A Novel Thermal Rearrangement of Allylic Nitro Derivatives into Allylic Alcohols

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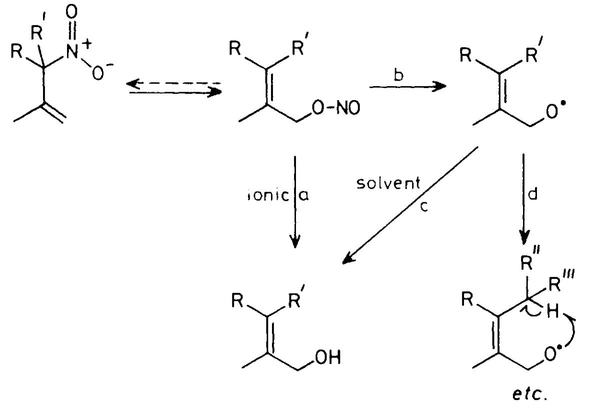
Heating secondary and tertiary allylic nitro compounds gives the corresponding rearranged allylic alcohols in moderate to good yield.

We reported a few years ago that ethylenediamine and some of its congeners were efficient catalysts for the condensation of nitromethane with ketones[1] leading to α,β-unsaturated or allylic nitro-derivatives depending on the starting ketone. The conjugated nitro olefin can be converted into its allylic isomer by quenching the corresponding nitronate salt with a weak acid. With such a ready access to allylic nitro compounds, we considered the possibility of converting them into allylic alcohols *via* a [2,3] sigmatropic rearrangement to the allylic nitrite, as shown in Scheme 1. Apart from the feasibility of the

Table 1. Results of thermal rearrangement of allylic nitro derivatives into allylic alcohols.

Starting material	Solvent	Reaction temp./°C	Reaction time/min	Products (% yield)
(1)	Tetralin	190	15	**(2)** and **(3)** (85) (72 : 13)
(1)	*o*-Dichlorobenzene	180	15	**(2)** (74)
(5)	Tetralin	190	75	**(6)** (33)[a]
(8)	Tetralin	190	10	**(9)** (67)
(10)	Tetralin and acetamide (5 equiv.)	200	30	**(11)** (53)
(12)	Mesitylene	165	120	**(13a)** and **(13b)** (37) (4 : 1)
(14)	Tetralin	190	15	**(15)** (42)

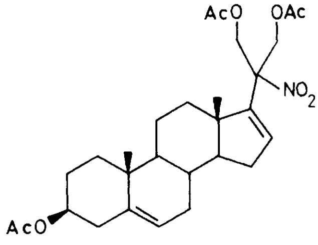
[a] Yield 43% based on recovered starting material.



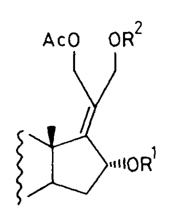
Scheme 1

rearrangement, the success of this conjecture will greatly depend on the subsequent behaviour of the nitrite at the temperature necessary for the first step. Kinetic work[2] on the pyrolysis of simple alkyl nitrites (mostly in the gas phase) pointed to an initial fragmentation to the highly reactive alkoxyl radicals. In some cases, the formation, *inter alia*, of the corresponding alcohols has been observed, especially in the presence of an added hydrogen atom donor. However, unlike the very useful photolytic variant (the Barton reaction[3]), thermolysis of alkyl nitrites has not attracted much attention as a synthetic tool. Allylic nitrites in particular seem to have been almost completely neglected. In a photochemical study of a steroid example, Nussbaum and co-workers[4] also noted its extreme lability towards acid promoted hydrolysis. In our case, we were worried by the possibility that the putative alkoxyl radical intermediate would prefer to abstract an internal allylic hydrogen available to it through a six-membered transition state (path d) as in the Barton reaction.

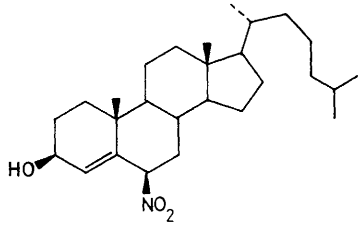
Heating compound **(1)**[1b] in tetralin at 200 °C for 15 minutes indeed gave the corresponding allylic alcohol **(2)** in good yield (75%). A small amount (10%) of the *trans*-esterified alcohol **(3)** was also produced bringing the total yield of rearranged product to 85%. Acetylation of the mixture gave a single tetra-acetate **(4)**. Under similar conditions, 3β-hydroxy-6β-cholest-4-ene **(5)**[5] rearranged more slowly and less efficiently (33%) to give diol **(6)** with hardly any of its 4a-isomer **(7)** as shown by chromatographic comparison with authentic material.[6] The high stereoselectivity in these two examples, and especially the latter, strongly point to a suprafacial [2,3] sigmatropic transposition in the first step.



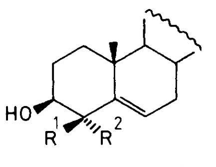
(1)



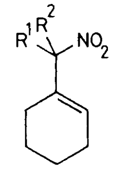
(2) $R^1 = H$, $R^2 = Ac$
(3) $R^1 = Ac$, $R^2 = H$
(4) $R^1 = R^2 = Ac$



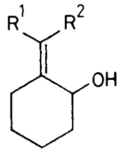
(5)



(6) $R^1 = OH$, $R^2 = H$
(7) $R^1 = H$, $R^2 = OH$



(8) $R^1 = R^2 = CH_2CH_2CO_2Me$
(10) $R^1R^2 = CH_2OC(Me)_2OCH_2$
(12) $R^1 = Me$, $R^2 = H$
(14) $R^1 = CH_2CH_2CO_2Me$, $R^2 = H$



(9) $R^1 = R^2 = CH_2CH_2CO_2Me$
(11) $R^1R^2 = CH_2OC(Me)_2OCH_2$
(13) a; $R^1 = Me$, $R^2 = H$
b; $R^1 = H$, $R^2 = Me$
(15) $R^1 = CH_2CH_2CO_2Me$, $R^2 = H$

This transformation was successfully extended to a number of other allylic nitro derivatives as shown by the examples in Table 1. Yields are variable and depend on the structure of the starting material. In examples with **(12)** or **(14)** as the starting material, the major product appears to be the *anti*-isomer as indicated by n.m.r. spectroscopy.

With regard to the fate of the intermediate allylic nitrite, we assumed at first that tetralin, with its four benzylic hydrogens, was acting as the final hydrogen atom donor to quench the intermediate alkoxyl radical. However, chromatographic analysis of the crude reaction mixture indicated the presence of only traces, if any, of α-tetralone oxime, the logical end product of such a radical process. Furthermore, performing the rearrangement of (**1**) in *o*-dichlorobenzene, which does not relinquish its hydrogens easily, nevertheless afforded the same allylic alcohol in a comparable yield (74%). These observations and the apparent absence of the unwanted allylic hydrogen abstraction (path d) may be construed as evidence against the predominance of the radical process (path b) and in support of an ionic mode of decomposition (path a) as the major reaction pathway. However addition of excess of acetamide, as scavenger for nitrosonium ions, prior to thermolysis did not increase the yield in allylic alcohol. Acetamide reacts with nitrosating agents to give nitrogen and acetic acid.[7] Other additives such as *O*-ethyl carbamate or dodecylamine tended to complicate the purification of the products without any added benefit.

Preliminary experiments with a primary allylic nitro derivative have so far not been very promising. Despite these limitations, this novel rearrangement, which is akin to that of allylic amine oxides, sulphoxides, and selenoxides, provides a convenient entry into a variety of functionalised allylic alcohols and reveals another facet of the exceptionally rich chemistry of the nitro group. The scope and various mechanistic aspects of this process are currently under study.

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References

1 (a) D. H. R. Barton, W. M. B. Motherwell, and S. Z. Zard, *J. Chem. Soc., Chem. Commun.*, 1982, 551; (b) *Bull. Soc. Chim. Fr.* (II), 1983, 61. For a recent application of this procedure, see: R. Tamura, M. Sato, and D. Oda, *J. Org. Chem.*, 1986, **53**, 4368.

2 For a recent review, see: L. Batt, in 'The Chemistry of Amino, Nitro, and Nitroso Compounds and their Derivatives,' ed. S. Patai, Wiley Interscience, 1982, suppl. F, vol. 1, p. 417.

3 A. L. Nussbaum, E. P. Yuan, C. H. Robinson, A. Mitchell, E. P. Oliveto, J. M. Beaton, and D. H. R. Barton, *J. Org. Chem.*, 1962, **27**, 20; R. H. Hess, *Adv. Free Radical Chem.*, 1969, **3**, 83; Y. L. Chow, in 'The Chemistry of Amino, Nitro, and Nitroso Compounds and their Derivatives,' ed. S. Patai, Wiley Interscience, 1982, suppl. F, Vol. 1, p. 181.

4 A. L. Nussbaum, R. Wayne, E. Yuan, O. Zagneetko Sarre, and E. P. Oliveto, *J. Am. Chem. Soc.*, 1965, **87**, 2451.

5 A. Shafiullah, *J. Ind. Chem. Soc.*, 1987, **64**, 707.

6 A. Viger, A. Marquet, D. H. R. Barton, W. B. Motherwell, and S. Z. Zard, *J. Chem. Soc., Perkin Trans. 1*, 1982, 1937.

7 G. A. Olah and J. A. Olah, *J. Org. Chem.*, 1965, **30**, 2386.