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# INTRAMOLECULAR CYCLIZATION OF ALKENYL RADICALS GENERATED BY 1,5-HYDROGEN TRANSFER TO ALKOXY RADICALS

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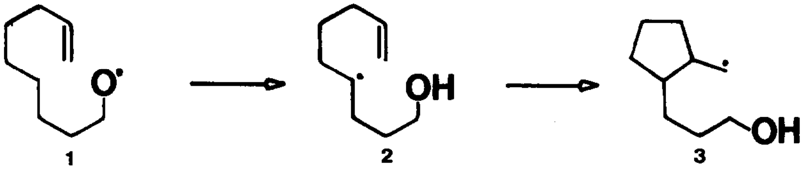
Abstract: Alkoxy radicals generated from the alkenyl nitrites or hypochlorites, possessing an olefinic bond in the position 8 or 9, by intramolecular 1,5-hydrogen transfer undergo the transposition of radical centre to the $\delta$-carbon atom. These alkenyl radicals undergo the 5- or 6-exo-cyclization and 1,2-disubstituted cyclopentane or cyclohexane derivatives are formed, respectively, in addition to the corresponding $\delta$-substituted open chain unsaturated alcohols.

It was found that free carbon radicals generated by intramolecular 1,5-hydrogen abstraction by alkoxy radicals could be intercepted by an electron-transfer or ligand-transfer oxidizing reagents[1-3]. It is also well known that 5-hexenyl type radicas, independently of its precursors, undergo predominantly the 5-exo-cyclization thus closing a cyclopentane ring[4-8].

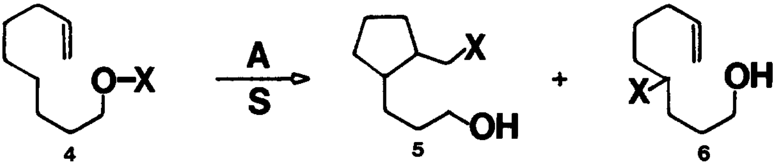
Our present contribution concerns the cyclization of carbon radicals 2, generated by 1,5-transposition of radicals centre from alkoxy radicals 1 onto the $\delta$-carbon atom. Thus intramolecular hydrogen abstraction and intramolecular addition reactions could be achieved in one sequence of reactions, in order to obtain 1,2-disubstituted cyclopentane derivatives, starting from an acyclic compounds (Scheme 1.). Intramolecular addition of carbon radical, generated by hypoiodite reaction, on the acetylenic bond was observed in the systems with fixed reactive centres[9].



Scheme 1.

Investigation of this sequence of free radical reactions was carried out with alkenyloxy radicals generated from the corresponding alkenyl nitrites 4a and alkenyl hypochlorites 4b (Scheme 2.). These substrates were selected because it was supposed that intermediary carbon radicals of type 2 can be quenche by olefinic bond[2,3].

By photolytical decomposition of 8-nonenyl nitrite 4a in benzene solution[10] the cyclic 5a and open chain nitrozo alcohols 6a were obtained as principal reaction products[11]. In addition to these reaction products, 8-nonenol and high boiling point products were also present in the reaction mixture. However in the ferrous ion induced decomposition of 8-nonenyl hypochlorite 4b[12] cyclic 5b and acyclic chlorohydrine 6b were also obtained as the products of this rearrangement-cyclization reaction (Scheme 2.)[11]. When 2.5 x $10^{-2}$ M carbontetrachloride solution of starting 8-nonenyl hypochlorite was used the ratio of cyclic 5b vs acyclic chlorohydrine 6b of 1.5 : 1 was obtained, however by increasing concentration of alkenyl hypochlorites (0.25 M) the ratio of cyclic to acyclic chlorohydrines was decreased.

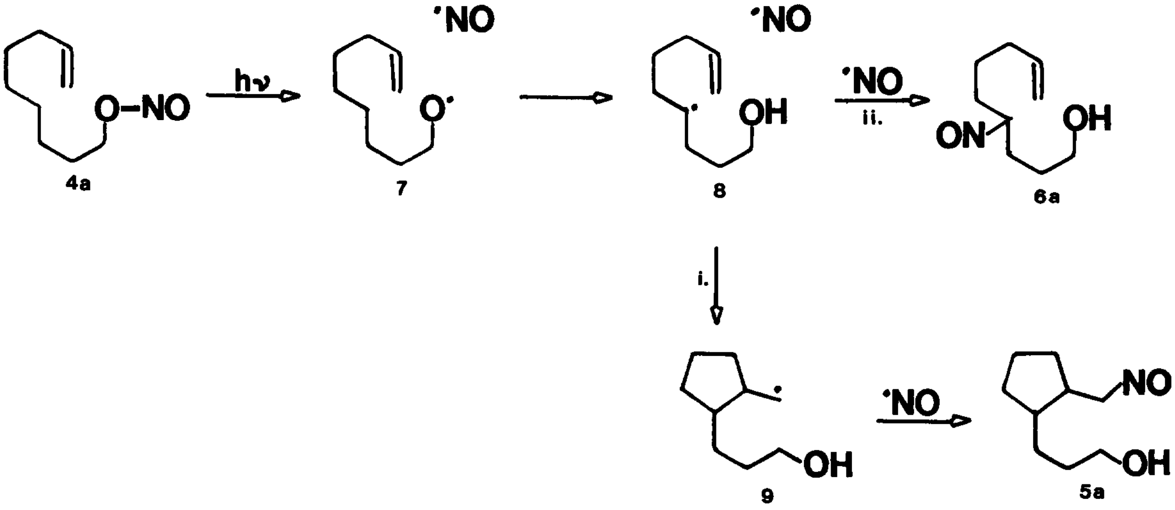


a. X = NO, A = hν, S = $C_6H_6$ 32% 14%

b. X = Cl, A = $Fe^{2+}$, S = $CCl_4$ 25% 19%

Scheme 2.

By photolitically induced homopolar decomposition of 8-nonenyl nitrite 4a, the alkoxy radical 7 was formed (Scheme 3.)[10]. In the subsequent intramolecular 1,5-hydrogen migration the transposition of radical centre from the oxygen to the δ-carbon atom occurs and 5-hexenyl type radical 8 arised[13,14]. This alkenyl radical has enough freedom, and possessing an olefinic bond in the position 5 and hydroxylic group in the position 4 (in respect to the radical carbon atom), it undergoes two competing reactions: i- intramolecular addition reaction giving



Scheme 3.

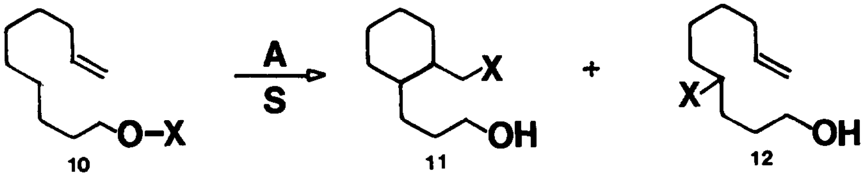
cyclopentylmethyl radical 9 and ii. coupling reaction with nitrozo radical producing acyclic nitrozo alcohol 6a.

The portion of carbon radical 8, possessing appropriately oriented olefinic double bond has necessary conformational distance requiered for the intramolecular addition and 5-exo-cyclization takes place. The cyclopentylmethyl radical 9, generated by this reaction, was quenched by nitrozo radical thus affording 2-(3-hydroxypropyl)-cyclopentylmethyl nitrozo compound 5a as a final reaction product (Scheme 3.). The second portion of alkenyl radical 8 which has not conformattion in which olefinic bond is facing carbon radical in 5-position undergoes directly the coupling with nitrozo radical as is the case in the "normal" Barton's reaction and open chain $\delta$-nitrozo alcohol 6a is formed[10].

Formation of cyclic 5b and open chain chlorohydrine 6b can also be explained by a similar sequence of reactions.

In the oxidation of 8-nonenol by lead tetraacetate the intermediary alkenyl radical of type 8 does not undergo the intramolecular addition and carbocyclic products were not obtained[15]. The carbocyclization does not occur because the alkenyl radical 8, in this case, is in the tight radical pair with lead triacetate species, and it rather undergoes the oxidative tetrahydrofuran ring closure than it could be quenched by olefinic bond[14-16].

Using 9-decenyl nitrite 10a and hypochlorite 10b as a precursors of the decenyloxy radical, 1,5-transposition of radical centre was also followed by cycloaddition reaction and cyclic 11a and acyclic nitrozo alcohol 12a and chlorohydrines 11b and 12b, respectively, were also obtained (Scheme 4.). In this case 6-exo cyclization takes place and cyclohexylmethyl derivatives 11 were formed by similar sequence of reactions as it was shown on Scheme 3.



| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| a. | X | NO, | A | $h\nu$, | S | $C_6H_6$ | 25& | 14% |
| b. | X | Cl, | A | $Fe^{2+}$, | S | $CCl_4$ | 29% | 16% |

Scheme 4.

However, when 8-octenyloxy radical was generated from the corresponding nitrite or hypochlorite, poor yields (up to 4%) of carbocyclic products were obtained. In this case intermolecular stabilization of $\delta$-carbon radical predominates (up to 47%) over 5-endo-cyclization.

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