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THE VAPOR PHASE OXIDATION OF ALCOHOLS BY CUPRIC OXIDE. A CONVENIENT PREPARATION OF ALDEHYDES AND KETONES

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There are numerous examples of the vapor phase oxidation of alcohols over a variety of metals (e.g., Cu,Fe,Al,Mn,Zn) and metal oxides (e.g., CuO,Fe_2O_3,Al_2O_3,Cr_2O_3).[1] Although of some industrial importance, vapor phase oxidation has found little application to practical laboratory procedures, probably because of the frequently elaborate procedures employed for the preparation of catalysts,[1] the utilization of elevated reaction temperatures (500-1,000°)[1], and the frequent occurrence of side reactions[2] (e.g., the formation of acids, dehydrogenation, coupling, and ether formation).

We wish to report a simple, high-yield laboratory procedure for the oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones. Our procedure involves passing a mixture of inert carrier gas (conveniently helium) and alcohol vapors through a 6 foot column loosely packed with cupric oxide wire worms.* A vapor phase chromatograph provides accurate temperature and helium flow rate control; injection of 5 to 100 µl of alcohol onto a column maintained at 250 - 300° with a helium flow rate of four to twenty ml/min. generally produced satisfactory results. The effluent vapors were passed through a Dry-Ice-acetone cooled trap to condense the product aldehyde or ketone. Yields were insensitive to minor variations in reaction conditions; raising the column temperature above 350° produced significant

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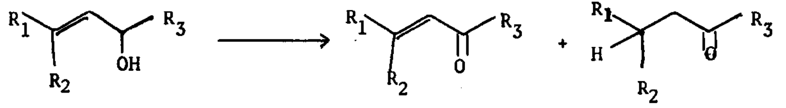
* Purchased from Allied Chemical Co., General Chemical Division, New York, N. Y., U.S.A.

overoxidation of primary alcohols to the corresponding acids, while lower temperatures or more rapid helium flow rates resulted in the recovery of unreacted alcohol. The minimum temperature for complete conversion of the alcohol increased gradually with column use, as the surface layers of cupric oxide were reduced to elemental copper. Repacking the column with fresh cupric oxide restored its original activity.

The results obtained in the oxidation of a number of alcohols are presented in Table I. n-Hexanol, n-heptanol, and n-octanol were converted to the corresponding aldehydes in almost quantitative yield. Secondary aliphatic alcohols, such as 2-octanol and 4-nonanol, and alicyclic alcohols such as cyclohexanol and 2-methylcyclohexanol furnished the corresponding ketones in yields in excess of 90%. Aromatic alcohols, such as benzyl alcohol and phenyl ethyl alcohol, could be smoothly converted to the corresponding aldehydes. Unsaturated aliphatic alcohols with two or more methylene units interpolated between the double bond and the hydroxyl-bearing carbon, such as 4-penten-1-ol and 5-hexen-1-ol, could be converted to the corresponding unsaturated aldehydes in quantitative yield.

The vapor phase reaction of allylic and homoallylic alcohols with cupric oxide proceeds in a more complicated manner. Allylic alcohols react at lower temperatures (complete consumption of starting material at 200 - 250°) to produce a mixture of saturated and unsaturated carbonyl compounds (Eq. 1). The composition of the mixture was a function of column temperature, and of alcohol structure. Higher temperatures invariably favored the production of the unsaturated ketone or aldehyde, but in every case a mixture of saturated and unsaturated compounds was obtained. Homoallylic alcohols give rise to similar product mixtures, but require higher temperatures to initiate reaction. These results are consistent with the mechanism depicted in Eq. 2.[3] An alternative mechanism involving dehydrogenation-hydrogenation is excluded by the aforementioned conversion of 5-hexen-1-ol to 5-hexen-1-al.



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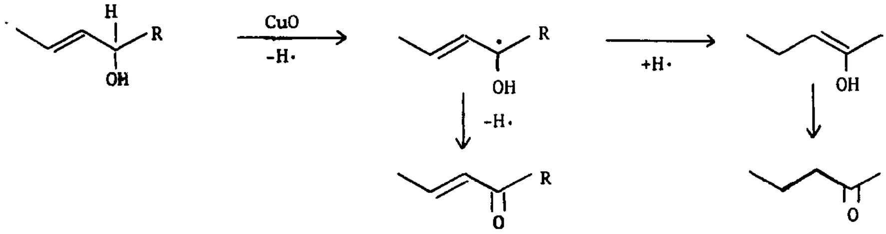
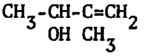
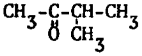
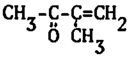
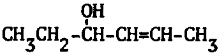
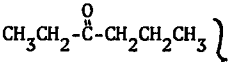
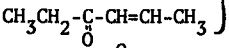
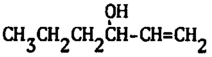
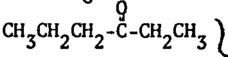
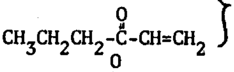
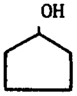
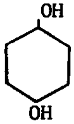
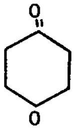
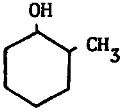
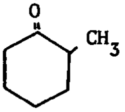
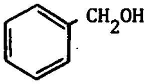
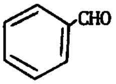
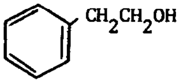
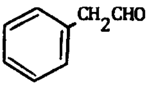


(2)

Table 1

Vapor Phase Oxidation of Some Primary and Secondary Saturated and Unsaturated Alcohols over Cupric Oxide (250-300°C)

	Compound	Product	% Yield*
1	$CH_3(CH_2)_3CH_2OH$	$CH_3(CH_2)_3CHO$	99
2	$CH_3(CH_2)_4CH_2OH$	$CH_3(CH_2)_4CHO$	99
3	$CH_3(CH_2)_5CH_2OH$	$CH_3(CH_2)_5CHO$	98
4	$CH_3(CH_2)_6CH_2OH$	$CH_3(CH_2)_6CHO$	98
5	$CH_3CHOH(CH_2)_6CH_3$	$CH_3CO(CH_2)_6CH_3$	96
6	$CH_3(CH_2)_2CHOH(CH_2)_4CH_3$	$CH_3(CH_2)_2CO(CH_2)_4CH_3$	100
7	$CH_2{=}CH\text{-}(CH_2)_2CH_2OH$	$CH_2{=}CH\text{-}(CH_2)_2CHO$	99
8	$CH_2{=}CH\text{-}(CH_2)_3CH_2OH$	$CH_2{=}CH\text{-}(CH_2)_3CHO$	100
9	 $CH_3\text{-}\underset{OH}{CH}\text{-}\underset{CH_3}{C}{=}CH_2$	 $CH_3\text{-}\underset{\overset{\|}{O}}{C}\text{-}\underset{CH_3}{CH}\text{-}CH_3$	90
		 $CH_3\text{-}\underset{\overset{\|}{O}}{C}\text{-}\underset{CH_3}{C}{=}CH_2$	5
10	 $CH_3CH_2\text{-}\overset{OH}{CH}\text{-}CH{=}CH\text{-}CH_3$	 $CH_3CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_2CH_2CH_3$	85
		 $CH_3CH_2\text{-}\underset{\overset{\|}{O}}{C}\text{-}CH{=}CH\text{-}CH_3$	10
11	 $CH_3CH_2CH_2\overset{OH}{CH}\text{-}CH{=}CH_2$	 $CH_3CH_2CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_2CH_3$	87
		 $CH_3CH_2CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH{=}CH_2$	10
12			92
13			90
14			92
15			92
16			90

* All yields were determined by analytical glc of the oxidation mixture.

Because of the experimental simplicity and high yield of the cupric oxide oxidation of alcohols, it is anticipated that the reaction will find wide application in synthetic organic chemistry. An obvious application of the procedure is the preparation of deuterated aldehydes and ketones (cf. Table II for the yields and isotopic purtiy of products). The advantages of this procedure over those previously utilized are obvious; the difficult and time-consuming problem of separating a small amount of a volatile compound from a complex reaction mixture is circumvented.

Table II

Vapor Phase Oxidation of Deuterated Alcohols
Over Cupric Oxide (300°C); Deuterium Retention

No.	Deuterated Compound	Product	% Yield	% Retention of Deuterium*
1	$CH_3(CH_2)_3CD_2OH$	$CH_3(CH_2)_3CDO$	98	
2	$(CH_3)_2CH(CH_2)_2CD_2OH$	$(CH_3)_2CH(CH_2)_2CDO$	99	98-99
3	$CH_3(CH_2)_4CD_2CH_2OH$	$CH_3(CH_2)_4CD_2CHO$	87	97-98
4	$CH_3CH_2CD_2(CH_2)_2OH$	$CH_3CH_2CD_2CH_2CHO$	90	98
5	$CH_3(CH_2)_3CD_2(CH_2)_2OH$	$CH_3(CH_2)_3CD_2CH_2CHO$	86	95

* Retention of deuterium in the products was determined from the mass spectra of the corresponding 2,4-dinitrophenylhydrazones.

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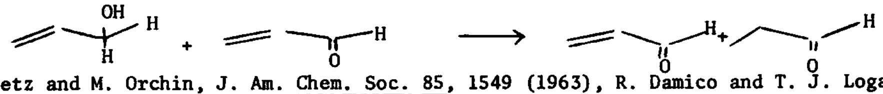

(i)

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