A New Method for Nitration of Alkenes to α,β-Unsaturated Nitroalkenes

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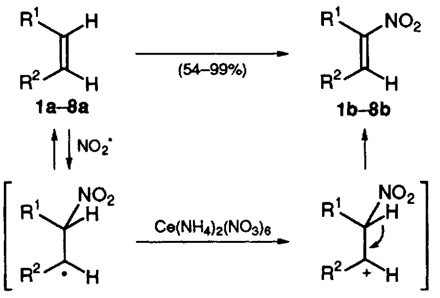
α,β-Unsaturated nitroalkenes were synthesized in 54–99% yields by sonication of a chloroform solution containing the corresponding alkenes, $NaNO_2$ (10 equiv.), $Ce(NH_4)_2(NO_3)_6$ (2.0 equiv.), and acetic acid (12 equiv.) in a sealed tube at 25–73 °C.

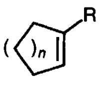
α,β-Unsaturated nitroalkenes are frequently used as versatile intermediates in organic synthesis.[1,2] Various approaches can lead to this class of compounds;[1,3] however, much demand still exists for their preparation in high yields under mild conditions. Herein we report a new and regioselective method for the synthesis of α,β-unsaturated nitroalkenes from the corresponding alkenes.

We treated an alkene (0.49 mmol, 1.0 equiv.) with sodium nitrite (10 equiv.), cerium(IV) ammonium nitrate (CAN, 2.0 equiv.), and acetic acid (12 equiv.) in chloroform (7.0 ml) in a sealed tube. After sonication (600 W) at 25–73 °C for 4 h, the corresponding α,β-unsaturated nitroalkenes were obtained upon aqueous workup and purification with silica gel chromatography (Scheme 1).

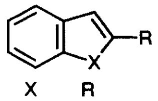
By this new method, we obtained cyclic nitroalkenes **1b**[4] (86%) and **2b**[5] (99%) in high yields. The same reaction conditions also allowed the conversion of acyclic, terminal alkenes attached with an alkyl or an aryl group (*e.g.*, **3a** and **4a**) to 1-nitro-2-organylalkenes (*i.e.*, **3b**[6] and **4b**[5]). Furthermore, we extended this method successfully to the synthesis of new compounds 1-nitro-3-silyl-1-propenes **5b** (81%) and **6b** (86%). The ^{13}C NMR spectrum of **5b** exhibited five sets of peaks at δ 11.10 (d, SiCH), 14.17 (t, $SiCH_2$), 18.46 (q, CH_3), 137.29 (d, CH=) and 143.98 (d, $=CHNO_2$).[7] Its high-resolution mass spectrum showed the molecular ion peak at 243.1658 (*cf.* the exact mass calculated for $C_{12}H_{25}NO_2Si$: 243.1654). These results clearly indicate the existence of the nitro and the silyl groups in the desired products. In addition, we obtained 2-nitroindene **7b**[8] (54%) and 2-nitrobenzofuran **8b**[9] (62%) from the corresponding fused bicyclic compounds **7a** and **8a**, respectively.



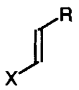
Scheme 1 Sonochemical nitration of alkenes to give the corresponding α,β-unsaturated nitroalkenes in a sealed tube by use of the following conditions: $NaNO_2$ (10 equiv.), $Ce(NH_4)_2(NO_3)_6$ (2.0 equiv.), AcOH, chloroform; 25–73 °C; 4 h



	n	R
1a	1	H
1b	1	NO_2 (86%)
2a	2	H
2b	2	NO_2 (99%)



	X	R
7a	CH_2	H
7b	CH_2	NO_2 (54%)
8a	O	H
8b	O	NO_2 (62%)



	X	R
3a	$C_6H_{13}^n$	H
3b	$C_6H_{13}^n$	NO_2 (99%)
4a	Ph	H
4b	Ph	NO_2 (82%)
5a	$CH_2SiPr^i_3$	H
5b	$CH_2SiPr^i_3$	NO_2 (81%)
6a	$CH_2SiBu^t_3$	H
6b	$CH_2SiBu^t_3$	NO_2 (86%)

The $NO_2\cdot$ radicals can be generated by reaction of nitrite ions with protons.[10,11] Accordingly we used an excess of sodium nitrite and acetic acid in a sealed tube for increasing the concentration of the $NO_2\cdot$ radicals in chloroform. After these radicals reacted with alkene substrates, CAN can oxidize the resultant carboradical intermediates[12] *in situ* to give the corresponding carbocationic species (Scheme 1). The possibility was thus decreased for the unfavourable reversion of carboradical intermediates to alkenes and $NO_2\cdot$ radicals. Finally, elimination of the α proton to the nitro group in the carbocationic species led to the desired α,β-unsaturated nitroalkenes. In the absence of CAN, we were able to convert **5a** to **5b** in 45% yield only (*cf.* 81% by the standard procedure). The application of ultrasound to the heterogeneous solutions significantly increased the reaction rates[13] and thus offered a chance to produce the desired, labile products in good yields.

Before this method was developed, we had failed to obtain 1-nitro-3-silyl-1-propenes, a new class of compounds, by use of numerous established procedures.[1,3] The conjugated nitroalkenyl and the allylsilane moieties therein seemed labile towards the reaction conditions employed. The success in the preparation of **5b** and **6b** in high yields by this newly developed method indicates its mild nature.

For certain non-symmetric alkenes, nitration by the mixture of sodium nitrite, acetic acid and CAN took place with high regioselectivity. For example, the nitro group was introduced to the mono-substituted alkyl or aryl alkenes **3a**–**6a** at the terminal vinylic carbons exclusively. The products possessed a coupling constant of 12.8–14.0 Hz resulting from the vicinal vinylic protons with a *trans* relationship.[14] The chemical shift of the two vinylic protons in **3b**, **5b** and **6b** which were in the ranges δ 6.90–6.96 and δ 7.26–7.48 provided extra evidence to support our identification of their structures.[15] Furthermore, we obtained 2-nitroindene **7b** from **7a** and 2-nitrobenzofuran **8b** from **8a** as the only regioisomers, as indicated by characteristic peaks for the vinylic proton at δ 7.95 for **7b**[8] and at δ 7.66 for **8b**.[9]

This newly developed sonochemical method for the synthesis of α,β-unsaturated nitroalkenes by use of sodium nitrite, CAN and acetic acid possesses the following advantages: mild reaction conditions, high regioselectivity, good to excellent yields and a short period of reaction time.

For financial support, we thank the National Science Council of Republic of China (Grants NSC 83-0208-M007-101).

Received, 14th March 1994; Com. 4/01509F

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