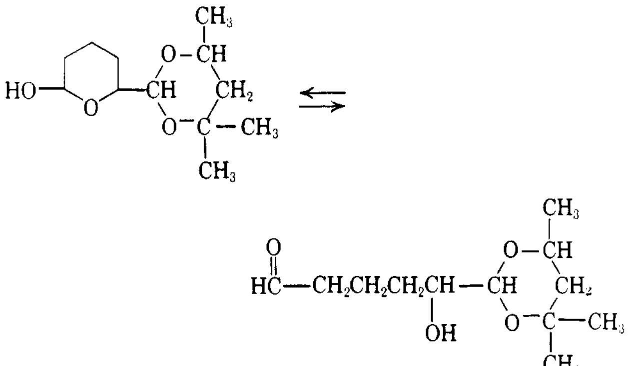

V

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

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During the course of studies of the reduction of enamines with sodium borohydride,[1] we observed that reaction occurred only *after* acetic acid was added to the mixture. Since we also observed the formation of by-products that contained boron bonded to the substrate, we suspected that diborane or a related species was involved. Although this hypothesis proved to be incorrect, it nevertheless led to the discovery that sodium borohydride with acetic acid is, in fact, a hydroborating agent.

It is well known that sodium borohydride in conjunction with various strong acids is an effective hydroborating agent.[2] Furthermore, Brown and Subba Rao[3] have shown that sodium borohydride and propionic acid probably react as follows:

$$CH_3CH_2CO_2H + NaBH_4 \longrightarrow H_2 + [CH_3CH_2CO_2BH_3]^{\ominus}Na^{\oplus}$$

We have noted that the analogous reaction between sodium borohydride and acetic acid produces a species which, perhaps by its decomposition into diborane and sodium acetate, is capable of effecting hydroboration. This fact was demonstrated by treating hexene-1 with a twofold excess of sodium borohydride and acetic acid. The product was then oxidized with hydrogen peroxide to give hexanol-1 in 75% yield.

The observation that a mixture of sodium borohydride and acetic acid can effect hydroboration is especially important in view of the fact that one of the frequently employed procedures for carrying out "conventional" reductions with sodium borohydride is to decompose the excess reagent with acetic acid. In view of our findings, this procedure affords the possibility of introducing serious complications when the aim is to effect selective hydride reduction in systems containing groups (such as olefinic linkages) that are susceptible to attack by diborane. Our findings may also serve to rationalize certain hitherto inexplicable reactions with sodium borohydride[4]—*e.g.*, the facile reduction of certain lactone to lactols and of the olefinic bond of α,β-unsaturated ketones. The vital role played by the acid would be either to protonate the substrate, thus rendering it more susceptible to attack by hydride as appears to be the case with enamines,[1] or to produce diborane, or a related species, which in turn attacks the substrate (or its protonated form).

Experimental

To a stirred suspension of 1.90 g. of sodium borohydride (Metal Hydrides, Inc.) and 2.10 g. of hexene-1 (Aldrich Chemical Co.) in 25 ml. of anhydrous tetrahydrofuran (distilled from lithium aluminum hydride) was added 3.00 g. of glacial acetic acid over a period of 45 min. The mixture was stirred under an atmosphere of nitrogen for 3 hr. at room temperature; then 25 ml. of 10% sodium hydroxide solution and 10 ml. of 30% hydrogen peroxide were very carefully added (violent gas evolution). The mixture was stirred for 1 hr. at room temperature, diluted with saturated brine, and thoroughly extracted with ether. The combined ether layers were washed with saturated brine and dried over anhydrous sodium sulfate. Most of the solvent was removed by distillation at atmospheric pressure through a 25-cm. Vigreux column. The residue was distilled through a short column and afforded 1.36 g. of a liquid, b.p. 155–162°, which was identified as hexanol-1 by infrared and vapor phase chromatographic comparison with authentic material and by conversion to the α-naphthylurethane derivative, m.p. 57–59°.[5] The residue from the distillation amounted to 0.54 g. of nearly pure hexanol-1, identified as described above.

The infrared spectra of the forerun fractions from the distillation described above showed bands due to unreacted hexene-1, but no absorption in the 2.5–3.3-μ region was observed, indicating the absence of ethanol in the reduction mixture.

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(2) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, 1962, chap. 5, p. 97.

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(4) N. A. Atwater, *J. Am. Chem. Soc.*, **83**, 3071 (1961) and examples cited therein.

(5) S. M. McElvain, "The Characterization of Organic Compounds," The Macmillan Company, New York, N. Y., 1958, p. 202.

Reactions of Epithioethylbenzene (Styrene Sulfide)

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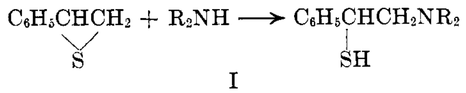
The preparation of epithioethylbenzene (styrene sulfide) has been reported by Guss and Chamberlain,[1] using the reaction of epoxyethylbenzene with potassium thiocyanate in water–dioxane solution. These authors attempted the addition of piperidine and morpholine to the styrene sulfide, but obtained only sulfur-free products which were not identified. It was of interest to this investigator to verify these results, to attempt to find conditions under which amines and styrene sulfide would undergo addition reactions to furnish aminesubstituted mercaptans, and to determine which, if any, of the common ring opening reactions of olefin sulfides styrene sulfide would undergo.

When the reactions of dimethylamine and piperidine with styrene sulfide were carried out in the absence of a solvent, hydrogen sulfide was evolved, no addition products could be obtained, and the products appeared to be polymeric in nature. However, when a solution of the sulfide in 90% benzene–10% ethanol was added slowly to an excess of secondary amine in the same solvent mixture and at various temperatures, aminomercaptan addition products (I) were obtained.



$$C_6H_5\underset{\diagdown S \diagup}{CHCH_2} + R_2NH \longrightarrow C_6H_5\underset{SH}{CH}CH_2NR_2$$

I

The yields obtainable seemed to be controlled mainly by steric factors—dimethylamine, piperidine, and morpholine giving good yields, diethylamine giving a much lower yield, and di-*n*-butylamine giving no addition product. Neither acidic nor basic types of catalysts appeared to improve the yields. The structure I shown is for the so-called "normal" cleavage of the sulfide ring, taking place at the primary carbon atom. This would be expected by analogy to reactions of epoxyethylbenzene (styrene oxide) with amines.[2] This structure was also proved for the reaction product of piperidine and styrene sulfide by desulfurizing the addition compound with Raney nickel and identifying the resulting product

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(2) W. S. Emerson, *ibid.*, **67**, 516 (1945).