[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Dioxane Sulfotrioxide, a New Sulfating and Sulfonating Agent

BY C. M. SUTER, P. B. EVANS AND JAMES M. KIEFER

The observation that di-(β-chloroethyl) ether may be converted into di-(β-chloroethyl) sulfate in high yields by the action of sulfur trioxide[1] led us to examine the behavior of dioxane toward this reagent. The addition of sulfur trioxide to pure dioxane at ordinary temperatures produces considerable charring but if the dioxane is first dissolved in an inert solvent such as carbon tetrachloride or ethylene chloride there results an addition product which separates out in white flakes or crusts.

$$O(CH_2CH_2)_2O + SO_3 \longrightarrow O(CH_2CH_2)_2OSO_3 \quad (1)$$

$$O(CH_2CH_2)_2O + 2SO_3 \longrightarrow O_3SO(CH_2CH_2)OSO_3 \quad (2)$$

If the dioxane is present in excess the composition of the precipitate corresponds to (1), while with the addition of more than one equivalent of sulfur trioxide (2) begins to be formed. The addition of dioxane to a suspension of (2) in carbon tetrachloride results in the evolution of heat, (1) being produced. Under anhydrous conditions both compounds are stable at room temperature, but upon heating to 75° in carbon tetrachloride decomposition ensues with formation of water soluble products. Both compounds react with water instantly to give sulfuric acid and regenerate dioxane.

These characteristics indicated that the dioxane sulfotrioxide and disulfotrioxide[2] might have interesting properties as sulfonating and sulfating agents. A similar addition compound obtained from pyridine[3] has long been known as a reagent for introducing the sulfotrioxide group into various types of compounds. The compounds obtained from dioxane are, however, much more reactive than that from pyridine as the pyridine sulfotrioxide[4] is reported to be insoluble in cold water[3] while the dioxane derivatives decompose instantly.

Sulfonation Reactions.—Thus far no difference in reactivity has been observed for the two dioxane addition products. In what follows the "D.S. reagent" refers to either or a mixture of both.

The addition of benzene to a suspension of the D.S. reagent in carbon tetrachloride at room temperature produces no immediate change but after standing for a day the solid reagent has disappeared and an oily upper layer has separated. This with a saturated sodium chloride solution gives a high yield of sodium benzenesulfonate. The sulfonation of *m*-xylene and of anisole is complete in a few minutes under these conditions, while chlorobenzene is not affected after a day's standing. Naphthalene sulfonates somewhat more rapidly than does benzene.

Phenol is converted into phenyl hydrogen sulfate, isolated as the potassium salt. Similarly aniline yields phenylaminosulfonic acid. Benzoic acid reacts instantly to give a water-soluble solid that hydrolyzes rapidly when the aqueous solution is boiled. Acetophenone also gives a readily hydrolyzable addition product.

$$2C_6H_5COOH + O_3SO(CH_2CH_2)_2OSO_3 \longrightarrow 2C_6H_5COOSO_3H + O(CH_2CH_2)_2O$$

$$C_6H_5COOSO_3H + H_2O \longrightarrow C_6H_5COOH + H_2SO_4$$

Sulfation Reactions.—The reaction of the D.S. reagent with alcohols is immediate. Practically quantitative yields of the alkyl hydrogen sulfates were obtained from *n*-butyl and *n*-lauryl alcohols. These were isolated as their potassium salts. Because of the high yield and purity of

$$RCH_2OH + O(CH_2CH_2)_2OSO_3 \longrightarrow RCH_2OSO_3H + O(CH_2CH_2)_2O$$

the products the D.S. reagent is of value in the preparation of detergents of the alkyl sodium sulfate type[5] from high molecular weight primary and secondary alcohols.

Reaction with Olefins.—The most interesting property of the D.S. reagent thus far investigated is its reaction with olefins. It has long been known[6] that sulfur trioxide reacts vigorously with ethylene to give carbyl sulfate. By the use of the D.S. reagent it is possible to extend this reaction to many types of olefinic compounds and at the same time avoid the undesirable side reactions attendant upon the use of sulfur trioxide itself.

It has been suggested[7] recently that the addition of sulfur trioxide to ethylene takes place

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[1] Suter and Evans, THIS JOURNAL, **60**, 536 (1938).

[2] These names were suggested by Professor Charles D. Hurd of this Laboratory to whom our thanks are due.

[3] Wagner, *Ber.*, **19**, 1158 (1886); Baumgarten, *ibid.*, **59**, 1976 (1926); Burkhardt and Lapworth, *J. Chem. Soc.*, 686 (1926).

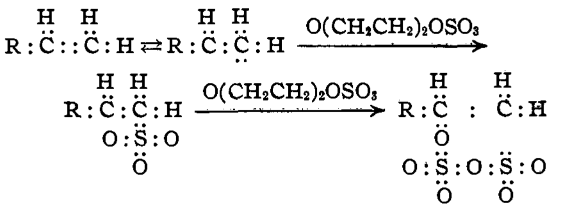
[4] This appears to be a more convenient and expressive name than the "anhydro-N-pyridinium sulfonic acid" previously used.

[5] Suter, U. S. Patent 2,098,114.

[6] Regnault, *Ann.*, **25**, 32 (1837).

[7] Michael and Weiner, THIS JOURNAL, **58**, 294 (1936).

through the bimolecular S_2O_6. Since there is presumably none of this present in the D.S. reagent which gives a similar product this formulation of the reaction is questionable. Several investigators[8] have suggested that addition at an olefin linkage is initiated by a polarization of the double bond followed by the attachment of a positive ion. Assuming that sulfur trioxide adds by a similar mechanism the reaction may be formulated as indicated in the equations.



Only the electron pairs involved in bonds are shown.

A study of the structure of the addition product obtained from propylene indicates that the carbon–sulfur bond is formed at the end carbon as shown in the equation. Hydrolysis of the primary addition product with alkali gave a hydroxypropanesulfonate which on oxidation was converted into the corresponding ketone, isolated as the barium salt. The structure of the barium acetonesulfonate was verified by analysis and by its behavior toward alkali which effects hydrolysis to sodium acetate. A sample of sodium acetonesulfonate prepared from chloroacetone and sodium sulfite decomposed in the same manner.

$$CH_3COCH_2SO_3Na + NaOH \longrightarrow CH_3COONa + CH_3SO_3Na$$

Isolation of the primary hydrolysis product, $CH_3CH(OSO_3H)CH_2SO_3H$, was not attempted in the case of propylene. Such a compound, a higher homolog of ethionic acid, was obtained as its sodium salt from 1-nonene by exact neutralization of the reaction mixture with cold alkali and evaporation of the aqueous solution below 50° under reduced pressure. Above 50° hydrolysis to the less soluble hydroxysulfonate becomes appreciable.

$$C_7H_{15}CH(OSO_3Na)CH_2SO_3Na + H_2O \longrightarrow C_7H_{15}CHOHCH_2SO_3Na + NaHSO_4$$

The alkali hydroxysulfonates obtained from olefins containing ten or more carbon atoms have marked detergent properties, those from 1-hexadecene and 1-heptadecene approximating the isomeric sodium alkyl sulfates in effectiveness.[9]

Experimental Procedure

Preparation of the D.S. Reagent.—For these experiments the dioxane was purified.[10] A solution containing 88 g. of dioxane in 300 cc. of ethylene chloride was chilled and stirred mechanically while sulfur trioxide was distilled into it from 60% oleum until the gain in weight was 80 g. As the liquid or gaseous sulfur trioxide strikes the solution, the white crystalline addition product separates. Ordinarily this mixture was prepared for immediate use but it could be preserved unchanged for several days in the ice box.

Reaction of Propylene with the D.S. Reagent.—Propylene was passed into a suspension of the reagent in ethylene chloride. No reaction occurred much below room temperature. When the reaction was complete all the solid had disappeared leaving a clear almost colorless solution. This was treated with an equal volume of water containing excess barium hydroxide and the mixture refluxed for an hour. The barium sulfate formed was removed by filtration, the ethylene chloride by steam distillation and carbon dioxide passed into the aqueous solution to remove excess barium hydroxide. Evaporation of the filtrate from the barium carbonate gave pure barium 2-hydroxypropane-1-sulfonate.

Anal. Calcd. for $C_6H_{14}O_8S_2Ba$: Ba, 33.37. Found: Ba, 32.90, 32.86.

Oxidation of Hydroxypropanesulfonic Acid.—Twenty grams (0.048 mole) of barium hydroxypropanesulfonate was dissolved in 50 cc. of water and acidified with sulfuric acid. After removal of the barium sulfate 3.4 g. of chromic acid was added and the mixture heated on the steam-bath for several days. The solution was diluted to 250 cc. and neutralized with barium carbonate. Evaporation of the filtrate to dryness gave a product containing a mixture of barium acetonesulfonate and unoxidized material. Refluxing a sample with 20% sodium hydroxide followed by acidification and distillation gave a 40% yield of acetic acid identified as the *p*-toluidide. Since sodium acetone sulfonate gave an 87% yield of acetic acid under like conditions the product was reoxidized, which increased the yield of acetic acid to 56%.

Reaction of Liquid Olefins with the D.S. Reagent.—The 1-nonene was prepared from *n*-hexylmagnesium bromide and allyl bromide according to the method of Wilkinson.[11] Gradual addition of the olefin to the reagent in ethylene chloride with stirring at room temperature gave a clear light-yellow solution. When this reaction mixture was hydrolyzed with barium hydroxide the resulting mixture of barium sulfate and barium hydroxynonanesulfonate was difficult to separate completely by extraction of the precipitate with hot water. It was therefore warmed with a slight excess of aqueous sodium sulfate. Upon cooling the filtrate the sodium hydroxysulfonate

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[8] Lowry, *J. Chem. Soc.*, 822 (1923); Kharasch and Reinmuth, *J. Chem. Ed.*, **8**, 1703 (1931).

[9] A study of the detergent properties of these compounds is being made by Dr. Walter H. McAllister, The Procter and Gamble Company, Ivorydale, Ohio. We are grateful for his permission to include a preliminary report of his results here.

[10] Eigenberger, *J. prakt. Chem.*, **130**, 75 (1931).

[11] Wilkinson, *J. Chem. Soc.*, 3052 (1931).

readily crystallized. Both the barium and sodium salts were analyzed.

Anal. Calcd. for $(C_7H_{15}CHOHCH_2SO_3)_2Ba$: Ba, 23.54. Found: Ba, 23.49, 23.55. Calcd. for $C_7H_{15}CHOHCH_2SO_3Na$: Na, 9.35. Found: Na, 9.34, 9.12.

When the reaction mixture was hydrolyzed with cold sodium hydroxide, the ethylene chloride layer separated and the aqueous solution evaporated to dryness under reduced pressure in a water-bath held at 40–50° the product was the sodium sulfate–sulfonate, $C_7H_{15}CH(OSO_3Na)CH_2SO_3Na$, mixed with a few per cent. of sodium sulfate. Due to the high solubility in water of the former, purification was not possible. Hydroxysulfonates were prepared from higher olefins by the same procedure used for 1-nonene.

Sulfation and Sulfonation Reactions.—The reactions of aromatic compounds and of alcohols with the D. S. reagent require no detailed description. In the case of the anisole sulfonation the product was identified as the para compound by conversion into the sulfonamide. The other sulfation and sulfonation products are well-known compounds.

Summary

1. Dioxane reacts with either one or two molecules of sulfur trioxide to give compounds of the coördination type.

2. Either of these addition compounds serves as a reagent for sulfonation of various types of aromatic compounds. In the case of aniline, phenol and benzoic acid reaction occurs with the substituents rather than the benzene nucleus.

3. Primary alcohols are converted into alkyl hydrogen sulfates. Since the higher members of this series are valuable detergents, this reaction has practical significance.

4. Olefins are converted into compounds of the carbyl sulfate type. Hydrolysis of these yields hydroxysulfonates. Those from high molecular weight olefins have detergent properties. Further investigation of these compounds is in progress.

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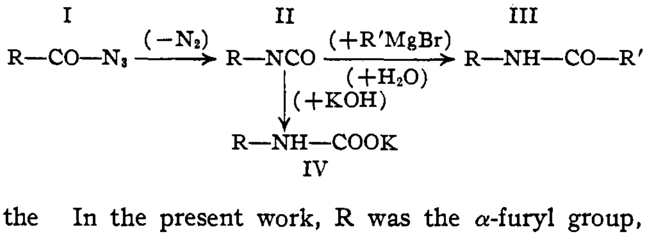
[CONTRIBUTION FROM THE CHARLES EDWARD COATES LABORATORY OF CHEMISTRY AT LOUISIANA STATE UNIVERSITY]

Preparation and Properties of Some Derivatives of 2-Aminofuran

BY H. M. SINGLETON[1] AND W. R. EDWARDS, JR.

Desiring to prepare and study derivatives of furan containing nitrogen in the α-position, and to ascertain to some extent the suitability of these products for further synthetic work, the authors applied the Curtius reaction, with variations, to furoic acid. This general means of approach has been employed by a number of investigators, but frequently the results with α-substituted furans have been discouraging. To simplify resultant observations and to make their possible application more general, the present work was confined to monosubstituted furans, though this involved waiver of the stabilizing influences sometimes exerted by additional substituent groups.

A preliminary comparison of the original method of Curtius for the preparation of 2-furoyl azide with the more recent method of Schroeter,[2] Naegeli,[3] and others, was made by reference and tested experimentally, and led to selection of the latter as more convenient, less expensive, and productive of a higher yield based on initial furoic acid. Starting with the azide, the primary reactions were



$$\begin{tikzcd} \text{I} & & \text{II} & & \text{III} \\ R{-}CO{-}N_3 \arrow[rr, "(-N_2)"] & & R{-}NCO \arrow[rr, "(+R'MgBr)", "(+H_2O)"'] \arrow[d, "(+KOH)"] & & R{-}NH{-}CO{-}R' \\ & & R{-}NH{-}COOK & & \\ & & \text{IV} & & \end{tikzcd}$$

In the present work, R was the α-furyl group, and R′ was either C_6H_5 or C_2H_5.

In proceeding from I to such products as III, IV and others, in the general employment of the Curtius reaction, the usual practice has been to omit isolation of II because of its objectionable nature, its instability when exposed to moist air, and the occasional difficulty of separating it from its solvent. It has been found commonly that when I has been decomposed thermally in suitable media, Grignard or other reagents can be added to the entire resultant mixtures with

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[1] This paper is an abstract of a portion of a thesis submitted by H. M. Singleton to the Graduate Faculty of Louisiana State University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, in June, 1937. It was presented at the Chapel Hill meeting of the American Chemical Society, April, 1937.

[2] Schroeter, *Ber.*, **42**, 3356 (1909).

[3] Naegeli and Stefanovitsch, *Helv. Chim. Acta*, **11**, 609 (1928); Naegeli, Grüntuch and Lendorff, *ibid.*, **12**, 227 (1929).