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2,2,2-TRINITRO ETHYL ALKYL SULFIDES

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This invention relates to a new class of 2,2,2-trinitroalkyl sulfides, and to a method of making them from nitroform, a mercaptan and an aldehyde having at least two carbon atoms.

These new sulfides are useful as explosives, propellants and propellant plasticizers.

The new compounds of my invention are the 2,2,2-trinitroalkyl sulfides having the structure

$$(NO_2)_3C-\underset{\displaystyle R}{\underset{|}{C}}H-S-R'$$

wherein R is an alkyl, benzyl, furyl or phenyl group; and R' is an alkyl or lower alkenyl group.

My new compounds are conveniently made by mixing the appropriate reagents in a suitable solvent such as diethyl ether, carbon tetrachloride or chloroform. The solvent is not an essential part of my invention, but I prefer to carry out the reaction in solution because of the explosive properties of nitroform and the products. It is also more convenient to carry out the reaction in solution when any of the reagents or the product are solid at the reaction temperature.

The reaction is carried out at a temperature in the range from room temperature to about 100° C. Below room temperature the reaction is very slow. Above 100° C. undesirable side reactions decrease the yield and increase the explosion hazard. My preferred temperature range is from room temperature to about 75° C.

Some of the compounds covered by my invention are more useful as explosives than as propellants and propellant plasticizers, whereas others of these compounds are useful chiefly in the latter field. The "oxygen balance" of any compound shows in general in which field of usefulness that compound is likely to fall. The oxygen balance is calculated according to the equation:

$$\text{Oxygen balance} = (O - 2C - \tfrac{1}{2}H - 2S^*)\ \frac{100 \times 16}{M.W.}$$

wherein O, C, H and S are the numbers of oxygen, carbon, hydrogen and sulfur atoms respectively in a compound of molecular weight M.W. The oxygen balance of most of the compounds used as explosives, propellants and propellant plasticizers is negative. In general, nitrogenous compounds with a relatively small negative balance; i.e., below —100, are likely to be useful as explosives, whereas compounds having negative oxygen balances of —200 or even more are often useful as propellant plasticizers whether or not they contain nitrogen. For example, trinitrotoluene has an oxygen balance of —74 and dimethyl phthalate, a plasticizer for propellants, has one of —173. As one ascends a homologous carbon series the oxygen balance becomes more negative. Therefore, it is evident that the compounds of this invention containing usually not more than seven carbon atoms are most likely to be used as explosives and propellants, whereas those containing a greater number of carbon atoms probably will have their chief use as propellant plasticizers. (Oxygen balance of $C_7H_{13}N_3O_6S$=—99. One isomeric material having this empirical formula is made from nitroform, acetaldehyde and n-butylmercaptan, as described hereinafter in Example 4.)

*This equation is slightly different from the usual one, because most previously known explosive compounds do not contain sulfur. The change in the equation used herein is derived by assuming that free sulfur oxidizes to sulfur dioxide.

The aldehyde used can be any aldehyde having at least two carbon atoms per molecule; i.e., formaldehyde is not operable in my invention. Typical aldehydes which can be used in my invention are the saturated aliphatic aldehydes such as acetaldehyde, propionaldehyde, n-butyraldehyde, isobutyraldehyde, n-hexaldehyde and n-heptaldehyde; the aralkyl aldehydes such as benzaldehyde and phenylacetaldehyde; and the heterocyclic aldehydes such as furfural.

Typical mercaptans which can be used in my invention are the alkyl mercaptans such as methylmercaptan, ethylmercaptan, n-propylmercaptan, n-butylmercaptan, tert. butylmercaptan, and n-dodecylmercaptan; and the lower alkenylmercaptans; i.e., those containing not over 4 carbon atoms, e.g., allylmercaptan and methyllylmercaptan.

The relative proportions of the three reagents are not critical. However, I often prefer to use an excess of nitroform because it appears to minimize the formation of undesirable by-products which do not contain nitrogen. These by-products are believed to be thio-acetals. The excess nitroform can be recovered easily by fractional distillation in vacuo. Usually, it is not even necessary to separate the unused nitroform and other reagents from the solvent or from each other, for the mixture can be used for the next batch of the same trinitroalkyl sulfide.

The following examples illustrate my invention. All parts are by weight.

Example 1

A solution of 7.5 parts of nitroform, 3 parts of propionaldehyde, 4 parts of ethylmercaptan and 80 parts of carbon tetrachloride was heated for an hour at 70–80° C., and then was fractionally distilled in vacuo. Two parts of unreacted nitroform and 5.5 parts of an amber-colored liquid were isolated. This liquid is the desired new compound, 2,2,2-trinitro-1-ethylethyl ethyl sulfide. The yield, based on unrecovered nitroform, was 59% of theory; the conversion was 44%; boiling point 85–88° C. at 1.5 mm. Hg, and 84–85° C. at 0.8 mm; refractive index n_D^{20} 1.4890. It flashes on a hot plate. However, it is quite stable toward mechanical shock; i.e., it can be detonated by a hammer blow only with difficulty. Oxygen balance —85.

Analysis.—Calcd. for $C_6H_{11}N_3O_6S$: C, 28.48%; H, 4.35%; N,16.60%; S, 12.65%. Found: C, 28.59%; H, 4.33%; N, 16.45%; S, 12.49%.

Example 2

A solution of 6 parts of nitroform, 4.2 parts of benzaldehyde and 3.6 parts of n-butylmercaptan in 30 parts of ether was left overnight at room temperature. The volatile materials then were evaporated off in vacuo. The residual amber-colored oil was dissolved in Skellysolve B (a petroleum fraction which is chiefly n-hexane). The solution was chilled, thus causing crystallization of the desired white product, 2,2,2-trinitro-1-phenylethyl n-butyl sulfide. It melted at 23–24° C. The yield was 6.5 parts, or 50% of theory. It burns, and is stable toward hammer blows. Oxygen balance —134.

Analysis.—Calcd. for $C_{12}H_{15}N_3O_6S$: C, 43.8%; H, 4.6%; N, 12.7%; S, 9.7%. Found: C, 43.5%; H, 4.5%; N, 11.8%; S, 8.9%.

Example 3

The process of Example 2 was repeated except that tert.-butylmercaptan was used instead of n-butylmercaptan. The residue from the low-pressure evaporation of the volatile material was a yellow solid. Recrystallization from Skellysolve B removed the yellow color. The new product, 2,2,2-trinitro-1-phenylethyl tert.-butyl sulfide, melted at 62–63° C. The yield was 9.0 parts, or 69%

of theory. It burns, and is stable toward hammer blows. Oxygen balance —134.

Analysis.—Calcd. for $C_{12}H_{15}N_3O_6S$: C, 43.76%; H, 4.56%; N, 12.73%; S, 9.72%. Found: C, 43.58%; H, 4.70%; N, 12.71%; S, 9.69%.

Example 4

A mixture of 8 parts of freshly distilled acetaldehyde, 5.5 parts of n-butylmercaptan, 9.1 parts of nitroform and 40 parts of ether was kept at room temperature over night. Then the solution was fractionally distilled in vacuo, thereby recovering 3.6 parts of unreacted nitroform. The desired product, 2,2,2-trinitro-1-methylethyl n-butyl sulfide, and a by-product, which contains no nitrogen and is believed to be a thio-acetal of acetaldehyde and n-butylmercaptan, were found to distil at almost the same temperture, thus making difficult the isolation of the desired compound. Three closely-boiling fractions were analyzed quantitatively. From this analysis, it was found that about 49% of the unrecovered nitroform was converted to to 2,2,2-trinitro-1-methylethyl n-butyl sulfide; i.e., the three fractions contained a total of about 4.8 parts of the said sulfide. The fraction which had the highest boiling point has the following properties: boiling point 70–75° C. at 0.15 mm. Hg.; n_D^{20} 1.4876.

Analysis.—Calcd. for $C_7H_{13}N_3O_6S$: C, 31.4%; H, 4.9%; N, 15.7%. Found: C, 32.6%; H, 5.2%; N, 14.5%.

The analysis shows that this fraction consists of the desired sulfide contaminated with a small amount of an impurity, presumably the proposed thio-acetal.

It flashes on a hot plate. It can be detonated by a hammer blow only with difficulty. Oxygen balance —99.

Other trinitroalkyl sulfides which can be prepared by the method of my invention are 1,1,1-trinitro-2-propyl methyl sulfide, 1,1,1-trinitro-2-propyl ethyl sulfide, 1,1,1-trinitro-2-propyl n-heptyl sulfide, 1,1,1-trinitro-2-propyl n-dodecyl sulfide, 1,1,1-trinitro-2-propyl allyl sulfide, 1,1,1-trinitro-2-propyl methallylsulfide, 1,1,1-trinitro-3-methyl-2-butyl ethyl sulfide, 2,2,2-trinitro-1-phenylethyl-allyl sulfide, 1,1,1-trinitro-3-phenyl-2-propyl ethyl sulfide and 2,2,2-trinitro-1-furylethyl methyl sulfide.

I claim:

1. A chemical compound having the formula

$$(NO_2)_3C-\underset{\displaystyle R}{\underset{|}{CH}}-S-R'$$

wherein R is selected from the group consisting of alkyl, benzyl, furyl and phenyl radicals and R′ is selected from the group consisting of alkyl and lower alkenyl radicals.

2. 2,2,2-trinitro-1-ethylethyl ethyl sulfide.

3. 2,2,2-trinitro-1-phenylethyl n-butyl sulfide.

4. 2,2,2-trinitro-1-phenylethyl t-butyl sulfide.

5. 2,2,2-trinitro-1-methylethyl n-butyl sulfide.

6. The process of making a chemical compound having the formula

$$(NO_2)_3C-\underset{\displaystyle R}{\underset{|}{CH}}-S-R'$$

wherein R is selected from the group consisting of alkyl, benzyl, furyl and phenyl radicals and R′ is selected from the group consisting of alkyl and lower alkenyl radicals, which comprises bringing together at a temperature of from room temperature to 100° C. an aldehyde, R—CHO wherein R is as already defined, and a mercaptan, R′—SH wherein R′ is as already defined in the presence of nitroform.

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