The reaction was conveniently carried out in an Erlenmeyer flask by means of a magnetic stirrer. The infrared spectrum exhibited the characteristic strong N—H band at 3320 cm.$^{-1}$.

N-Nitroso-N-benzyl-p-toluenesulfonamide.—A solution of 10.5 g. (0.04 mole) of N-benzyl-p-toluenesulfonamide in 50 ml. of glacial acetic acid and 200 ml. of acetic anhydride, was prepared in a three-necked flask equipped with a stirrer, a thermometer, and a solid addition funnel. The flask was cooled to around 5°. Then 60 g. (0.85 mole) of powdered sodium nitrite was added in portions over a period of 6 hr. The temperature was kept below 10° at all times; the mixture turned green. After the addition of sodium nitrite was completed, the reaction mixture was stirred overnight. The mixture was then poured over an excess of ice water with vigorous stirring and cooled for 1 hr. in an ice bath. The pale yellow precipitate was filtered, washed several times with water, and dried overnight in vacuum. The crude product was then recrystallized from ethanol to give 9.4 g. (81%) of tiny yellow needles, m.p. 90–92° (m.p. 89–90°[6] by nitrosation in aqueous sodium nitrite) after drying in vacuum overnight; the infrared spectrum was free of N—H and showed a strong band at 1387 cm.$^{-1}$, assigned to the N–NO group. This nitrosation was carried out in much larger scale with comparable yields; it should be done in the hood because of the evolution of oxides of nitrogen.

Benzyl Ester of 3,5-Dinitrobenzoic Acid.—N-nitroso-N-benzyl-p-toluenesulfonamide (14.5 g., 0.05 mole) was added in portions over a period of 1 hr. to a stirred mixture of 2.7 g. (0.05 mole) of sodium methoxide, 10 ml. of methanol, and 60 ml. of ether. Within 5 min., a pinkish color was visible. After the addition was completed, the mixture was stirred under reflux for 15 or 20 min. After cooling the mixture, 100 ml. of water was added to dissolve the salts and the water layer discarded. The ethereal solution of phenyldiazomethane was washed three times with 75-ml. portions of water and dried for 30 min. over anhydrous sodium sulfate. It was then filtered and added dropwise with stirring to a suspension of 11 g. of 3,5-dinitrobenzoic acid in 50 ml. of ether. The disappearance of the red color was accompanied by a copious evolution of nitrogen. The mixture was stirred overnight and then enough ether was added to give a clear solution which was extracted with dilute base, then with water until neutral and dried over anhydrous sodium sulfate. The ether was removed under vacuum and 9.1 g. (60%) of the benzyl ester of 3,5-dinitrobenzoic acid, m.p. 111–113°[9] (mixed m.p. 111–112°) were obtained.

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A Convenient Synthesis of Aromatic and Aliphatic Sodium Sulfinates

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Recent interest in aliphatic and aromatic sulfinic acids[1–3] has prompted us to report a simple method of converting readily available thiols to the corresponding sodium sulfinates in good yield.

Methods now available for the synthesis of these compounds include reduction of the appropriate sulfonyl chloride,[4] treatment of organometallic reagents with sulfur dioxide,[5] reaction of diazonium compounds with sulfur dioxide,[6] and cleavage of 1,2-disulfones with alkaline potassium cyanide.[7]

The present method consists of adding the thiol to acrylonitrile,[8] oxidizing the resulting sulfide to its sulfone by means of hydrogen peroxide in glacial acetic acid,[8] followed by treating the β-sulfonylnitrile with an equivalent amount of the sodium salt of a thiol.

$$\mathrm{RSH + CH_2{=}CH{-}CN \xrightarrow{\text{base}} \underset{\text{I}}{RSCH_2{-}CH_2CN}}$$

$$\mathrm{RSCH_2{-}CH_2{-}CN + H_2O_2 \xrightarrow{CH_3CO_2H} \underset{\text{II}}{RSO_2CH_2CH_2CN}}$$

$$\mathrm{RSO_2CH_2CH_2CN + R'SNa \xrightarrow{C_2H_5OH} RSO_2Na + \underset{\text{III}}{R'SCH_2CH_2CN}}$$

$$\text{I, II, III} \left\{\begin{array}{l} \mathrm{R} = n\text{-}\mathrm{C_4H_9} \\ \mathrm{R} = n\text{-}\mathrm{C_3H_7} \\ \mathrm{R} = p\text{-}\mathrm{CH_3C_6H_4} \\ \mathrm{R} = o\text{-}\mathrm{CH_3C_6H_4} \end{array}\right.$$

Other bases have been used to effect the elimination of the sulfinate but sodium thiolate also regenerates I which can be oxidized to II and thus serve as precursor for more III. The over-all yields for the transformation of thiol to sodium sulfinate are 70–75%.

The structure of each of the aromatic sulfinates was established by the isolation of the free sulfinic acid, melting point determination and determination of the infrared absorption spectrum (strong band at 1090 cm.$^{-1}$).[9]

Because of the instability of the free aliphatic sulfinic acids,[10] the sodium salts were treated directly with benzyl chloride to form the known alkyl benzyl sulfones.

In a similar fashion, aromatic and aliphatic sulfinic acids can be made by the action of RSNa on compounds of type V. The reaction sequence is outlined below. The yields are comparable.

$$\mathrm{RSH + HC{\equiv}C{-}CO_2C_2H_5 \xrightarrow[\text{cat.}]{\text{base}} \underset{\text{IV}}{RSCH{=}CHCO_2C_2H_5}}$$

$$\mathrm{RSCH{=}CHCO_2C_2H_5 + H_2O_2 \xrightarrow{CH_3CO_2H} \underset{\text{V}}{RSO_2CH{=}CHCO_2C_2H_5}}$$

$$\mathrm{RSO_2CH{=}CHCO_2C_2H_5 + R'SNa \xrightarrow{C_2H_5OH} RSO_2Na + R'SCH{=}CHCO_2C_2H_5}$$

Thiols add readily to ethyl propiolate[11] in high yield, and the adducts are oxidized to the corresponding sulfones in yields of 85–90%. The reaction of RSNa with V gives the sodium sulfinate in 85–90% yield. However, the availability of acrylonitrile makes the first route more accessible.

Experimental[12]

Addition of Thiols to Acrylonitrile.—The method used was that described by Hurd and Gershbein.[8] "Triton B" (40% aq., 3 drops) was used as catalyst. The acrylonitrile used was ob-

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(6) L. Gatterman, *Ber.*, **32**, 1136 (1899).

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(12) All melting points and boiling points are uncorrected.

tained from American Cyanamid Co. The thiols were obtained from Matheson, Coleman and Bell.

Oxidation of β-Aryl- or Alkylmercaptopropionitriles.—The β aryl- or alkylmercaptopropionitriles were oxidized to the sulfonyl derivatives in good yield using the method described by Hurd and Gershbein.[8]

Reaction of β-*p*-Tolylsulfonylpropionitrile with Sodium 1-Propanethiolate.—In a 100 ml. three neck flask fitted with a reflux condenser and a magnetic stirrer was placed 4 g. (0.019 mole) of β-*p*-tolylsulfonylpropionitrile suspended in 50 ml. of alcohol. A solution of the sodium thiolate was made from 10 ml. of ethanol, 0.44 g. of sodium and 1.45 g. of 1 propanethiol. This solution was added slowly at first and then more rapidly to the stirred solution of the sulfone. This mixture was refluxed for 5 hr., ethanol removed under reduced pressure and the white solid suspended in ether and filtered. The white salt was dried and weighed 3.1 g. (91% yield). On acidification of a small portion there was no odor of 1-propanethiol indicating that the salt was free of sodium 1-propanethiolate. From the acidified portion the free sulfinic acid was isolated, m.p. 81–83°, (lit.,[13] 84°). The infrared spectrum had a strong absorption at 1090 cm.$^{-1}$, characteristic of sulfinic acids.[9] The ether residue after filtration was evaporated on the steam bath. The remaining oil was shown to be β-propylmercaptopropionitrile by vapor phase chromatographic analysis and by comparison with a known sample. Infrared analysis showed a small amount of sulfone present (weak -SO$_2$-absorption).

In the like reaction between β-propylsulfonylpropionitrile and 1-propanethiolate, the resulting salt was converted to benzyl *n*-propyl sulfone, (58% yield, m.p. 87–89°, lit.,[14] 88–89°) by refluxing with benzyl chloride in aqueous alcohol.

Reaction of Ethyl β-*p*-Tolylsulfonylacrylate with Sodium Thiophenoxide.—The addition of thiols to ethyl propiolate and the oxidation of the adducts has been reported elsewhere.[11] The procedure for the displacement reactions was exactly the same as that for the acrylonitrile reactions. The product was identified by isolation and the ester residue was shown to be a mixture of the ethyl *cis*- and *trans*-β-phenylmercaptoacrylate by vapor phase chromatographic analysis.

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2-Methyl-2,4-pentanediol, a Useful Aldehyde Reagent

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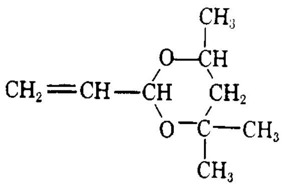
The unsaturated acetal, 2-vinyl-4,4,6-trimethyl-1,3-dioxane (I) is obtained in 98% yield from an equimolar mixture of acrolein and 2-methyl-2,4-pentanediol.[1]



I

The fact that the yield is 10–30% better than those obtained from other glycols under similar conditions in the face of acrolein's well known reactivity at the ethylenic bond led us to investigate the behavior of this glycol with other aldehydes.[2]

Since, with a single exception so far, the reaction with aldehydes has been shown to be quite general, 2-methyl-2,4-pentanediol may now be numbered among the stable aldehyde reagents. Although there are already many such reagents, this example possesses the following unique set of properties: (1) very high specificity for the aldehyde function; (2) high concentration of derivative at equilibrium; (3) derivative formation under mild conditions; (4) ready conversion of derivative to standard aldehyde derivatives.

This combination makes 2-methyl-2,4-pentanediol useful in several operations commonly encountered in organic chemistry: (1) conversion of unstable aldehydes to stable acetals; (2) removal of water-soluble aldehydes from solution; (3) separation of aldehydes from ketones.

This paper is concerned with a few examples of each of these operations; forthcoming publications will deal with more complex problems solved by application of this reagent.

The stable acetals of acrolein, β-chloropropionaldehyde, and β-hydroxypropionaldehyde have already been described.[1] β-Phenoxypropionaldehyde (II) originally prepared by Smith and Ballard[3] is readily prepared from acrolein and phenol over a basic ion exchange resin catalyst. When this adduct was found to revert to its components on attempted distillation, it was converted to the distillable 2-methyl-2,4-pentanediol acetal for identification.

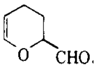
$$C_6H_5O—CH_2CH_2CHO$$

II

Not only are 2-methyl-2,4-pentanediol acetals easily formed, but once formed, they are not readily hydrolyzed. This combination allows one actually to form acetals in aqueous solution. The products are generally water-insoluble and can be extracted with benzene or other solvent. The diol is usually also extractable, leaving the original solution uncontaminated.

For example, we have lowered the concentration of an aqueous solution of formaldehyde from 3 to 0.8% simply by stirring the solution at pH 3 with this glycol and benzene. The product, 4,4,6-trimethyl-1,3-dioxane (III), was isolated in fair yield (65%).

As another example, α-hydroxyadipaldehyde, the hydrolysis product of the thermal dimer (IV) of acrolein is stable only in aqueous solution. Attempts to distil it or otherwise separate it from water have always led to condensations. If, however, the glycol and benzene are added to the acidic solution, the half acetal V is obtained in 90–95% yields.



IV

Although the reactions were run with excess glycol, only very small amounts of bisacetal were formed. Furthermore, little or no reaction occurred between the

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[2] R. F. Fischer and C. W. Smith (to Shell Development Co.), U. S. Patents 2,888,492 (1959) and 2,987,524 (1961).

[3] C. W. Smith and S. A. Ballard (to Shell Development Co.), U. S. Patent 2,500,582 (1950).