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Microwave–assisted transformation of α,β- and β,γ-unsaturated nitroalkenes into carbonyl compounds

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Vinyl and allylic nitroalkenes have been converted into the corresponding carbonyl compounds in good yield using tin(II) chloride dihydrate under microwave irradiation.

Keyword: irradiation, microwave oven, α,β-unsaturated nitroalkenes, β,γ-unsaturated nitroalkenes, tin(II) chloride dihydrate

Conversion of a nitro functionality into another functional group, most notably the carbonyl group, is an important transformation in organic synthesis. Due to their high electrophilicity, nitroalkenes are valuable precursors to a large number of target molecules as well as important intermediates in organic synthesis.[1] The conversion of conjugated nitroalkenes into carbonyl compounds is an important transformation and literature reveals the use of various reagents. The methods[2] are shown to be unsatisfactory involving stringent conditions and long reaction times. Moreover, only a very few reagents are reported[3] for the conversion of β,γ-unsaturated nitro compounds into α,β-unsaturated ketones and these involve long reaction times.

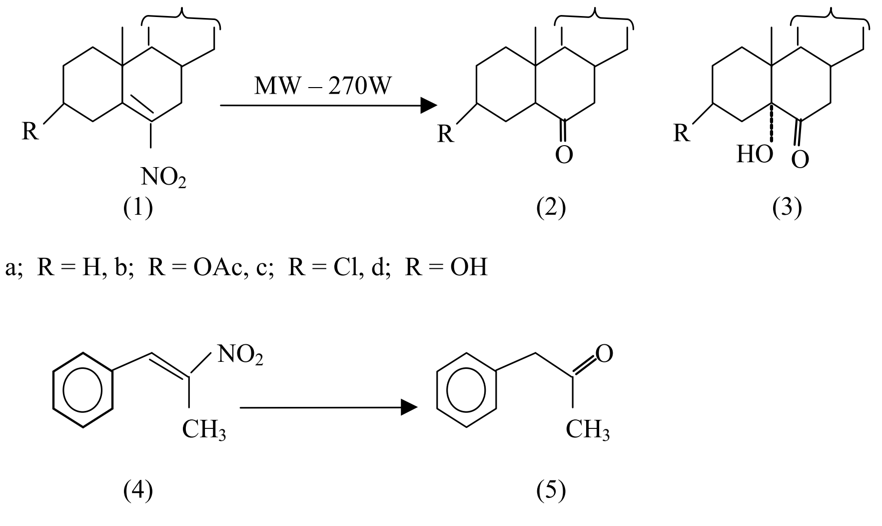
Microwave irradiation in chemical reactions is receiving increasing interest[4] due to its novelty, simplicity, reproducibility and eco-friendliness. Moreover, microwave-assisted reactions are completed in minutes compared to hours and days with conventional methods. Here we report the data from our observation that tin(II) chloride dihydrate can facilitate the transformation of α,β- and β,γ-unsaturated nitroalkenes into the corresponding carbonyl compounds under microwave irradiation. The present transformation has been reported[3c] earlier using stannous chloride dihydrate at longer reaction times. The microwave-assisted conversion requires comparatively much less time which has prompted us to put our results on record.

Microwave-assisted irradiation has induced the conversion of 6-nitro-Δ^5-steroids (**1a–d**) into the mixture of two major products, the 5α-cholestan-6-one[5] (**2a–d**) and the 5α-hydroxy cholest-6-one[6] (**3a–d**) in presence of $SnCl_2.2H_2O$. Similarly β-methyl-β-nitrostyrene (**4**) gave phenyl acetone[7] (**5**) as a major product (Scheme 1). The reaction with β,γ-unsaturated nitro steroids (**6b–c**) furnished the corresponding α,β-unsaturated ketones (**7b–c**). However, in the case of the compound (**6a**), α,β-unsaturated aldehyde (**7a**) is obtained along with small quantity of α,β-unsaturated alcohol (**8**) which has been confirmed by the sodium borohydride reduction of (**7a**) to (**8**). Similarly β,γ-unsaturated nitroalkenes (**9a,b**) gave α,β-unsaturated ketones (**10a,b**) as the major products (Scheme 2). In the formation of carbonyl compounds, the water of crystallisation in stannous chloride dihydrate probably plays a vital role by conjugate addition of water to the nitroalkenes followed by hydrolysis of the intermediate stannylnitronate[8] salt. It is apparent that this reagent is mild and not sensitive to other functionalities like double bonds and acetate groups under microwave irradiation. This unconventional microwave reaction has better selectivity than the conventional method and due to its novelty is an attractive avenue for the rapid generation of structural diversity.

This simple and mild procedure for converting α,β- and β,γ-nitroalkenes to the corresponding carbonyl compounds under the microwave irradiation is a useful addition to existing methods.

Experimental

The products were characterised by m.p., b.p., spectroscopic data and by direct comparison with authentic samples. IR spectra were recorded on a JASCO FT/IR – 5300 instrument and ^{1}H NMR spectra were recorded in deuteriochloroform on a JEAL FX – 90 instrument. The reactions were carried out in a domestic microwave oven (Kelvinator – T 37).



a; R = H, b; R = OAc, c; R = Cl, d; R = OH

Scheme 1

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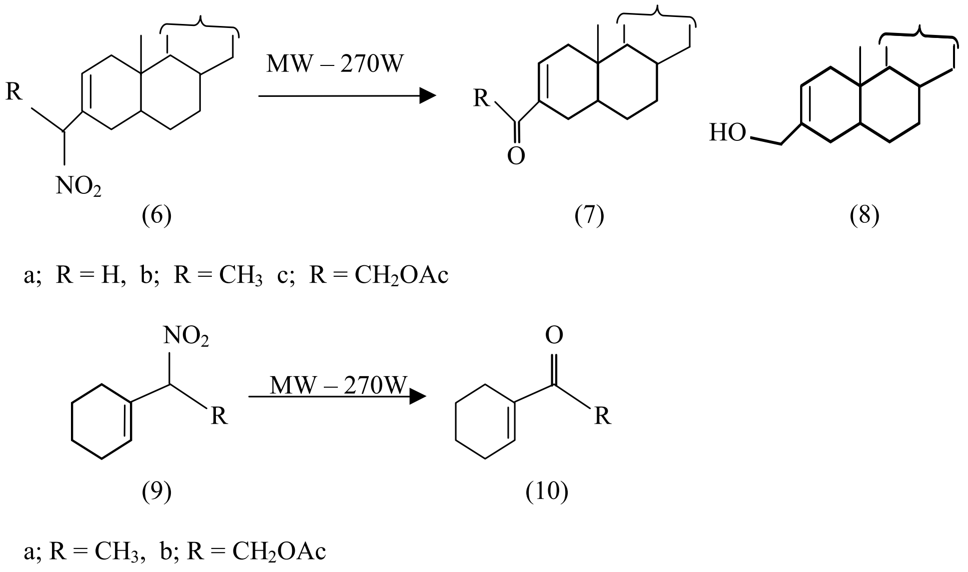

Scheme 2

General procedure

CAUTION: Due precautions should be taken when using volatile solvents in a microwave oven.

In a typical procedure, the nitroalkene (1 mmol), tin(II) chloride dihydrate (10 mmol), soaked with few drops of tetrahydrofuran (0.5 ml) were taken in a 50 ml. Erlenmeyer flask. The mixture was then irradiated at 270 W for 15 minutes inside the microwave oven. The reaction was carried out inside the fume cupboard for safety reasons. The reaction mixture was cooled and diluted with 50 ml water and then extracted with dichloromethane (100 ml). The organic layer was washed with water, dried and evaporated under reduced pressure to obtain the crude products that were purified by silica gel preparative TLC using an ethyl acetate and petroleum ether mixture as eluting solvent. The yield of the purified products are incorporated in the Table 1.

7a: IR(KBr) 1668, 1585 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.75 (s, 3H), 0.86 (s, 3H), 0.92 (d, J = 6.6 Hz, 6H), 1.2 (d, J = 6.6 Hz, 3H), 3.12 (d, J = 6 Hz, 2H), 3.52 (d, J = 5.8 Hz, 2H), 5.98 (t, J = 5.8 Hz, 1H), 9.62 (s, 1H, CHO). Anal. Calcd for $C_{28}H_{46}O$: C, 84.4; H, 11.55. Found: C, 84.2; H, 11.5. MS: 398 (M^{+}).

7b: IR(KBr) 1670, 1585 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.77 (s, 3H), 0.87 (s, 3H), 0.93 (d, J = 6.4 Hz, 6H), 1.5 (d, J = 6.5 Hz, 3H), 2.26 (s, 3H), 3.16 (d, J = 6.1 Hz, 2H), 3.58 (d, J = 5.9 Hz, 2H), 5.98 (t, J = 5.9 Hz, 1H). Anal. Calcd for $C_{29}H_{48}O$: C, 84.5; H, 11.65. Found: C, 84.4; H, 11.6. MS: 412 (M^{+}).

7c: IR(KBr) 1755, 1675, 1585, 1215 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.76 (s, 3H), 0.86 (s, 3H), 0.95 (d, J = 6.7 Hz, 6H), 1.4 (d, J = 6.5 Hz, 3H), 2.32 (s, 3H), 3.22 (d, J = 6 Hz, 2H), 3.61 (d, J = 5.7 Hz, 2H), 4.90 (s, 2H), 5.96 (t, J = 5.7 Hz, 1H). Anal. Calcd for $C_{31}H_{50}O_3$: C, 79.15; H, 10.6. Found: C, 79.0; H, 10.6. MS: 470 (M^{+}).

Table 1 Conversion of vinyl and allylic nitroalkenes into carbonyl compounds using tin(II) chloride dihydrate

Reactant	Product[a]/Yield[b]%
1a	**2a** (70), **3a** (25)
1b	**2b** (78), **3b** (15)
1c	**2c** (68), **3c** (18)
1d	**2d** (80), **3d** (15)
4	**5** (78)
6a	**7a** (75), **8a** (20)
6b	**7b** (65)
6c	**7c** (82)
9a	**10a** (65)
9b	**10b** (70)

[a] All products were characterised by IR, NMR spectral analysis and direct comparison with authentic samples.

[b] Reactions were monitored by TLC and the reaction time was common (15 min) for all the substrates.

8: IR(KBr) 3400, 1580 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.64 (s, 3H), 0.81 (s, 3H), 0.86 (d, J = 6.5 Hz, 6H), 0.94 (d, J = 6.5 Hz, 3H), 2.90 (d, J = 8 Hz, 2H), 3.58 (d, J = 7 Hz, 2H), 3.16 (br. s, -OH), 4.12 (m, 2H), 5.94 (t, J = 7 Hz, 1H). Anal. Calcd for $C_{28}H_{48}O$: C, 83.9; H, 12.1. Found: C, 84.0; H, 12.0. MS: 400 (M^{+}).

10a: IR(KBr) 1684, 1565 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.45–1.86 (br. m, 4H), 2.30 (s, 3H), 2.34–2.60 (br. m, 4H) 6.28 (t, J = 7.8 Hz, 1H). Anal. Calcd for $C_8H_{12}O$: C, 77.4; H, 9.7. Found: C, 77.4; H, 9.65. MS: 124 (M^{+}).

10b: IR(KBr) 1752, 1680, 1565, 1210 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.52–1.88 (br. m, 4H), 2.28 (s, 3H), 2.44–2.82 (br. m, 4H), 4.94 (s, 2H), 6.42 (t, J = 7.7 Hz, 1H). Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.9; H, 7.7. Found: C, 65.9; H, 7.6. MS: 182 (M^{+}).

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