

borane to be oxidized quantitatively. Indeed, when 3 mol of sodium hydroxide (3 M solution) was used in the above reaction, oxidation of thioether was totally suppressed and the tri-*n*-octylborane was quantitatively oxidized to the corresponding alcohol (98% yield by GC).

We have therefore demonstrated that from a solution of organoborane and thioether, by a careful choice of reagent, it is possible to oxidize the organoborane in the presence of the thioether or to oxidize the thioether in the presence of the organoborane.

### Experimental Section

All operations were carried out under nitrogen. THF, Et<sub>2</sub>O and 1-octene were distilled from lithium aluminum hydride and stored under nitrogen. Methyl sulfide and 1,4-oxathiane were distilled from 9-borabicyclo[3.3.1]nonane (9-BBN) and stored under nitrogen. Commercial Clorox (5.25% sodium hypochlorite in water) was used as the source of sodium hypochlorite.

**Tri-*n*-octylborane.** To a well-stirred solution of borane-methyl sulfide (5.4 mL, 50 mmol) at 20 °C there was added under nitrogen 1-octene (23.6 mL, 150 mmol) dropwise over a period of 15 min. The reaction mixture was stirred at this temperature for an additional 15–20 min. Methyl sulfide was removed under vacuum (15 mm, 1 h) to leave essentially pure tri-*n*-octylborane (100%) in the flask.

**Oxidation of Thioether from a Solution of Tri-*n*-octylborane in 1.0 M THF with Sodium Hypochlorite.** Oxidation of methyl sulfide in the presence of tri-*n*-octylborane is described as representative. With the usual experimental setup,<sup>10</sup> the reaction flask was charged with tri-*n*-octylborane (2.21 mL, 5 mmol), methyl sulfide (0.38 mL, 5 mmol), *n*-decane (0.38 mL, 2 mmol), and THF (2.03 mL) to make the reaction mixture 1.0 M in borane. The flask was surrounded by a water bath (20 °C) and sodium hypochlorite (7.2 mL, corresponding to 5 mmol of NaOCl) was added dropwise over a period of 10–12 min while the contents of the flasks were stirred. After 15 min, the aqueous layer was saturated with anhydrous potassium carbonate and the organic layer was analyzed by GC using 10% SE-30 on Chromosorb (60/80), 6 ft × 0.25 in. column. GC analysis revealed the absence of methyl sulfide, indicating thereby its 100% conversion to the sulfoxide. The <sup>11</sup>B NMR spectrum of the organic layer indicated the presence of only trialkylborane at δ +85.7 (relative to BF<sub>3</sub>·OEt<sub>2</sub>) and no oxidation product arising from the trialkylborane.

For the isolation of tri-*n*-octylborane or its oxidation product, 1-octanol, after the selective removal of methyl sulfide, the following experiments were done. Tri-*n*-octylborane (6.63 mL, 15 mmol) and methyl sulfide (1.14 mL, 15 mmol) in THF (7.23 mL) were placed in a flask surrounded by a water bath (20 °C). Sodium hypochlorite (21.6 mL, 15 mmol of NaOCl) was added dropwise over 25–30 min. After 10 min at this temperature, the aqueous layer was saturated with anhydrous potassium carbonate. The THF layer was separated under nitrogen. The aqueous layer was washed with 2 × 5 mL of THF and the washings were transferred to the main solution. The organic layer was dried over anhydrous magnesium sulfate under nitrogen and filtered, and removal of the solvents yielded 5.05 g (96%) of the tri-*n*-octylborane. Alternatively, the above tri-*n*-octylborane (4.42 mL, 10 mmol) was dissolved in THF (5.58 mL) and the reaction mixture was oxidized by adding 3 M sodium hydroxide (3.7 mL, 11 mmol) followed by 30% hydrogen peroxide (4.0 mL, 32 mmol). After 1 h at 50 °C, the aqueous layer was saturated with anhydrous potassium carbonate and the organic layer was separated. The aqueous layer was extracted with two 15-mL portions of ether and the combined extract was washed with saturated brine solution (15 mL). The organic layer was dried over anhydrous magnesium sulfate. Removal of solvent and distillation afforded 3.28 g of 1-octanol (84%) (containing 5–6% of 2-octanol), bp 85–87 °C (15 mm).

**Oxidation of Tri-*n*-octylborane from a Solution of Thioether in 0.5 M THF with Alkaline Hydrogen Peroxide.** The oxidation of tri-*n*-octylborane from a solution of 1,4-oxathiane is described as representative. The reaction flask containing

tri-*n*-octylborane (2.21 mL, 5 mmol), 1,4-oxathiane (0.47 mL, 5 mmol), *n*-tetradecane (0.52 mL, 2 mmol), and THF (6.8 mL) was surrounded by a water bath (20 °C). Sodium hydroxide (3 M, 5.0 mL, 15 mmol) was added followed by 30% hydrogen peroxide (1.88 mL, 15 mmol) dropwise over a period of 10 min. After an additional 2 h at 25 °C, the aqueous layer was saturated with anhydrous potassium carbonate. Analysis of the organic layer by GC revealed 14.67 mmol of 1-octanol and 2-octanol (93:7), a yield of 98%.

**Registry No.** Borane-methyl sulfide, 13292-87-0; 1-octene, 111-66-0; tri-*n*-octylborane, 3248-78-0; methyl sulfide, 75-18-3; methyl sulfoxide, 67-68-5; 1-octanol, 111-87-5; 2-octanol, 123-96-6; borane-1,4-oxathiane, 72525-30-5.

### Anhydrous Copper(II) Sulfate: An Efficient Catalyst for the Liquid-Phase Dehydration of Alcohols

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A fundamental organic transformation for which a great number of methods have been reported is the conversion of alcohols to olefins. These methods include both direct dehydration of the alcohol with numerous reagents and elimination in alcohol derivatives, usually esters.<sup>1</sup> New procedures and reagents appear regularly, each of which offers certain advantages over other methods.<sup>2</sup> We wish to report that anhydrous copper(II) sulfate, prepared by heating copper(II) sulfate pentahydrate at 200–300 °C for 2 days, serves as an effective catalyst for the dehydration of secondary, tertiary, benzylic, and allylic alcohols to the corresponding olefins. This reagent was first employed with tertiary alcohols in 1933<sup>3</sup> and has been nearly ignored since. We find that it is a valuable alternative to other dehydration reagents and works for a variety of alcohol types.

Of greatest note is the extreme simplicity of the method. The neat alcohol and the solid catalyst are heated at an appropriate temperature (vide infra), and the olefin distills from the reaction mixture. Dehydration occurs in the liquid phase so that gas-phase flow systems are unnecessary, the conditions are fairly mild (100–160 °C), and the time required is relatively short (0.5–15 h). Furthermore, the olefin product is uncontaminated with byproducts other than the evolved water; filtration through a cotton pad gives pure product.

**Experimental Guidelines.** Anhydrous copper(II) sulfate can be prepared in large batches and stored indefinitely in a desiccator. It was found that an alcohol-catalyst ratio of 1:0.75 gave the best results. The temperature required for smooth dehydration varies with the alcohol structure—the order of reactivity being tertiary ≈

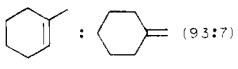
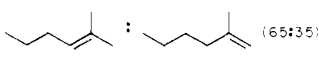
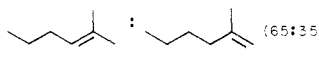
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Table I. Dehydration of Alcohols Catalyzed by Anhydrous  $\text{Cu}^{\text{II}}\text{SO}_4$ 

entry	alcohol	P, mm	T, °C	t, h <sup>a</sup>	products	yield, %
1	1-phenylethanol	25	120	1.5	styrene	65
2	1-phenyl-1-propanol	25	125	2	$\beta$ -methylstyrene ( <i>trans/cis</i> , 91:9)	69
3	$\alpha$ -tetralol	25	140	0.5	1,2-dihydronaphthalene	95
4	2-phenyl-2-propanol	25	95	1	$\alpha$ -methylstyrene	83
5	1,1-diphenylethanol	0.4	100	1	1,1-diphenylethylene	92
6	1-methylcyclohexanol	660 <sup>b</sup>	130	1.5	 (93:7)	76
7	2-methyl-2-hexanol	660 <sup>b</sup>	125	1	 (65:35)	76
8	cyclohexanol	660 <sup>b</sup>	165	15	cyclohexene	77
9	2-octanol	660 <sup>b</sup>	180	5	1-octene (21%), 2-octene (79%)	78
10	1-hexen-3-ol	660 <sup>b</sup>	130	5	1,3-hexadiene	45
11	2-cyclohexenol	660 <sup>b</sup>	120	1.5	cyclohexadiene	52
12	geraniol	25	125	1.5	myrcene	25
13	linalool	25	100	3	myrcene	4
14	2-phenyl-2-propanol	660	95	1	$\alpha$ -methylstyrene	70
15	1,1-diphenylethanol	660	100	1	1,1-diphenylethanol	87
16	1-methylcyclohexanol	660	130	1.5	1-methylcyclohexene	70
17	2-methyl-2-hexanol	660	125	1	 (65:35)	70

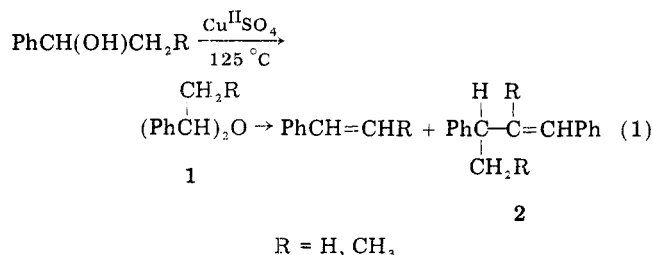
<sup>a</sup> Time required for olefin evolution to cease. <sup>b</sup> The normal atmospheric pressure in these laboratories.

benzylic > allylic > secondary. The reaction temperatures found to be best were about 120–130 °C for the tertiary, benzylic, and allylic types and 160–180 °C for secondary alcohols. Higher temperatures lead to somewhat decreased yields in cases of easily polymerized olefins.

The olefin product was collected at atmospheric pressure or under reduced pressure for olefins with boiling points greater than ~120 °C. The pressure was chosen so that the reaction temperature was at or near the boiling point of the starting alcohol, allowing smooth distillation of the olefin from the reaction mixture. Table I lists the results of our dehydration reactions (entries 1–13).

When the olefin product is not readily polymerized, the reaction can be carried out under reflux and the olefin recovered by working up the reaction mixture. Entries 14–17 of Table I refer to this method, and it is seen that only slightly lower yields are observed.

**General Comments.** The general reactivity order suggests that carbenium ion formation is the key step. The regiochemistry (Saytzeff orientation favored, entries 6, 7, and 9) and stereochemistry (*trans* olefin favored, entry 2) support this interpretation.<sup>4</sup> In addition, the dehydrations of 1-phenylethanol and 1-phenylpropanol lead to side products uniquely indicative of carbenium ion intermediates. Heating either of these alcohols with anhydrous copper(II) sulfate yields first the bis ether 1, which then undergoes smooth cracking to the olefin. Furthermore, examination of the reaction residue reveals that the major byproduct is a styrene dimer, 2 (eq 1).<sup>5</sup> Both products



can result from the capture of a benzylic carbenium ion. Capture by alcohol in the early stages of the reaction gives the ether; in the later stages of the reaction, when the alcohol is depleted, capture by styrene gives the styrene dimer after proton elimination. Finally, the production of dienes from allylic alcohols (entries 10–13) is characterized by lower yields and increases in polymeric side products.

The exact catalytic species is not known at this time, nor is the role of copper understood. When very small amounts of pyridine are added to the reaction mixture, nearly complete destruction of the catalytic activity follows. It is therefore possible that in the preparation of anhydrous copper(II) sulfate, small amounts of strong, proton acids are formed which are responsible for the catalytic activity. The products of dehydration are similar in nature to those of other acid-catalyzed dehydrations of the same alcohols.

What is notable is that anhydrous copper(II) sulfate is a general dehydration catalyst that equals or surpasses other common catalysts in yields and is often more efficient (lower temperatures and/or shorter times).<sup>6</sup> For example,  $\beta$ -methylstyrene is produced in 69% yield in the present work while potassium bisulfate gives 55–60% yields.<sup>7</sup> Styrenes can be prepared from 1-arylethanol in 33–80% yields with potassium bisulfate at 220 °C in 5–8 h.<sup>8</sup> For the parent system, we observe a comparable yield and greatly decreased temperature requirements. Copper(II) sulfate is also superior to  $\text{Me}_2\text{SO}$  and  $\text{H}_2\text{SO}_4$  in the dehydration of 2-methyl-2-hexanol<sup>9</sup> and 1-methylcyclohexanol.<sup>10</sup> These selected examples illustrate that  $\text{Cu}^{\text{II}}\text{SO}_4$  is an excellent first choice as an alcohol dehydration catalyst.

### Experimental Section

**Materials.** All the alcohols used in this study were purchased from Aldrich and used as received. Anhydrous copper(II) sulfate was prepared by heating  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (Fisher, ACS grade) in a

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(5) These products have been fully characterized by their IR, NMR, and mass spectra.

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porcelain dish at 275 °C for 2 days. The off-white solid was stirred several times during heating to help break up the lumps and was stored in a desiccator.

**General Dehydration Procedure.** The alcohol to be dehydrated was placed in a round-bottomed flask containing a magnetic stirring bar and anhydrous copper(II) sulfate (0.75 molar equiv). A 7-cm Vigreux column and condenser was attached, and the mixture was immersed with vigorous stirring in an oil bath preheated to the desired reaction temperature. Heating was continued until the distillation of volatile products into an ice-cooled receiver stopped. The majority of the water layer of the product was removed by pipet, and the olefin product was filtered through a plug of cotton. In all cases the olefin product was pure as determined by NMR spectroscopy, which was also used to calculate ratios of isomeric products. Where the olefin product was higher boiling (>120 °C), aspirator vacuum (25 mm) was applied to the same experimental setup.

When dehydrations were carried out under reflux (entries 14-17), the alcohol and catalyst were heated together in a flask fitted with a condenser. The temperature and reflux time utilized were those determined for complete distillation of product in the above distillation method. The reaction mixture was cooled, ether was added, and the copper sulfate was filtered. Fractional distillation of the ether solution yielded the olefin product.

**Registry No.** 1-Phenylethanol, 98-85-1; 1-phenyl-1-propanol, 93-54-9;  $\alpha$ -tetralol, 529-33-9; 2-phenyl-2-propanol, 617-94-7; 1,1-diphenylethanol, 599-67-7; 1-methylcyclohexanol, 590-67-0; 2-methyl-2-hexanol, 625-23-0; cyclohexanol, 108-93-0; 2-octanol, 123-96-6; 1-hexen-3-ol, 4798-44-1; 2-cyclohexenol, 822-67-3; geraniol, 106-24-1; linalool, 78-70-6; styrene, 100-42-5; (*E*)- $\beta$ -methylstyrene, 873-66-5; (*Z*)- $\beta$ -methylstyrene, 766-90-5; 1,2-dihydronaphthalene, 447-53-0; 2-methylstyrene, 300-57-2; 1,1-diphenylethylene, 530-48-3; 1-methylcyclohexene, 591-49-1; methylenecyclohexane, 1192-37-6; 2-methyl-2-hexene, 2738-19-4; 2-methyl-1-hexene, 6094-02-6; cyclohexene, 110-83-8; 1-octene, 111-66-0; 2-octene, 111-67-1; 1,3-hexadiene, 592-48-3; cyclohexadiene, 592-57-4; myrene, 123-35-3; Cu<sup>II</sup>SO<sub>4</sub>, 18939-61-2.

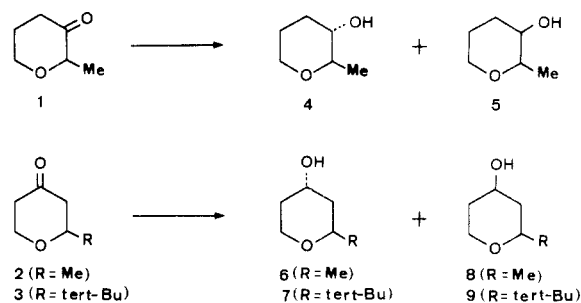
### Steric Course of the Reductions of 2-Alkyltetrahydropyranones

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The stereoselectivity of the reductions of substituted cyclohexanones has received considerable attention over the years<sup>1</sup> but is still not completely understood. Our interest in the synthesis of substituted tetrahydropyrans and deoxy sugars<sup>2-5</sup> prompted an investigation of the stereochemistry of the reduction of alkyl-substituted tetrahydropyranones 1-3. In particular, we have been concerned with the effect, if any, of a ring heteroatom on the stereochemical course of these reactions in comparison with those of the corresponding alkylcyclohexanones. Briefly, we found no significant deviation between the alicyclic and heterocyclic systems. Table I,<sup>11-19</sup> incorporating our studies and literature values, summarizes results with six reducing agents. As seen, the only differences are that the carbocyclic cases often give somewhat higher percentages of the



less stable (axial hydroxyl) isomers.

However, a recent report<sup>6</sup> concluded that the reduction of 2 with L-Selectride<sup>7</sup> affords predominantly the *cis* isomer 8 (equatorial OH), in contrast to the predominant attack from the equatorial side usually obtained with this bulky reagent (i.e., 85-95% equatorial attack on 3-methylcyclohexanone). This abnormal behavior was attributed to the intervention of complexation with the ring oxygen and hydride delivrance through a boat conformation.

We have carefully reexamined the reduction of 2 with L-Selectride and conclude that the *trans* isomer 6 is the major product in THF at -78 °C<sup>8</sup> and ether at room temperature.<sup>6</sup>

As previously observed,<sup>6</sup> direct NMR analysis of the alcohols 6 and 8 was hampered by overlap of the C-2 and C-6 protons with the diagnostic ones at C-4. However, this problem was conveniently overcome by conversion to the *p*-nitrobenzoates which shifted the signals of the C-4 protons away from the offending peaks of C-2 and C-6.

In this manner, assignment of the proper configurations was straightforward and confirmed the previous determinations; the signals for the protons at C-4 of the esters had exactly the same shapes as those reported for the corresponding hexadeuterated alcohols.<sup>6</sup> Likewise, analysis of mixtures of 6 and 8 by GLC was difficult, as reported.<sup>6</sup> However, the corresponding trimethylsilyl ethers were readily separated (OV-17 column), and this provided a convenient and accurate method of analysis. As indicated in Table I, L-Selectride consistently afforded a predominance of the *trans* alcohol 6, in accord with results with cyclohexanones and other tetrahydropyranones. We conclude that a ring oxygen in position 3 or 4 of a six-membered-ring ketone has no significant effect on the stereochemistry of reductions.

The discrepancy between our and previous<sup>6</sup> results is perhaps due to the latter's analysis by NMR. The presence of 2-butanol, produced in the peroxide oxidation of L-Selectride reductions, would artificially enhance the perceived amount of *cis* isomer 8 since the CHOH proton

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