is a further object of this invention to provide processes for preparing these novel sulfonamide compounds.

It is another object of this invention to provide a class of novel sulfonamide compounds which are useful in promoting and/or accelerating the release of oxygen from oxygen-releasing compounds in water.

It is a further object of the present invention to provide a class of novel N-acyl, alkylsulfonamides which will increase the bleaching and washing efficiency of oxygen releasing agents in water at temperatures as low as 50° C.

Still further objects and advantages of the present invention are disclosed in and will become apparent from the following description and the appended claims.

The present invention provides a class of N-substituted, N-acyl alkylsulfonamides having the general formula



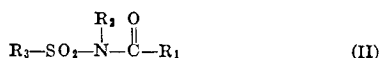
where R₁ and R₂ are organic radicals, at least one of which is an aliphatic radical, and where R₃ is an alkyl group. Compounds of this class are generally stable, crystalline solids when pure, have a limited, but effective, solubility in water and are useful in increasing the bleaching efficiency of oxygen-releasing compounds when incorporated therewith in water. Such compounds, where R₃ is an alkyl group containing 10 carbon atoms or less, are usually readily obtainable in crystalline form. Alkyl sulfonamides of this class may also be employed in dry compositions containing oxygen-releasing compounds and such compositions are generally stable with respect to loss of available oxygen when stored under ordinary storage conditions for prolonged periods of time, that is, generally for periods of six months or longer.

The term "N-acyl" as used herein is intended to include the structure designated parenthetically in Formula I. Thus when R₁ is an aliphatic group or radical the N-acyl structure is an alkanoyl group or radical. When R₁ is an aromatic group or radical the N-acyl structure is an aroyl group or radical. In the above formula, the alkyl group designated as R₃ may have as many as 20 or more carbon atoms, however, compounds in which R₃ contains more than 10 carbon atoms often have limited water solubility and thus are not as useful for oxygen-releasing compound formulations. Thus, particularly suitable alkyl-sulfonamides are those in which the alkyl group (R₃) in

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the above structure), includes, alkyl groups having a straight or branched chain for example, methyl ethyl, n-propyl, isopropyl, n-butyl, isobutyl, secbutyl, t-butyl, n-amyl, iso-amyl, n-hexyl, isohexyl, n-heptyl, isoheptyl, n-octyl, iso-octyl, 2-ethyl hexyl, etc. groups or radicals.

Particularly advantageous N-substituted N-acyl alkylsulfonamides of the present invention and falling within the scope of the above formula are N-substituted, N-acyl alkylsulfonamides having the general formula



where R_1 and R_2 are organic radicals at least one of which is a aliphatic radical and where R_3 is an alkyl group preferably having from 1 to 10 carbon atoms. Compounds of this class include, for example, N-substituted N-acyl methyl-, ethyl-, or butylsulfonamides and, when pure, are stable crystalline solids. When the compounds contain impurities, some of them are sometimes oily liquids. However, all such compounds generally have sufficient water solubility to be useful in increasing the bleaching efficiency of oxygen-releasing compounds in water at relatively low temperatures, e.g., temperatures as low as 40° C.

One particularly useful group of novel N-substituted, N-acyl alkylsulfonamides falling within the scope of Formula I comprises compounds where one of the organic radicals R_1 or R_2 is an aliphatic radical and the other is an aromatic radical, preferably R_2 is an aliphatic and R_1 is an aromatic radical, and where R_3 is an alkyl group. Another group of particularly useful compounds falling within the scope of Formula I comprises compounds where R_1 and R_2 are like or dissimilar aliphatic radicals and R_3 is an alkyl group.

The aliphatic radicals of R_1 and/or R_2 in either or both of the above formulae preferably contain from 1 to 10 carbon atoms in the aliphatic group. Although such aliphatic radicals may contain more than 10 carbon atoms, for example, up to 30 carbon atoms, compounds containing more than 10 carbon atoms, often have limited water solubility. Thus, the unsubstituted aliphatic hydrocarbon groups or radicals in the above structure may, and, preferably do, include, for example, alkyl groups or radicals having a straight or branched chain, e.g., methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, secbutyl, t-butyl, n-amyl, iso-amyl, n-hexyl, isohexyl, n-heptyl, isoheptyl, n-octyl, iso-octyl, 2-ethyl hexyl, etc. groups or radicals.

The substituents of the substituted aliphatic groups or radicals may be, for example, halogen atoms, hydroxyl, sulfo, nitro, carboxy-, alkoxy-, carbalkoxy-, amino, alkyl or carboxyl groups or radicals to provide the aforementioned substituted groups or radicals.

The unsubstituted aromatic groups or radicals may be, for example, phenyl, pyridyl, benzyl, alpha and beta naphthyl, quinolyl, anthryl, benzquinolyl and the like. The substituents of substituted aromatic groups or radicals may include halo-, hydroxyl, nitro-, sulfo- and alkyl substituted groups or radicals. The alkyl substituted aromatic groups or radicals preferably contain from 1 to 20 carbon atoms in the alkyl group.

Illustrative examples of some specific N-substituted, N-acyl alkylsulfonamides of this invention falling within the scope of Formula I and which are contemplated by this invention are:

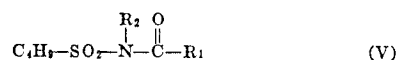
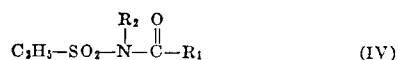
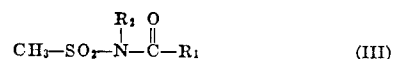
N-ethyl, N-acetyl, methyl-, ethyl, or propylsulfonamide
N-ethyl, N-benzoyl, methyl-, ethyl-, or butylsulfonamide
N-phenyl, N-propionyl, methyl-, ethyl-, or propylsulfonamide
N-n-propyl, N-acetyl, methyl-, ethyl-, or butylsulfonamide
N-isopropyl, N-chloroacetyl, methyl-, ethyl-, or propylsulfonamide
N-hydroxymethyl, N-benzoyl, amyl-, hexyl-, or heptylsulfonamide

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N-ethyl, N-beta-phenylacetyl, methyl-, ethyl, or propylsulfonamide
N-methyl, N-hydrocinnamoyl, methyl-, or ethylsulfonamide
N-(4-hydroxycyclohexyl), N-chloroacetyl, methyl-, or ethylsulfonamide
N-(beta-carboxymethyl), N-(benzoyl)-methyl-, ethyl-, or butylsulfonamide
N-(4-pyridyl), N-propionyl, methyl-, ethyl-, or propylsulfonamide
N-formyl, N-(p-bromobenzoyl), methyl-, or ethylsulfonamide
N-carbethoxymethyl, N-(alpha-naphthoyl) methyl-, or ethylsulfonamide
N-methyl, N-(p-nitrobenzoyl), methyl-, or ethylsulfonamide
N-acetyl, N-p-hydroxymethyl, methyl-, ethyl-, or butylsulfonamide
N-phenyl, N-butyroyl, methyl-, ethyl-, or propylsulfonamide
N-nitroethyl, N-acetyl, methyl, ethyl-, or butylsulfonamide

A preferred group of N-substituted, N-acyl, alkylsulfonamides falling within the scope of Formula II are compounds where R_1 or R_2 , or both, are unsubstituted aliphatic radicals, and R_3 is an alkyl group. Another preferred group of compounds are those where R_1 or R_2 is an unsubstituted aliphatic radical and the other is an unsubstituted aromatic radical, preferably R_1 is an unsubstituted aromatic radical and R_2 is an unsubstituted aliphatic radical, and R_3 is an alkyl group.

Particularly preferred compounds of this invention which have been found to be especially useful in promoting or accelerating the release of oxygen from oxygen-releasing compounds are N-substituted, N-acyl alkylsulfonamides having the following general formulae



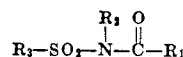
where R_1 and R_2 are as above-described.

Specific N-substituted, N-acyl, alkylsulfonamides which have been found to be particularly suitable in promoting or accelerating bleaching properties and the release of oxygen from oxygen-releasing compounds are:

N-methyl, N-acetyl, methylsulfonamide
N-phenyl, N-acetyl, methylsulfonamide
N-methyl, N-benzoyl, methylsulfonamide
N-methyl, N-benzoyl, ethylsulfonamide
N-methyl, N-benzoyl, butylsulfonamide

The N-substituted, N-acyl, alkylsulfonamides of this invention may be prepared by a process which comprises mixing and reacting an N-substituted alkylsulfonamide such as an N-aliphatic or an N-aromatic substituted sulfonamide with an acyl compound such as, for example, an alkanoyl or an aroyl compound. In such reaction the N-substituted alkylsulfonamide and the acyl compound should be so selected and reacted that a compound char-

fonamides having the following general formulae



where R_1 or R_2 , or both, are aliphatic radicals, and R_3 is an alkyl group, is formed. Although the amounts of N-substituted alkylsulfonamides and acyl compounds may vary widely, they are preferably reacted in a mol ratio of from about 1.5:1 to 1:1.5, more preferably a mol ratio of about 1:1.

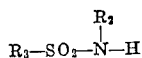
A suitable process for preparing an N-aliphatic, N-alkanoyl, alkylsulfonamide of this invention comprises mixing and reacting an N-aliphatic alkylsulfonamide with

an alkanoyl compound such as, for example, an alkanoyl halide until an N-substituted, N-acyl alkylsulfonamide having the above general formula is formed. In the product formed by this process, R_1 and R_2 in the above described formula are aliphatic radicals and R_3 is an alkyl group.

A suitable process for preparing an N-aliphatic, N-aroyl sulfonamide of this invention comprises mixing and reacting an N-aliphatic alkylsulfonamide with an aroyl compound, for example, an aroyl halide, until an N-substituted, N-acyl sulfonamide having the above described general formula is formed. In the product formed by such a process, R_1 of the above formula is an aromatic group or radical and R_2 is an aliphatic group or radical and R_3 is an alkyl group.

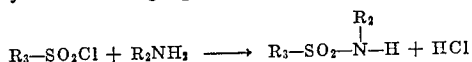
A suitable process for preparing an N-aromatic, N-alkanoyl sulfonamide of this invention comprises mixing and reacting an N-aromatic alkylsulfonamide with an alkanoyl compound, until an N-substituted, N-acyl alkylsulfonamide having the above general formula is formed. In the product formed in this process R_1 in the above formula is an aliphatic group or radical and R_2 is an aromatic group or radical.

The N-substituted alkylsulfonamides which may be employed in such process are characterized in having the formula:



where R_3 is an alkyl group as hereinbefore described and R_2 is an organic radical, e.g., either an aliphatic or an aromatic radical as hereinbefore described.

The N-substituted alkylsulfonamides may be readily obtained by reacting a suitable alkylsulfonyl chloride or a mixture of alkylsulfonyl chlorides with an organic amine in a liquid alkaline medium, the reaction being exemplified by the following equation



where R_2 and R_3 have the same meaning and significance as hereinbefore described.

The organic amines which may be employed in the above process include, for example, alkylamines such as methylamine, ethylamine, butylamine, cyclohexylamine and the like and arylamines such as, for example, aniline, naphthylamine, aminopyridine, amino-anthracene, etc.

The acyl compounds which may be reacted with the above-described N-substituted alkylsulfonamides in accordance with the processes of this invention include organic acid anhydrides having the formula $(R_1CO)_2O$, organic esters having the formula R_1COOX , and acyl halides having the formula R_1COY . In the above formula R_1 is an organic radical as hereinbefore described, and X is an alkyl or an aryl group or radical and Y is a halogen preferably chlorine or bromine.

Examples of acyl compounds which may be employed in the processes of this invention include alkanoyl compounds, for example, alkyl acid anhydrides such as acetic anhydride, butyric anhydride and the like; alkanoyl halides such as acetyl chloride, acetyl bromide, the corresponding butyryl halides and the like; aroyl compounds such as, for example, benzoic anhydrides, benzoyl chloride or bromide and the like; mixed anhydrides, for example, acetyl benzoate, butyryl benzoate, etc., and aroyl esters such as benzoyl acetate, benzoyl butyrate, etc.; carboxylic acid esters, such as ethyl benzoate, benzyl propionate, ethyl acetate, ethyl propionate and the like.

The particular N-substituted alkylsulfonamide or mixture of N-substituted alkylsulfonamides and the particular acyl compound employed in the processes of this invention will depend upon the particular N-substituted, N-acyl, alkylsulfonamide desired. When the N-substituted alkylsulfonamide is an N-aromatic alkylsulfonamide the acyl compound is an alkanoyl compound. However,

when the N-substituted alkylsulfonamide is an N-aliphatic alkylsulfonamide the acyl compound may be either an alkanoyl or an aroyl compound.

The N-substituted, alkylsulfonamide may be mixed and reacted with any of the above-described acyl compounds either in situ, that is, in the above-described liquid alkaline medium or alternatively such sulfonamide may be recovered as a solid and thereafter reacted with the acyl compound. When it is desired to carry out the reaction in situ the acyl compound, for example, either an alkanoyl compound or an aroyl compound, is slowly added, with agitation to a mixture comprising a liquid alkaline medium and the N-substituted alkylsulfonamide. During and/or after the addition of the acyl compound the mixture may be heated or maintained at a temperature in the range of between 30° C. and 200° C. until the N-substituted, N-acyl, alkylsulfonamide is formed. Although temperatures below 30° C. may be employed the reaction tends to proceed more slowly than may be desirable. Higher temperatures which may be employed are, in general, limited by the boiling point of the liquid alkaline medium.

The time required for the N-substituted, alkylsulfonamide to completely react with the acyl compound will vary considerably depending upon the amount of the reagents to be reacted, the alkaline medium used and the temperature employed. Complete reaction normally occurs over a period of from about 30 minutes to 4 hours, the smaller quantities of reagents and higher temperatures of the reaction medium requiring shorter reaction times.

After the reaction is completed the N-substituted, N-acyl, alkylsulfonamide may be recovered by neutralizing the liquid alkaline medium with a suitable acid and thereafter concentrating and cooling the neutralized medium to precipitate out the crystalline compound. Alternatively, the N-substituted, N-acyl, alkylsulfonamides may be recovered from the neutralized medium by extraction in a water-immiscible, low boiling point solvent such as, for example, ligroin, carbon tetrachloride or chloroform which can be readily cooled and/or evaporated and from which crystalline compounds may be directly recovered.

When the N-substituted alkylsulfonamides are available or have been previously prepared such compounds may be dissolved in a liquid alkaline medium and mixed and reacted with an acyl compound as above-described or alternatively, since the acyl compounds are usually liquid organic solvents having boiling points ranging from about 30° C. to 200° C., the N-substituted alkylsulfonamide may be added directly to an excess of the acyl compound and heated, preferably at or near the boiling point of the acyl compound, more preferably by refluxing for from 30 minutes to 4 hours, until the reaction is completed. The excess acyl compound may then be removed by distillation to obtain the crystalline N-substituted, N-acyl, alkylsulfonamide.

Where the boiling point of the acyl compound is below 30° C., the acyl compound may be mixed with a higher boiling liquid, such as for example, glacial acetic acid and the N-substituted alkylsulfonamide added thereto and heated, preferably by refluxing, until the desired compound is formed. The compound may then be separated or crystallized as above-described.

The N-substituted alkylsulfonamides may be prepared by a process which comprises mixing and reacting about one molecular proportion of a hereinafter described organic amine, e.g., an alkyl or an aryl amine, with about one molecular proportion of an alkylsulfonyl chloride in a liquid alkaline medium until an N-alkyl or an N-aroyl alkylsulfonamide is formed and thereafter mixing and reacting the N-substituted alkylsulfonamide so formed with a hereinbefore described acyl compound, e.g., an alkanoyl or an aroyl compound, at a temperature in the range of from about 50° C. to about 200° C., until an N-substituted, N-acyl, alkylsulfonamide is formed. The particular organic amine and acyl compound are so se-

lected so that a compound falling within the general scope of Formula I, hereinbefore described, is formed.

A wide variety of liquid alkaline media may be employed in such process including non-aqueous, water-soluble, alkaline organic liquids such as pyridine or lutidine or aqueous alkaline liquids such as aqueous solutions of alkali metal hydroxides or alkali metal carbonates. It is preferred that the liquid alkaline medium be one in which the organic amine is soluble for the reaction usually proceeds slowly if the organic amine is insoluble or partially soluble in the medium. In order to insure a relatively rapid reaction between the organic amine and the alkylsulfonyl chloride, it is preferred that the organic amine be soluble in the liquid alkaline medium in an amount of at least 5%, preferably at least 10%, by weight in the medium. Since the reaction between the organic amine and the alkylsulfonyl chloride is exothermic, it is preferred that the organic amine be first dissolved in the liquid alkaline medium and that the alkylsulfonyl chloride be slowly added with agitation, preferably by mechanical means, to the solution. If desirable, the liquid medium may be cooled during the addition of the alkylsulfonyl chloride and maximum yields of N-substituted, alkylsulfonamide are usually obtained when the process is carried out at temperatures below 45° C., preferably at temperatures in the range of about 30° C.-45° C. Although temperatures below 30° C. may be employed there is no significant advantage and the reaction time is usually significantly prolonged.

Thus, by way of illustration, N-methyl, N-acetyl alkylsulfonamides or mixtures thereof may be prepared by mixing and reacting an appropriate alkylsulfonyl chloride, for example, methyl-, or 1-butylsulfonyl chloride or mixtures thereof and methylamine in a liquid alkaline medium in a molecular ratio of about 1:1 to obtain an N-methyl alkylsulfonamide which in turn may be reacted with alkanoyl compounds such as acetic anhydride or acetyl chloride to obtain an N-methyl, N-acetyl alkylsulfonamide. Also by way of further illustration, N-methyl, N-benzoyl, alkylsulfonamides may be prepared by mixing and reacting an appropriate alkylsulfonyl chloride and methylamine in a liquid alkaline medium in a molecular ratio of about 1:1 to obtain an N-methyl alkylsulfonamide which may then be mixed and reacted with aroyl compounds such as benzoic anhydride, benzoyl chloride or benzoyl acetate to form an N-methyl, N-benzoyl, alkylsulfonamide.

Any of the N-substituted, N-acyl, alkylsulfonamides of this invention or mixtures thereof may be mixed with a wide variety of organic and/or inorganic oxygen-releasing compounds to provide novel bleaching compositions. However, the alkylsulfonamides of Formulae II or III, hereinbefore described have been found generally preferable. Examples of organic oxygen-releasing compounds include organic peroxides such as urea peroxide, benzoyl peroxide, methyl ethyl ketone peroxide and the like. Examples of inorganic oxygen-releasing compounds include inorganic peroxides such as alkaline-earth metal peroxides, for example, calcium, magnesium, zinc and barium peroxides. Other suitable inorganic peroxides include alkali metal carbonate peroxides such as sodium carbonate peroxide, and alkali metal pyrophosphate peroxides such as sodium pyrophosphate peroxide. Particularly suitable inorganic oxygen-releasing compounds include inorganic per-salts such as ammonium and metal persulfates, perchlorates and perborates. Of these per-salts, water soluble alkali metal persulfates and perborates are preferred and alkali metal perborates, especially sodium and potassium perborates are particularly preferred.

Useful bleaching compositions comprise, as noted above, a mixture of an oxygen-releasing compound and one or more of the novel compounds of this invention. These ingredients can be used in the compositions in various proportions depending upon whether the compositions are to be used as a bleaching composition or a washing composition or both. However, in most instances, the

compositions contain either an organic or an inorganic oxygen-releasing compound and from about 0.1 to about 2.0 mols, per mol of oxygen-releasing compound of any of the N-substituted N-acyl sulfonamides.

The novel compounds of this invention promote and accelerate the release of a greater amount of oxygen from oxygen-releasing compounds in water at 50° C.-80° C. than occurs when such oxygen-releasing compounds are dissolved in water at these temperatures in the absence of such novel compounds.

Suitable compositions comprise a mixture of an inorganic per-salt such as an alkali metal perborate and from about 0.1 to about 2.0 mols, per mol of perborate of any one or more of the novel compounds of this invention and one or more of an inorganic detergent builder salt and/or an inorganic diluent salt, and/or an organic surfactant.

A further understanding of the novel compounds of this invention as well as the utility and the processes of preparing such compounds may be obtained from the following specific examples which are intended to illustrate the invention, but not to limit the scope thereof, parts and percentages being by weight unless otherwise indicated.

Example I

To a 2 liter reaction vessel containing 1.5 liters of a 5 weight percent solution of sodium hydroxide, there was added, with agitation 105 grams of an aqueous solution containing 30 percent by weight (1 gram mol) of monomethyl amine. Thereafter, at room temperature (25° C.) and while agitation was continued, there was slowly added 115 grams (1 gram mol) of methylsulfonyl chloride. The resulting reaction mixture was stirred for 4 hours at room temperature (25° C.) and filtered. The filtrate was slightly acidified by the slow addition of 180 grams of concentrated hydrochloric acid.

N-methyl-methylsulfonamide did not separate at this point in view of its water solubility. The solution was thus evaporated almost to dryness and the mushy residue extracted with four 100 ml. portions of methyl alcohol. The extracts were combined, the methyl alcohol distilled off and the residue, consisting of N-methyl-methylsulfonamide, transferred to a 2 liter reaction vessel equipped with a heater and reflux condenser. To this reaction vessel containing N-methyl, methylsulfonamide, there was slowly added 800 grams of acetic anhydride. The reaction mixture was heated at a temperature of about 140° C. for 3.5 hours and thereafter cooled in an ice bath. After the reaction mixture had cooled, ice water (3° C.) was slowly added to the reaction mixture to convert the excess acetic anhydride to acetic acid. During the addition of the ice water a white crystalline material precipitated from the aqueous acetic acid solution. The crystals were separated from the cold (5° C.) aqueous acetic acid solution and recrystallized in 70% aqueous ethanol. A yield of 115 grams of white crystalline N-methyl, N-acetyl, methylsulfonamide was obtained. The melting point of the crystals was determined and found to be about 40° C.

Elemental analysis of a portion of the crystalline material showed it to contain the following elements in the amounts given below and compared with the theoretical elemental content of N-methyl, N-acetyl methylsulfonamide.

Element	Actual (found) (percent)	Theoretical (percent)
Carbon.....	31.53	31.79
Hydrogen.....	5.75	6.00
Nitrogen.....	9.34	9.27
Sulfur.....	10.5	10.6

The elemental analysis was in substantial agreement with the formula for N-methyl, N-acetyl, methylsulfon-

amide. The yield of 115 grams was 75% of that theoretically possible based on the methylsulfonyl chloride charged.

The infrared absorption of the compound of this example was determined using potassium bromide pellets. The infrared absorption peaks established the presence of SO₂, the C—N bond and the acyl structure of the compound.

Example II

To a 4 liter, three necked glass reaction vessel equipped with a mechanical stirrer, thermometer, reflux condenser and heater there was charged 1,000 ml. of pyridine and 90 grams (2.9 mols) of anhydrous liquified methylamine which immediately dissolved in the pyridine. To this solution there was slowly added with cooling and agitation 322 grams (2.8 mols) of methylsulfonyl chloride. The addition took place over a 15 minute period in order to prevent the reaction, which was exothermic, from causing the temperature of the contents of the reaction vessel to rise above 30° C. After the addition was completed, the reaction mixture which consisted of a solution of N-methyl, methylsulfonamide in pyridine was heated to 45° C. and stirred for 30 minutes. Thereafter there was slowly added with continuous agitation over a 15 minute period, 394 grams (2.8 mols) of benzoyl chloride. The resulting reaction mixture was stirred for 3 hours during which time it was continuously maintained at a temperature of 100° C. The reaction mixture was a solution comprising N-methyl, N-benzoyl, methylsulfonamide in pyridine.

The solution was cooled and the methylsulfonamide compound was extracted from the pyridine into chloroform by adding the pyridine to a separatory funnel containing 8 liters of chloroform thereby forming a chloroform solution of the methylsulfonamide. Reaction impurities, including residual pyridine were extracted and/or washed from the chloroform solution with 2 liters of an aqueous solution containing 10% hydrochloric acid. This procedure was repeated twice after which the chloroform solution was washed two more times with 1.5 liters of a saturated solution of sodium bicarbonate and finally washed three additional times with water. The water was removed from the chloroform solution by drying it over magnesium sulfate. After refluxing with 25 grams of decolorizing charcoal for 2 hours, the solution was filtered and concentrated by evaporating 7.5 liters of the chloroform. The residue was recrystallized from boiling ethyl alcohol, and fine white crystals were obtained. The crystalline yield was 410 grams or 69% of that theoretically possible, based on the methylsulfonyl chloride initially charged. The melting point of the crystals was 101° C.

An elemental analysis was conducted on the crystalline material. The actual elemental content compared with the theoretical elemental content of N-methyl, N-benzoyl methylsulfonamide is given below:

Element	Actual (found) (percent)	Theoretical (percent)
Carbon.....	50.63	50.70
Hydrogen.....	5.09	5.20
Nitrogen.....	6.54	6.57

The elemental analysis was in substantial agreement with the formula for N-methyl, N-benzoyl, methylsulfonamide.

X-ray analysis of the crystals was conducted using nickel filtered copper K-alpha radiation at a wave length

of 1.541 angstroms, X-ray diffraction pattern (with intensities of 1% and greater) was as follows:

Interplanar spacings (d) Angstroms	Relative intensity, percent
9.21	100
18.79	94
4.60	80
6.15	12
3.93	11
7.89	7
5.68	4
4.33	3
3.07	3
4.53	3
3.52	3
3.00	3
4.72	2
4.11	2
2.77	2
3.68	2
3.26	2
2.61	2
5.04	1
2.96	1
2.40	1
1.76	1

Infrared absorption analysis of the compound of this example was determined using KBr pellets. The infrared absorption peaks at the wave lengths indicated in the table below established the presence of SO₂, the C—N bond and the acyl structure of the compound.

Absorption peaks (wave length in microns)	Relative intensity
3.3.....	Weak.
6.0.....	Strong.
6.9.....	Weak.
7.5.....	Strong.
7.6.....	Medium.
7.7.....	Do.
7.8.....	Do.
8.7.....	Strong.
9.7.....	Medium.
9.9.....	Do.
10.2.....	Weak.
10.3.....	Medium.
12.3.....	Do.
12.8.....	Do.
13.0.....	Do.
14.0.....	Strong.
14.4.....	Do.

Example III

The procedure of Example II was repeated, except that ethylsulfonyl chloride was employed in place of methylsulfonyl chloride of Example II. The crystalline compound obtained was N-methyl, N-benzoyl ethylsulfonamide as indicated by the elemental analysis of the compound obtained. The compound had a melting point of 108° C.

The actual elemental content, analytically determined and compared with the theoretical elemental content of N-methyl-N-benzoyl, ethylsulfonamide is given below:

Element	Actual (found) (percent)	Theoretical (percent)
Carbon.....	52.77	52.86
Hydrogen.....	5.71	5.77
Nitrogen.....	6.05	6.17
Sulfur.....	14.0	14.1

X-ray diffraction analysis of the crystals, conducted using the procedures of the preceding examples (and with intensities of 3% and greater) was as follows:

Interplanar spacings (d) Angstroms	Relative intensities, percent
3.95	100
4.74	91
2.78	34
4.35	26
7.96	24
5.09	20
3.01	16
2.62	14
6.19	11
7.13	11
7.13	10
2.35	10
2.20	10
3.55	8
2.93	6
2.69	6
2.34	6
2.10	6
1.90	6
1.89	6
10.27	4
5.64	4
3.31	4
3.24	3
8.67	3

Infrared absorption analysis of the compound of this example was determined in KBr pellets. The infrared absorption peaks and wave lengths indicated in the table below established the general structure, e.g., the C—N bond, the SO₂ group and the acyl structure, of the compound.

Absorption peak (wave length in microns)	Relative intensity
3.3.....	Weak.
6.0.....	Strong.
6.3.....	Weak.
7.0.....	Medium.
7.1.....	Do.
7.7-7.8.....	Strong.
8.5.....	Medium.
8.6.....	Do.
9.6.....	Strong.
9.9.....	Do.
10.0.....	Weak.
10.3.....	Do.
10.7.....	Do.
10.8.....	Do.
11.8.....	Do.
11.9.....	Do.
12.5.....	Strong.
12.7.....	Medium.
13.6.....	Do.
13.9.....	Strong.
14.3.....	Do.
15.4.....	Do.

Example IV

The procedure of Example II was repeated, except that 1-butylsulfonyl chloride was employed instead of the methylsulfonyl chloride used in Example II. A yield of 71% of the possible theoretical yield of the crystalline compound N-methyl, N-benzoyl, 1-butylsulfonamide was obtained. The compound had a melting point of 123° C.

An elemental analysis was conducted on the crystalline material obtained. The actual elemental content of the crystals compared with the theoretical elemental content of N-methyl, N-benzoyl 1-butylsulfonamide is given below.

Element	Actual (found) (percent)	Theoretical (percent)
Carbon.....	56.38	56.46
Hydrogen.....	6.68	6.71
Nitrogen.....	5.36	5.49
Sulfur.....	12.9	12.6

An infrared absorption analysis of the compound was conducted as described in the previous example. The infrared absorption pattern obtained establishes the pres-

ence of pertinent structural elements, e.g., SO₂, the C—N bond and the acyl structure of the compound.

Example V

To a glass reaction vessel equipped with a mechanical stirrer, there was charged 8 liters of a 5% solution of aqueous sodium hydroxide after which 220 grams (2.4 mol) of aniline was added to the reaction vessel and dissolved in the NaOH solution. Thereafter there was slowly added over a 10 minute period at room temperature (25° C.) and with agitation 258 grams (2.25 mols) of methylsulfonyl chloride. The resulting mixture was mechanically agitated for 2 hours at room temperature (25° C.) after which time it was filtered and acidified with 1,000 grams of concentrated hydrochloric acid. A white precipitate consisting of N-phenyl, methylsulfonamide formed in the reaction mixture. The precipitate was filtered, dried and transferred to a second reaction vessel equipped with a heater and reflux condenser. One liter of acetyl chloride and 800 ml. of glacial acetic acid were added to the reaction vessel thereby dissolving the solid crystals. The resulting solution was refluxed at a temperature of 52° C. for 2.5 hours. At the end of this time the excess acetyl chloride was distilled off and 3 liters of cold (5° C.) distilled water was added to the liquid residue. A white crystalline precipitate which formed during the addition of the cold water was separated by filtration washed with a cold (5° C.) saturated solution of sodium bicarbonate and recrystallized from methyl alcohol. The crystalline material obtained which consisted of N-phenyl, N-acetyl methylsulfonamide weighed 375 grams amounting to a yield of 78% of that theoretically possible based on the methylsulfonyl chloride charged. The crystalline material had a melting point of 121° C.

The actual elemental content, analytically determined and compared with the theoretical elemental content of N-phenyl, N-acetyl methylsulfonamide is as follows:

Element	Actual (found) (percent)	Theoretical (percent)
Carbon.....	50.62	50.70
Hydrogen.....	5.11	5.20
Nitrogen.....	6.40	6.57

The elemental analysis was in substantial agreement with the formula for N-phenyl, N-acetyl, methylsulfonamide.

X-ray diffraction analysis resulted in the following X-ray diffraction pattern:

Interplanar spacings (d) Angstroms	Relative intensity, percent
5.37	100
6.96	87
8.34	37
4.62	29
4.39	29
3.68	25
3.86	24
4.33	18
4.50	17
3.44	17
2.92	11
2.86	10
3.56	7
3.62	6
4.98	6
4.15	6
3.36	6
3.03	6
2.29	6
3.10	5
2.98	5
2.66	5
2.61	5
2.40	5
2.74	3
2.13	3
2.07	3
1.98	3
2.53	2
2.45	2
2.37	1

The infrared absorption peaks obtained from infrared absorption analysis of the compound of this example establish the presence of pertinent structural elements, e.g., SO_2 , the C—N bond and the acyl structure of the compound.

Example VI

Two hundred grams of a mixture of alkylsulfonyl chlorides comprising 1-butyl sulfonyl chloride, 1-pentylsulfonyl chloride, 1-hexylsulfonyl chloride, 1-heptylsulfonyl chloride and 1-octylsulfonyl chloride, wherein the average molecular weight of the alkyl groups was 80, was reacted with 34 grams of methyl amine and 160 grams of benzoyl chloride in accordance with the procedure described in Example II. Two hundred-fifty grams (approximately 80% of the theoretical yield, based on the alkyl sulfonyl chloride mixture charged), of a yellowish waxy solid was obtained. This mixture consisted of a mixture of N-methyl, N-benzoyl alkylsulfonamides in which the alkyl groups corresponded to those of the starting alkylsulfonyl chlorides. This material was found to be effective in promoting and/or accelerating the bleaching activity of aqueous solutions of sodium perborate compositions at temperatures as low as 50° C.

The infrared absorption pattern of the mixture of this example established the presence of pertinent structural elements, e.g., the SO_2 group, the C—N bond and the acyl structure of the compound.

Example VII

Dry mixed compositions containing the following ingredients in the percentages given in the following table were prepared.

Ingredient	Composition Number				
	1	2	3	4	5
Sodium dodecylbenzene sulfonate.....	20.0	20.0	20.0	20.0	20.0
Sodium tripolyphosphate.....	24.0	24.0	24.0	24.0	24.0
Tetrasodium pyrophosphate.....	10.0	10.0	10.0	10.0	10.0
Sodium silicate.....	9.5	9.5	9.5	9.5	9.5
Sodium sulfate.....	24.0	21.6	21.6	21.1	20.0
Lauryl isopropanol amide.....	0.5	0.5	0.5	0.5	0.5
N-methyl, N-acetyl, methylsulfonyl amide.....	6.0				
N-phenyl, N-acetyl methylsulfonyl amide.....		8.4			
N-methyl, N-benzoyl methylsulfonyl amide.....			8.4		
N-methyl, N-benzoyl ethylsulfonyl amide.....				8.9	
N-methyl, N-benzoyl 1-butylsulfonyl amide.....					10.0
Sodium perborate.....	6.0	6.0	6.0	6.0	6.0

The bleaching capacity of each of compositions 1 through 5 was determined by dissolving 0.25% by weight of each composition in water in separate cylindrical receptacles. The receptacles were provided with mechanical agitation and the solutions therein were maintained at a temperature of 60° C. Each solution had an available oxygen concentration of about 11.5 parts per million. The solutions contained a mol ratio of sodium perborate to acyl sulfonamide of about 1:1.

Eight 5" x 5" swatches of unbleached naturally yellowed muslin were analyzed for reflectance (Rd) and (a)+(b) color values on a Gardner Automatic Color Difference Meter. Two swatches were placed in each of the 5 receptacles containing the dissolved compositions and washed for 10 minutes. After this period the swatches were dried, pressed and again analyzed on the Gardner Automatic Colorimeter. The reflectance ΔRd (brightening) and bleaching efficiency $\Delta(a)$ and $\Delta(b)$ were calculated by subtracting the difference in readings before and after the washing operation. The loss of available oxygen was also determined for each solution. The results are summarized in the accompanying table.

The Gardner Automatic Color Difference Meter is a tristimulus colorimeter, that is, it contains three photo

cells which measure (1) reflectance (Rd); (2) green to red color (a); (3) blue to yellow color (b).

Composition number	Available oxygen ¹ loss (percent)	ΔRd ²	$\Delta(a)$ ³	$\Delta(b)$ ³
1.....	69	+5.7	-0.2	-1.4
2.....	74	+6.3	-0.2	-1.5
3.....	91	+7.0	-0.4	-1.9
4.....	88	+6.8	-0.3	-1.7
5.....	82	+6.5	-0.3	-1.7

¹ Determined by Iodometric titration of spent wash solutions.

² Positive values indicate degree of increase of reflectance or brightening.

³ Negative values indicate the degree of color disappearance or bleaching.

The above values for loss of available oxygen indicate the release of oxygen from sodium perborate. By way of contrast a solution of a composition identical, except that it did not contain the sulfonamide, showed a loss of only 40% of available oxygen. The above results also demonstrate that the above compositions bleached and brightened the yellow unbleached muslin. However, solutions of compositions from which the acyl sulfonamides were omitted did not bleach or brighten the muslin to any appreciable extent.

Example VIII

The bleaching acceleration properties of some of the novel compounds of this invention are further indicated by the following:

To one liter of standard full strength borate-carbonate pH 10 buffer solution there was added the following.

(1) 0.460 gram of Orange II—[p(2-hydroxy-1-naphthyl-azo)-benzene sulfonic acid-sodium salt]

(2) 2 grams of a detergent having the composition

Ingredient:	Percent
Sodium dodecylbenzenesulfonate	25.0
Lauryl isopropanol amide	3.0
Sodium silicate	6.0
Sodium tripolyphosphate	28.0
Tetrasodium pyrophosphate	12.0
Anhydrous sodium sulfate	17.3
Sodium carboxymethyl cellulose	0.7
Moisture	8.0

A 100 ml. portion of this solution was added to each of seven individually numbered tubes which were mechanically shaken in a water bath maintained at 60° C. The initial color concentration was determined in a Bausch and Lomb spectrophotometer by measuring the intensity of its absorption maximum at 483 millimicrons. While recording the time, the materials indicated in the following table were added to the numbered tubes containing the orange dye-detergent solution.

Tube No.	Compound	Dye concentration (percent of original), minutes			
		0	20	60	160
1.....	Solution only.....	100	100	100	100
2.....	0.080 g. sodium perborate.....	100	81	63	53
3.....	0.080 g. sodium perborate + N-methyl, N-acetyl, methylsulfonyl amide.....	100	76	54	23
4.....	0.080 g. sodium perborate + N-phenyl, N-acetyl, methylsulfonyl amide.....	100	78	52	20
5.....	0.080 g. sodium perborate + N-methyl, N-benzoyl, methylsulfonyl amide.....	100	69	41	11
6.....	0.080 g. sodium perborate + N-methyl, N-benzoyl, ethylsulfonyl amide.....	100	73	45	14
7.....	0.080 g. sodium perborate + N-methyl, N-benzoyl, 1-butylsulfonyl amide.....	100	75	48	18

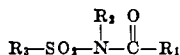
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In the above table the N-substituted N-acyl alkyl-sulfonamides were added in equimolar amounts with respect to the sodium perborate, that is, 0.00052 gram mol of each compound was added to the tube as indicated. The results demonstrate that the compounds of this invention effectively promote the bleaching of standard dyes when in solution at 60° C.

The novel compounds disclosed in this application have been disclosed as incorporated components of novel bleaching and washing compositions in my copending U.S. patent, application Serial No. 181.449, filed in the U.S. Patent Office, March 21, 1962.

What is claimed is:

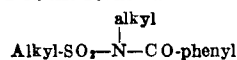
1. A compound of the formula



where R_1 is an aromatic group selected from the group consisting of phenyl, pyridyl, benzyl, alpha and beta naphthyl, quinolyl, anthryl, benzquinolyl groups and halo-, hydroxyl, nitro-, and sulfo-substituted phenyl, pyridyl, benzyl, alpha and beta naphthyl, quinolyl, anthryl, benzquinolyl groups; R_2 is selected from the group consisting of alkyl groups containing from 1 to 10 carbon atoms and halo-, hydroxyl, sulfo-, nitro-, carboxy- and alkoxy-substituted alkyl groups containing from 1 to 10 carbon atoms and R_3 is alkyl.

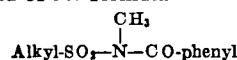
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2. A compound of the formula



wherein alkyl is from 1 to 10 carbon atoms.

3. A compound of the formula



wherein alkyl is from 1 to 10 carbon atoms.

4. N-methyl, N-benzoyl, methylsulfonamide.

5. N-methyl, N-benzoyl, ethylsulfonamide.

6. N-methyl, N-benzoyl, 1-butylsulfonamide.

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