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FORMATION OF REMOTE DOUBLE BONDS BY CUPRIC ACETATE CATALYZED PHOTOLYSIS OF ALKYL NITRITES

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Alkoxy radicals, which satisfy certain structural and geometrical requirements, undergo intramolecular hydrogen abstraction from nonactivated remote carbon atom, leading to the introduction of functional groups mainly at the δ-carbon atom[1-3]. The introduction of a double bond at the δ-carbon atom has been achieved by metal catalyzed decomposition of alkyl hydroperoxides[4,5]. Alkoxy radicals generated by the ferrous sulfate reduction of hydroperoxide undergo 1,5-hydrogen abstraction affording δ-carbon radicals. The trapping of these "out of cage" carbon radicals with cupric acetate furnished δ-olefinic alcohols[4,6]. It has been shown that the photolysis of ^{15}N labelled nitrite esters, involving intramolecular hydrogen abstraction by alkoxy radicals, proceeds through an "out of cage" free radical mechanism and that carbon radicals can be intercepted by chain transfer reagents[1,7,8].

Present investigation concerns the possibility of cupric acetate interception of δ-alkyl radicals, generated by the photolysis of alkyl nitrites whereby an oxidative elimination process of the intermediate was expected to occur. As may be seen from Table I these expectations were justified: the photolysis of nitrite esters in the presence of cupric acetate gave the unsaturated alcohols as the main intramolecular hydrogen abstraction product.

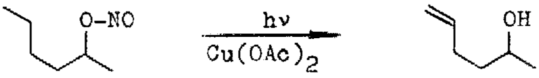
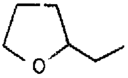
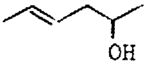
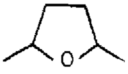
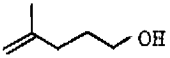
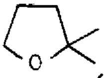
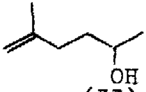
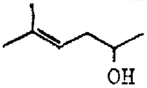
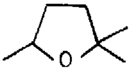
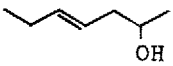
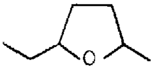
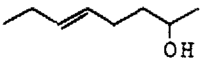
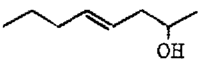
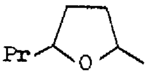


Table I[a,b]. Products (yield %)

Alkyl nitrites[c]	Unsaturated alcohols[d]		Cyclic ethers[d]	Saturated alcohols	Carbonyl compounds
n-Hexyl-	 (27)	 (5)	 (11)	26	15
2-Hexyl-[e]	 (35)	 (4)	 (9)	24	19
iso-Hexyl-	 (36)	 (9)	 (6)	30	15
5-Methyl-2-hexyl-	 (33)	 (13)	 (3)	29	14
2-Heptyl-	 (24)	 (4)	 (18)	35	14
2-Octyl-	 (23)	 (5)	 (10)	36	19

[a] The nearly quantitative return precludes the presence of other unidentified products.

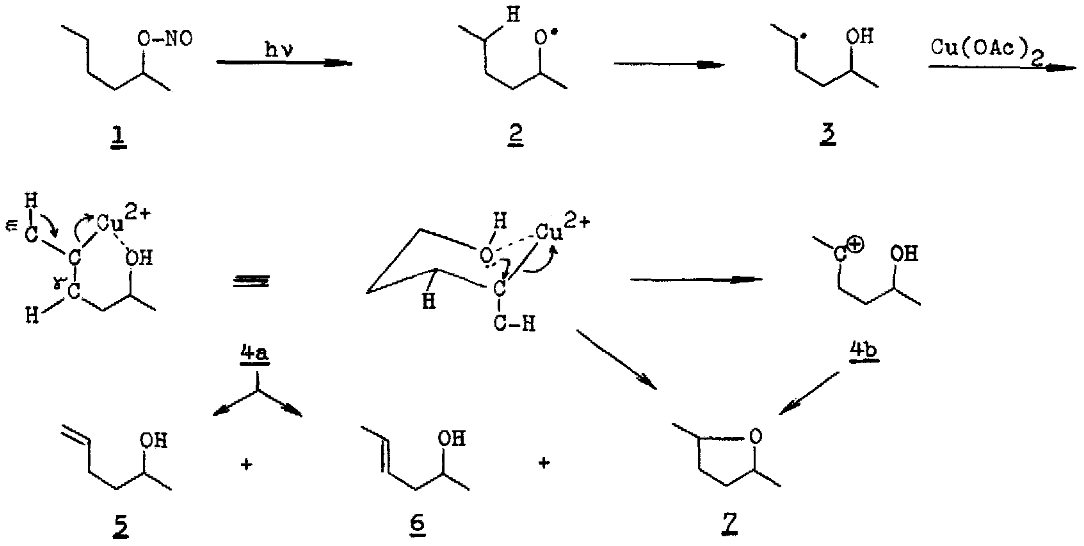
[b] The identification of products was achieved by comparison with available authentic samples and/or by their IR, NMR and mass spectra, which in each case were in agreement with the given structure.

[c] Alkyl nitrites were prepared by the treatment of the corresponding alcohols with saturated aqueous solution of sodium nitrite and 50% sulfuric acid; C. Hunter, J. Chem. Soc., 1936, 285.

[d] The unsaturated alcohols were compared with those obtained in the ferrous sulfate-cupric acetate promoted decomposition of corresponding alkyl hydroperoxides, ref. 4; the cyclic ethers were compared with those obtained in the lead tetraacetate oxidation of the corresponding saturated alcohols, M. Lj. Mihailović, Ž. Čeković. Z. Maksimović, D. Jeremić, Lj. Lorenc and R. I. Mamuzić, Tetrahedron, 21, 2799 (1965).

[e] Photolysis was also performed with cupric chloride and whereby 5-chloro-2-hexanol was obtained in 45% yield.

It is known that the photolysis of nitrite esters (1) affords alkoxy radicals (2) which undergo subsequent 1,5-hydrogen abstraction giving rise to δ-carbon radicals (3)^{1,9}. Similarly to the Barton reaction which proceeds through an "out of cage" free radical mechanism, the oxidative quenching of alkyl radicals by cupric acetate leads to the formation of the corresponding δ- (or γ-) olefinic alcohols (5, 6)^{4,10}, an alkylcopper intermediate 4a being involved in the electron transfer oxidation of alkyl radicals (3)^{6}. The elimination of hydrogen from ε- (or γ-) carbon atom, most probably takes place simultaneously with the heterolytic cleavage of the carbon-copper bond in the alkylcopper intermediate (4a). However, in case when δ-carbonium ion 4b is formed as a competing process, the cyclization occurs affording a cyclic ethers (7) as a ligand transfer product^{12}. In the photolysis of 2-hexyl nitrite in the presence of cupric chloride, 5-chloro-2-hexanol was obtained as a ligand transfer product. In the iso-hexyl systems (iso-hexyl nitrite and 5-methyl-2-hexyl nitrite) the intramolecular abstraction of the available tertiary hydrogen is favourable and a tertiary alkylcopper intermediate is involved, so that the oxidative elimination of hydrogen predominates over cyclization. The preference of δ-double bond formation is probably due to stereochemical requirements of the transition state which render the elimination of ε-hydrogen from alkylcopper intermediate 4a more favourable than that of γ-hydrogen.



The fact that nitrogen containing compounds have not been found among the reaction products, indicats clearly that nitrosyl radicals do not take part in the termination reaction.

In a typical experiment, a mixture of 3 g (0.01 mole) of cupric acetate hydrate, 0.02 mole of alkyl nitrite and 150 ml of benzene was irradiated by a high pressure mercury lamp (Hanovia Q 81) in a pyrex wessel during a period of 5-6 hrs under nitrogen, at running water temperature. The reaction mixture was then poured in water and worked up in the usual way; olefinic and saturated alcohols, cyclic ethers and carbonyl compounds were separated by preparative gas chromatography (XE-60, 2 m).

The synthetic attractivness of preparation of olefinic alcohols having remote double bonds and easy availability of alkyl nitrites suggest that this reaction is useful complementary reaction for the introduction of double bonds at nonactivated remote carbon atoms.

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12. In the alkylcopper intermediate (**4a**), copper ion is most probably coordinated with the hydroxylic oxygen forming a six-membered cyclic transition state. The heterolysis of carbon-copper bond proceeds with the simultaneous attack of oxygen, as a ligand, to form the ether ring.