The first [2,3]-sigmatropic rearrangement of allylic nitro compounds

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Allylic nitro compounds 1a–d undergo [2,3]-sigmatropic rearrangement in refluxing 1,2,4-trichlorobenzene, to afford rearranged alcohols 3a–d and carbonyl compounds 4a–d; the heating, under the same conditions, of a mixture of nitroalkenes 7a–c, propargyl alcohols or amine 8 and $\mathrm{Bu^tOK}$ promotes a one-pot formation of allylic alcohols 3a–c.

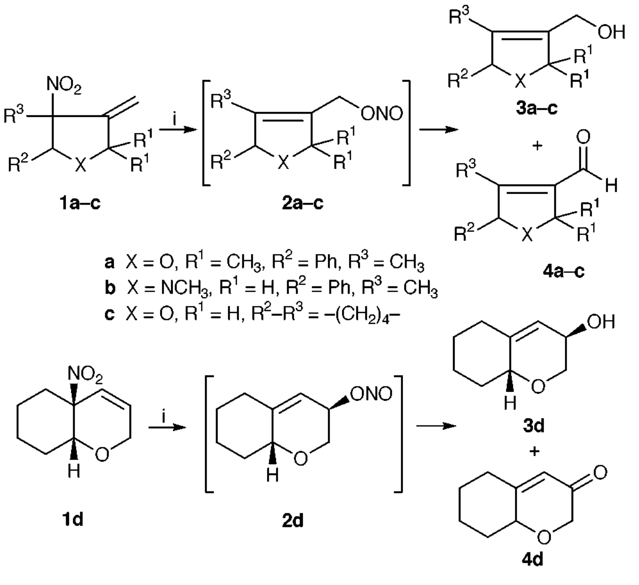
The influence of zwitterionic moities such as sulfoxides or amine oxides at the 3-position of hexa-1,5-dienes has been investigated and some interesting results showed that acceleration of either [3,3]- or [2,3]- sigmatropic rearrangement could be observed.[1a] Unlike for these substituents, it has been shown that allylic nitro compounds do not participate in [2,3]-sigmatropic rearrangements under thermolysis at 110 °C in toluene.[1b]

We have recently described the facile preparation of allylic nitro compounds **1a–d** by $\mathrm{Bu^tOK}$-promoted oxa- and aza-Michael addition–intramolecular carbocyclization of prop-2-ynyl alcohols or amines with α,β-disubstituted nitroalkenes.[2]

Here we report on our initial investigations of the first thermal conversion of these valuable substrates into allylic alcohols and the corresponding α,β-unsaturated carbonyl derivatives.

Heating a solution of nitro olefines **1a–d** in trichlorobenzene at 214 °C induces a rapid [2,3]-rearrangement providing nitrite intermediates which undergo homolytic fission of the O–NO bond. Subsequent disproportionation of the resulting alkoxyl radical thus derived gives rise to alcohols **3** (12–15%) and carbonyl compounds **4**[3] (13–18%) according to a well-known process[4] (Scheme 1).

The transient formation of alkyl nitrites was established by the isolation of **2a**† (10%) along with **3a** (13%) and **4a** (7%). A selective suprafacial [2,3]-sigmatropic rearrangement leading to **2d** accounts for the stereochemistry of **3d**.‡ Indeed, the homolytic fission does not alter the configuration of the functional carbon center.



Scheme 1 *Reagents and conditions*: i, 1,2,4-trichlorobenzene, 214 °C, 20–45 min (25–30%).

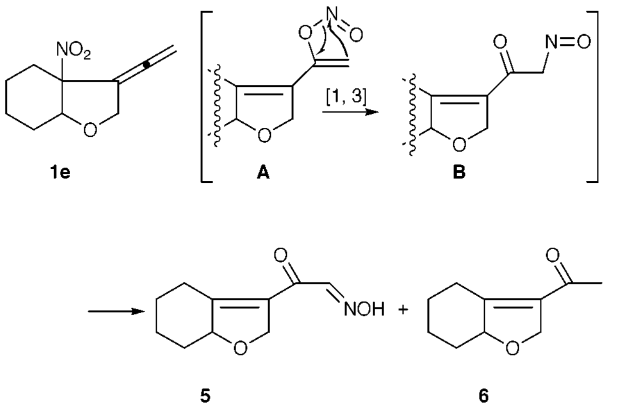
Because of their higher degree of unsaturation, we also decided to study under the same reaction conditions the behaviour of easily accessible allenyl nitro compound **1e**.[5] Interestingly, **1e** under thermolysis at 214 °C undergoes [2,3]-sigmatropic rearrangement and cleanly affords keto oxime **5**§ (23%), along with trace amounts of acetyl dihydrofuran **6** (Scheme 2).

Extensive studies[6] of either thermally or photochemically induced transformations of alkyl nitrites resulted in the observation that only photochemically generated ‘activated’ alkoxyl radical intermediates could lead to oximes by hydrogen-atom transfer reactions. Indeed, although thermally induced transformations afford carbonyl derivatives according to either disproportionation or acid catalysis, vapour-phase pyrolysis of nitrites with apropriate structures follows identical pathways and leads to identical products than photolysis.

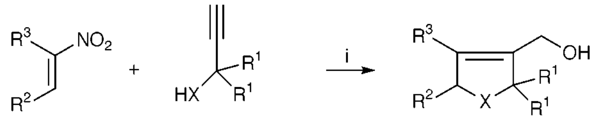
Thus, formation of oxime **5**, which formally results from incorporation of nitric oxide after homolytic scission, could be explained by a [1,3]-sigmatropic rearrangement of the vinyl nitrite unit in **A**. Although isolated in small amounts, the formation of acetyl dihydrofuran **6** could support the occurrence of an early homolytic fission stage.

In order to increase the efficiency of the overall process, we adapted our procedure previously developed for the preparation of allylic nitro compounds[2] through a domino reaction initiated by Michael addition of propargylic alcohols or amine **8** to nitroalkenes. We therefore discovered that exchanging THF for refluxing trichlorobenzene resulted in a one-pot formation of rearranged alcohols (8–13%), directly from nitroalkenes **7a–c** and propargylic alcohols or amine **8**. Interestingly, the formation of the corresponding aldehydes could not be detected under the reaction conditions, probably due to the rapid consumption of the nitrite intermediate in the presence of a strong base such as $\mathrm{Bu^tOK}$¶ (Scheme 3).

Similarly, the one-pot conversion of nitroalkene **7c** in the presence of chlorobutynol **9** and $\mathrm{Bu^tOK}$ afforded keto oxime **5** in 10% yield (Scheme 4).

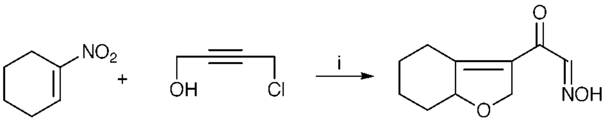


Scheme 2 *Reagents and conditions*: i, 1,2,4-trichlorobenzene, 214 °C, 5 min (**5**: 23%, **6**: trace).



7a–c **8** **3a–c**

Scheme 3 *Reagents and conditions*: i, **8** (X = NMe, O) (1.5 equiv.), 1,2,4-trichlorobenzene, Bu^{t}OK (1.2 equiv.), room temp., 5 min, then 214 °C, 45 min (8–13%).



7c **9** **5**

Scheme 4 *Reagents and conditions*: i, **9** (1.5 equiv.), 1,2,4-trichlorobenzene, Bu^{t}OK (1.2 equiv.), room temp., 5 min, then 214 °C, 2 min (10%).

In conclusion, the Bu^{t}OK/thermally induced one-pot reaction of nitroalkenes with alkynyl alcohols constitutes a new four-step domino reaction which involves [2,3]-sigmatropic rearrangement of allyl and allenyl nitro compounds and provides a new route to elaborated 2,5-dihydro-furans or -pyrroles.

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Notes and references

† *Selected data* for **2a**: δ_H(400 MHz, CDCl$_3$) 1.19 (s, 3H), 1.47 (s, 3H), 1.61 (s, br, 3H), 4.97 (d, *J* 13.6, 1H), 5.02 (d, *J* 13.6, 1H), 5.59 (s, 1H), 7.26–7.39 (m, 5H); δ_C(100 MHz, CDCl$_3$) 10.8, 27.0, 27.8, 70.5, 88.1, 89.0, 127.5, 128.7, 129.9, 129.4, 139.2, 140.0.

‡ *Selected data* for **3d**: δ_H(400 MHz, CDCl$_3$) 1.35 (m, 2H), 1.75 (m, 3H), 1.95 (m, 2H), 2.23 (ddt, *J* 13.9, 4.4, 2.2, 1H), 3.34 (dd, *J* 11, 6.9, 1H), 3.91 (br t, *J* 5.1, 1H), 3.95 (dd, *J* 11, 4.7, 1H), 4.18 (br s, 1H), 5.53 (br d, *J* 1.8, 1H); δ_H(400 MHz, C$_6$D$_6$) 1.23–1.05 (m, 2H), 1.54–1.31 (m, 3H), 1.72 (m, 1H), 2.02 (m, 2H), 3.27 (dd, *J* 10.6, 7.7, 1H), 3.75 (m, 1H), 3.92 (dd, *J* 10.6, 5.1, 1H), 4.10 (m, 1H), 5.41 (br d, *J* 1.6, 1H); δ_C(100 MHz, CDCl$_3$) 24.5, 27.3, 33.2, 33.5, 63.6, 68.3, 75.2, 120.4, 143.3; stereochemistry has been assigned by NOESY correlation (in C$_6$D$_6$).

§ *Selected data* for **5**: *m/z* (12 eV) 195.1 (1.5%), 179.1 (11.4), 178.1 (100), 150.1 (52.1), 123.1 (14.9); ν/cm^{-1} 3691, 3559, 3156, 2983, 1817, 1795, 1711, 1650, 1610, 1470, 1382, 1097; δ_H(400 MHz, CDCl$_3$) 1.18–1.46 (m, 5H), 1.99 (m, 1H), 2.25 (m, 1H), 3.57 (dm, *J* 14.5, 1H), 4.65 (m, 1H), 5.07 (dt, *J* 12, 3.5, 1H), 5.17 (ddd, *J* 12.0, 5.3, 1.8, 1H), 7.62 (s, 1H), 9.79 (br s, 1H); δ_C(100 MHz, CDCl$_3$) 23.1, 26.4, 26.9, 35.4, 75.9, 86.4, 126.4, 150.8, 157.9, 185.8.

¶ Alkyl nitrites have been shown to undergo nitrosyl transfer to alcohols (ref. 7) or amines (ref. 8) either in acidic or basic conditions (ref. 9).

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