

CATALYTIC REDUCTION OF OZONIDES. I. SYNTHESIS OF ALCOHOLS FROM OLEFINS

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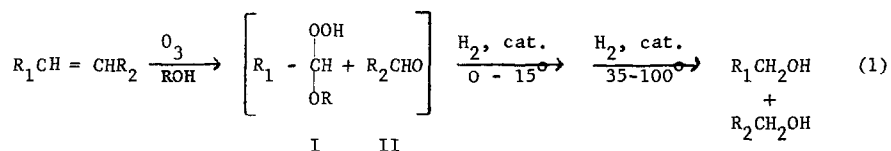
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Although the oxidation of ozonides to carboxylic acids is a standard preparative method,³ the one-step reductive cleavage of ozonides to alcohols has only recently been examined in detail.^{4,5} The results of these studies suggested that chemical reduction is preferred to catalytic hydrogenation for this purpose. Thus, a two-stage hydrogenation of the ozonolysis product from ethyl 10-undecenoate (in ethanol), first at room temperature and 2000 psi, and then at 130-150° using Raney nickel catalyst gave ethyl 10-hydroxydecanoate in 71% yield, whereas large-scale preparations produced impure product in yields of 40 to 66%.⁵ (The yield of pure ethyl 10-hydroxydecanoate in a large-scale preparation using sodium borohydride was 94%). On the other hand, a large-scale preparation of pentadecanol-1 in 72% yield by the two-stage hydrogenation of hexadecene-1 ozonide in the presence of a nickel catalyst is described in a patent.⁶ Similarly, the preparation of methyl 9-hydroxynonanoate from methyl oleate ozonide in 76-79.5% yields was reported in another patent.⁷ However, both patents dealt with the hydrogenation of the "classical" ozonides prepared in inert solvents.


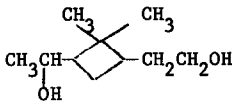
We have re-examined the ozonolysis of olefins in the reactive solvents methanol or 1-butanol followed by a one vessel, two-stage catalytic hydrogenation. Under carefully controlled conditions this sequence of reactions provides a general method for the synthesis of alcohols in excellent yield (eq. 1).



The ozonolysis is carried out between -78 and 20° to give a mixture of the corresponding alkoxyhydroperoxide (I) and aldehyde (II). The first-stage reduction of I occurred exothermically at 15-50 psi over platinum catalyst or 50-300 psi over Raney nickel catalyst

and the mixture was cooled to 0-15° to avoid the free radical decomposition of I to the corresponding ester, R_1CO_2R .^{5,8,9} After reduction of the hydroperoxide, the final stage of the hydrogenation is carried out at 35-50° and 50-150 psi with platinum catalyst or at 80-100° and 600-1000 psi with Raney nickel catalyst. When the reduction was completed (usually 1-4 hours), the catalyst was removed by filtration and pure products were isolated by solvent removal under vacuum without the need for any further purification steps such as those required in the work-up of sodium borohydride reductions.^{4,5} Results of this method for the synthesis of alcohols and glycols are shown in Table I.

TABLE I
SYNTHESIS OF ALCOHOLS FROM OLEFINS

Olefin	Catalyst	Products*	Yield, %
cyclopentene	Pt	$HO(CH_2)_5OH$	80
cyclohexene	Pt	$HO(CH_2)_6OH$	95
1-methylcyclohexene	Ni	$CH_3CH(OH)(CH_2)_5OH$	77
cyclooctene	Pt	$HO(CH_2)_8OH$	95
cyclooctene	Ni	$HO(CH_2)_8OH$	92
1,5-cyclooctadiene	Ni	$HO(CH_2)_4OH$	86
cyclododecene	Pt	$HO(CH_2)_{12}OH$	85
1,5,9-cyclododecatriene	Pt	$HO(CH_2)_4OH$	95
norbornene	Ni		91
α -pinene	Ni		85
octene-1	Ni	$CH_3(CH_2)_6OH$	80
methyl oleate	Ni	$CH_3(CH_2)_8OH$	82
		$HO(CH_2)_8CO_2CH_3$	91

* Physical constants of all products agreed with literature values. In most cases, purity was also established by vapor phase chromatography.

We conclude that ozonolysis in reactive solvents with subsequent hydrogenation provides a useful method for the large-scale conversion of olefins to alcohols and glycols in high yields. The excellent yields of glycols from cyclic and bicyclic olefins are noteworthy. Our yield of hexamethylene glycol (95%) is much better than that reported for the sodium borohydride reduction of cyclohexene ozonide (63%).^{4a} The yields of nonanol (82%) and methyl 9-hydroxynonanoate (91%) from methyl oleate are also better than those previously reported.^{5,7} Many such preparations have been carried out on a 1-2 mole scale with no diminution in yield.

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