

OXIDATION OF ALCOHOLS TO ALDEHYDES AND KETONES via aci-NITROESTERS OF
 ETHYL NITROACETATE UNDER NEUTRAL CONDITIONS

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Summary: The reaction of alcohols with ethyl nitroacetate, diethyl
 azodicarboxylate, and triphenylphosphine gave the corresponding
 aldehydes or ketones in 52-85% yields.

In spite of the development of effective reactions for the oxidation of
 alcohols to aldehydes and ketones,¹⁾ there still exists a need for new methods
 which proceed under mild neutral conditions. Recently, we reported that the
 reaction of an alcohol with 2,6-di-t-butyl-4-nitrophenol, diethyl azodicarboxylate
 (1) and triphenylphosphine (2) gave rise to an aci-nitroester which, on treatment
 with a base, decomposed into the corresponding carbonyl compound and an oxime.²⁾
 We now wish to report the oxidation of alcohols under neutral conditions.

The reaction of tetradecanol with ethyl nitroacetate (3),³⁾ 1, and 2 at room
 temperature for 2 h resulted in the formation of tetradecanal and aci-nitroester
 (4; R = C₁₃H₂₇, R¹ = H) in 66% and 19% yields, respectively. Although no oxime
 (6) could be isolated, the aldehyde would be formed by the decomposition of
 initially formed 4.⁴⁾ In order to facilitate the decomposition, the reaction
 mixture was refluxed for additional 2 h where tetradecanal was obtained in 85%
 yield. Similarly, various alcohols were successfully oxidized to aldehydes or
 ketones as summarized in Table 1. Neither 6 nor C-alkylated products (7) could
 be isolated in these reactions. The predominant O-alkylation could be rational-
 ized by assuming the intermediacy of a hard alkylating reagent, Ph₃P⁺-OR.^{5, 6)}

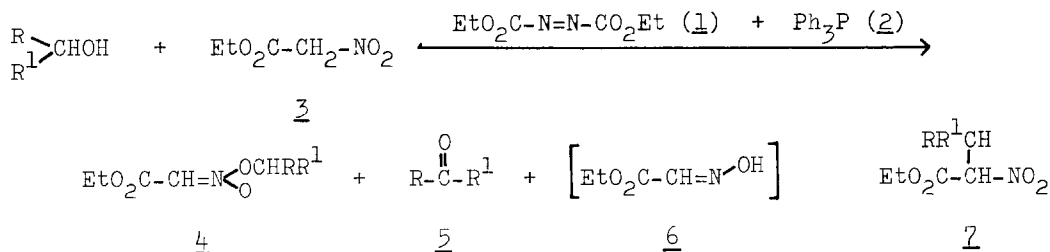


Table 1. Oxidation of Alcohols

Alcohol, RR ¹ CHOH R	R ¹	Aldehyde or Ketone <u>2</u>	Yield of <u>2</u> , (%) [*]	Solvent System Used for Isolation ^{**}
CH ₃ (CH ₂) ₆	H	CH ₃ (CH ₂) ₆ CHO	62	B-EA (10 : 1)
CH ₃ (CH ₂) ₁₂	H	CH ₃ (CH ₂) ₁₂ CHO	85	B-H (2 : 1)
C ₆ H ₅ CH ₂	H	C ₆ H ₅ CH ₂ CHO ^{***}	52	B-EA (10 : 1)
p-CH ₃ O-C ₆ H ₄	H	p-CH ₃ O-C ₆ H ₄ CHO	75	B-EA (10 : 1)
C ₆ H ₅	CH ₃	C ₆ H ₅ -CO-CH ₃	85	B-EA (10 : 1)
Citronellol		Citronellal	72	B-EA (10 : 1)
Cholestanol		Cholestan-3-one	77	H-E (10 : 1)

^{*} Yields were not optimized. ^{**} B = benzene, EA = ethyl acetate, H = hexane, E = ether. ^{***} The reaction was carried out at -20~-15°C for 1 h, and then at room temperature for 17 h. Compound 4 (R = C₆H₅CH₂, R¹ = H) was obtained in 27% yield.

General Procedure: A solution of 1 (261 mg, 1.5 mmol) in tetrahydrofuran (THF, 1 ml) was added dropwise to a solution of an alcohol (1 mmol), 2 (393 mg, 1.5 mmol), and 3 (200 mg, 1.5 mmol) in THF (2 ml) at room temperature. After the solution had been stirred for 2 h, it was refluxed for 2 h and the solvent was removed under reduced pressure. The products were isolated by preparative layer chromatography (silica gel) and identified by nmr and ir spectroscopies.

In view of the selectivity of the alkylation reaction by the use of 1 and 2,⁶⁾ the procedure described here indicates potential usefulness for the regioselective oxidation of di- and polyols.

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References and Note

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