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.

Acknowledgment.—This work was supported by the Air Force Office of Scientific Research under contract no. A.F. 49 (638) 531.

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(14) T. R. Lewis and S. Archer, *J. Am. Chem. Soc.*, **73**, 2109 (1951).

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

R. F. FISCHER AND C. W. SMITH

Shell Development Company, Emeryville, California

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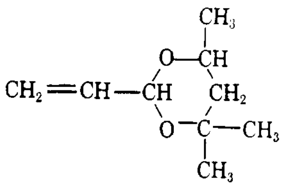
The unsaturated acetal, 2-vinyl-4,4,6-trimethyl-1,3-dioxane (I) is obtained in 98% yield from an equimolar mixture of acrolein and 2-methyl-2,4-pentanediol.[1]



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.

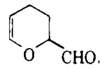
$$C_6H_5O-CH_2CH_2CHO$$

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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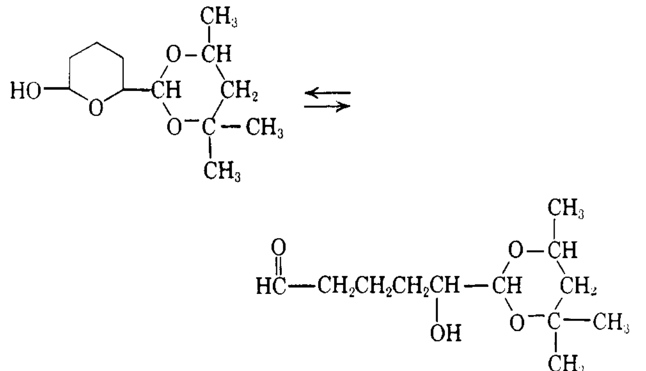
(1) R. F. Fischer and C. W. Smith, *J. Org. Chem.*, **25**, 319 (1960).

(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).



V

distilled product and 2-methyl-2,4-pentanediol. This suggests strongly that the cyclic form predominates.

This acetal can be distilled and stored without decomposition, but under acid conditions should give reactions characteristic of the free aldehyde. It might therefore be of special interest in anhydrous systems where the free aldehyde cannot be used.

The dimer IV itself is the only aldehyde so far tested which has failed to yield a 2-methyl-2,4-pentanediol acetal; only tars were obtained under the usual preparative conditions. If desired, the acetal could probably be prepared by special techniques, however.

Acetone does not react with 2-methyl-2,4-pentanediol under conditions which give good yields of acetals. Although other ketones were not tried, the reaction is probably restricted to aldehydes. In one case an equimolar mixture of acetone and acrolein was efficiently separated by formation of the acrolein acetal without affecting the ketone.

The basis for the efficiency of hexylene glycol in acetal formation is probably twofold. First, the tendency to form five- and six-membered rings gives 1,2- and 1,3-glycols an advantage over aliphatic alcohols in acetal formation. Thus even acrolein and ethylene glycol give 58% yields of the cyclic acetal.[1] The greater stability of the heavily substituted dioxane is undoubtedly the result of conformational control of the *gem*-dimethyl groups.[4]

Experimental

β-Phenoxypropionaldehyde Acetal.—A 1:1 molar mixture of acrolein and phenol was allowed to stand in contact[5] with a strongly basic ion exchange resin (Amberlite IRA 400, Rohm and Haas Co.). After 3 hr., 191 g. (1.27 moles) was drained off the resin and 150 g. (1.27 moles) of 2-methyl-2,4-pentanediol and 0.5 g. of *p*-toluenesulfonic acid were added. After 1 hr. at reflux under a phase-separating head, 25 ml. of water had been removed. The solution was washed twice with 30 ml. of 10% sodium hydroxide once with water and dried. After removal of solvent by distillation, the entire residue (235 g.) was charged to a 2-ft. helices-packed column, and 106 g. (0.69 mole) of 2-vinyl-4,4,6-trimethyl-1,3-dioxane (I), b.p. 65–67° (20 mm.), was removed. The residue was then transferred to a distillation vessel equipped with a Claisen head and distilled at reduced pressure. After 37 g. of phenol had been removed, the product, 2-(2-phenoxyethyl)-4,4,6-trimethyl-1,3-dioxane was obtained; yield 71 g. (49%, taking into account the recovered acrolein derivative).

Anal. Calcd. for $C_{15}H_{22}O_3$: C, 72.1; H, 8.8. Found: C, 71.8; H, 8.9.

Removal of Formaldehyde from Aqueous Solution.—Five hundred grams of a 2.96% solution of formaldehyde was prepared by diluting 41 g. of 37% solution to 500 g. (0.5 mole of aldehyde). The acidity was adjusted to pH 3 with 0.8 g. of sulfuric acid, and the solution was stirred for 2 hr. at 60° with 59 g. (0.5 mole) of 2-methyl-2,4-pentanediol and 150 ml. of benzene. Titration then showed 2.47% formaldehyde in the aqueous phase. A second 59-g. portion of glycol was added. After four additional hours at 60°, the formaldehyde concentration in the aqueous phase was 1.64 wt. %. Two further similar treatments reduced the formaldehyde to 1.38 and 1.21 wt. %. After separation, the aqueous layer was extracted three times with 150-ml. portions of benzene, leaving 1.02% formaldehyde in the aqueous layer. A single further treatment with 59 g. of diol in 100 ml. of benzene followed by three extractions with benzene lowered the formaldehyde concentration to 0.79%. Thus 74% of the formaldehyde was removed.

On fractionation of part of the extracts through a 2-ft. helices-packed column, 31 g. (65% yield, based on formaldehyde removed) of 4,4,6-trimethyl-1,3-dioxane was obtained, b.p. 56° (31 mm.), $n^{20}\mathrm{D}$ 1.4202.

Anal. Calcd. for $C_7H_{14}O_2$: C, 64.6; H, 10.8. Found: C, 64.3; H, 10.8.

Removal of α-Hydroxyadipaldehyde from Aqueous Solution.—A solution of α-hydroxyadipaldehyde was prepared by allowing 56 g. (0.5 mole) of the thermal acrolein dimer (IV) to react with 85 g. of water containing 0.5 g. of sulfuric acid. Heat evolution was controlled with ice cooling, after which the solution was stirred at room temperature for 45 min. After addition of a solution of 118 g. (1.0 mole) of 2-methyl-2,4-pentanediol in 150 ml. of benzene, the mixture was stirred under reflux for 1.5 hr. The layers were separated. After the aqueous layer had been washed with benzene, the combined benzene solutions were dried and filtered, and the solvent was distilled *in vacuo*.

The residue was distilled from a flask equipped with a Claisen head. The forecut, b.p. 68–71° (0.5 mm.), $n^{20}\mathrm{D}$ 1.4286 was 35 g. of 2-methyl-2,4-pentanediol (29% recovery). The yield of product (V), b.p. 120–150° (0.5 mm.), was 116 g. (100%, calcd. as half acetal). For analysis it was redistilled through a 2-ft. helices-packed column; b.p. 121° (0.8 mm.), $n^{20}\mathrm{D}$ 1.4632.

Anal. Calcd. for $C_{12}H_{22}O_4$: C, 62.7; H, 9.7; OH val., 0.43 eq./100 g. Found: C, 62.5; H, 9.7; OH val., 0.42 eq./100 g.

When freshly distilled the compound is a very viscous pale yellow oil. On standing it becomes more fluid and turns colorless.

A small amount of the bisacetal was obtained by redistillation of several of the accumulated highest boiling fractions; b.p. 158–160° (0.5 mm.), $n^{20}\mathrm{D}$ 1.4628.

Anal. Calcd. for $C_{18}H_{34}O_5$: C, 65.5; H, 10.4; OH val., 0.30 eq./100 g. Found: C, 65.4; H, 10.3; OH val., 0.29 eq./100 g.

Formation of an Acetal in the Presence of a Ketone.—A 500-ml. three-necked flask equipped with stirrer and phase-separating head was charged with 58 g. (1.04 moles) of acrolein, 58 g. (1.0 mole) of acetone, 114 g. (0.965 mole) of 2-methyl-2,4-pentanediol, 0.1 g. of *p*-toluenesulfonic acid, and 250 ml. of benzene. After 1.5 hr. under reflux, 18.5 ml. of water had been removed. A further 1.5 hr. gave only 0.5 ml. of water. The solution was then stirred with 2 g. of calcium carbonate, filtered, and concentrated to dryness. Bromine water–thiosulfate titration of the combined low boiling materials showed a maximum of 4.5 g. of acrolein.

The product was distilled through a 2-ft. helices-packed column. After a small (3 ml.) forecut the product distilled in the range 65–67° (20 mm.), $n^{20}\mathrm{D}$ 1.4373. The corresponding constants for 2-vinyl-4,4,6-trimethyl-1,3-dioxane are 62–64° (18 mm.), $n^{20}\mathrm{D}$ 1.4381.[1] The yield was 128 g. (85% conversion to product on glycol), and there was 12 g. of residue.

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(4) G. S. Hammond, in Newman's "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 458.

(5) R. F. Fischer and C. W. Smith (to Shell Development Co.), U. S. Patent 2,857,422 (1958).

The Hydroborating Properties of Sodium Borohydride and Acetic Acid

JAMES A. MARSHALL AND WILLIAM S. JOHNSON

Department of Chemistry, Stanford University, Stanford, California

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During the course of studies of the reduction of enamines with sodium borohydride,[1] we observed that