

Oxidation of Ethers by Nitrogen Dioxide in the Presence of Silica Gel

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Ethers are efficiently oxidized by nitrogen dioxide to give the corresponding aldehydes or ketones in the presence of silica gel under mild conditions.

Nitrogen dioxide (NO_2), which is usually equilibrated with dinitrogen tetroxide (N_2O_4), has been reported to cause the oxidation of some organic compounds.¹ Field and Grundy reported² that benzyl alcohols are oxidized to benzaldehydes by high concentrations of N_2O_4 but to the best of our

knowledge the oxidation of ethers by NO_2 and N_2O_4 has not been reported.¹ We inferred that NO_2 is an active intermediate in the oxidation of alcohols³ and ethers⁴ by metallic nitrates supported on silica gel. Here we report the efficient oxidation of ethers to aldehydes or ketones by NO_2 in the

Table 1 Oxidation of ethers by nitrogen dioxide^a

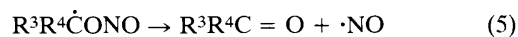
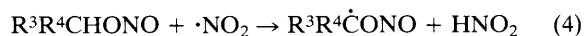
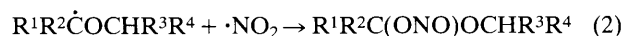
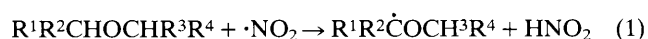
Ether	t/min	Product	Yield (%)
Cyclododecyl methyl	30	Cyclododecanone	88
Benzyl cyclohexyl	15	Benzaldehyde	94
		Cyclohexanone	36
		Cyclohexyl nitrite	13
Benzyl cyclohexyl ^b	15	Benzaldehyde	91
		Cyclohexanone	10
		Cyclohexyl nitrite	7
Benzyl cyclohexyl ^{b,c}	15	Benzaldehyde	4
Dibenzyl ^{b,d}	20	Benzaldehyde	194
1-Phenylethyl methyl	15	Acetophenone	85
Dihexyl ^{d,e}	60	Hexanal	32
(Cyclopentanol)	30	Cyclopentanone	70
(Cyclohexanol)	30	Cyclohexanone	80

^a The ether (1 mmol) and silica gel (1 g) were stirred at room temperature in CCl₄ (20 ml) under NO₂. ^b The reaction mixture was heated in refluxing CCl₄. ^c Silica gel was not added. ^d 100% ± 1 mol of product from 1 mol of ether. ^e The ether was detected in 42% recovery.

presence of silica gel. This oxidation may be of use for organic synthesis because it occurs under neutral and mild conditions.

The oxidations in this study were carried out by stirring an ether (1 mmol) and 230–400 mesh chromatographic silica gel (1 g) in CCl₄ (20 ml) at room temperature or at refluxing temperature under an atmosphere of NO₂. Benzyl and secondary ethers gave the corresponding aldehydes and ketones in high yields but primary alkyl ethers reacted more slowly (Table 1).[†] In the absence of silica gel the extent of oxidation was insignificant. The reactivity of ethers is nearly the same as that of alcohols. In the reactions of benzyl cyclohexyl ether the yields of cyclohexanone were much lower than those of benzaldehyde and a small amount of cyclohexyl nitrite was detected. Cyclohexanone was obtained in 28% yield when cyclohexyl nitrite⁵ (1 mmol) and silica gel (0.5 g) were heated in refluxing CCl₄ (10 ml) for 15 min under NO₂. In the absence of silica gel or NO₂ the nitrite was recovered. This fact shows that NO₂ promotes the decomposition of the

[†] Benzyl halides and benzyl esters gave the corresponding carbonyl compounds and the aromatic compounds underwent nitration in the reaction with NO₂ in the presence of silica gel. However, the rates of these reactions are much slower than those of the oxidation of ethers.



Scheme 1

nitrite to the ketone in the presence of silica gel and suggests the possibility that carbonyl compounds are formed at least partly *via* nitrites.

The logarithm of initial rates in the oxidation of *p*-methyl-, *p*-fluoro- and *p*-chloro-benzyl methyl ethers showed a roughly linear dependence on the Hammett substituent constants to give a ρ value of -0.7 . The fact that the electronic character of the substituents influenced the reaction rates to only a small extent suggests that radical rather than ions are formed as intermediates.⁶ Therefore, NO₂ is presumed to act in a radical manner, although NO₂ and N₂O₄ are known to undergo self-ionization to give nitrosyl and nitrate ions.^{1,7} Moreover, the oxidation of ethers and alcohols by silica gel-supported metallic nitrates is inferred to involve NO₂ and proceed *via* a radical process.^{3,4} Consequently, we propose the radical processes in Scheme 1 for the oxidative cleavage of ethers.

We infer a similar scheme for the decomposition of nitrites to carbonyl compounds which is promoted by NO₂ [reactions (4) and (5)].

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