Journal de la Société Chimique de Tunisie, **2009**, *11*, 37-43

MICHAEL ADDITIONS OF NITROALKANES TO CONJUGATED KETONES, CARBOXYLIC ESTERS AND NITRILES IN WATER AND BIPHASIC CONDITIONS (WATER-DICHLOROMETHANE)

Younes Moussaoui, Ridha Ben Salem *

Physical Organic Chemistry Laboratory, Science Faculty of Sfax, 3018 Sfax, Tunisia

(Reçu le 5 Mars 2009, accepté le 11 Avril 2009)

ABSTRACT: The Michael reaction involving nitroalkanes cannot occur without base and solvent. The low yields obtained in water are due to the limited solubility of nitroalkanes. To circumvent the drawback the reaction is studied in a biphasic medium (water-dichloromethane). The yields are considerably increased by addition of a phase transfer catalyst such as tetrabutylammonium chloride or bromide. The bromide being less efficient than the chloride.

Key words: Michael reactions, heterogeneous catalysis, nitroalkanes, tetrabutylammonium salt.

INTRODUCTION

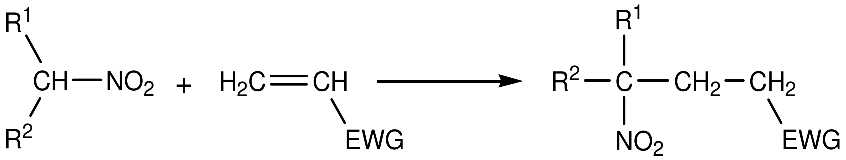
Michael reactions are fundamental reactions in organic synthesis [1-8]. The Michael addition of carbanions to the C-C double bond of α,β-unsaturated ketones, nitriles, amides and esters is a method of choice for the formation of C-C bonds [1,8,9]. It is a well known fact that 1,4-addition of nitroalkanes affords α,β-unsaturated carbonyl compounds [4,12-16] which lead to aminoalkanes after appropriate reduction [17,18] and other functionality that can be derived from the nitro group [7,8,19-22].

The Michael reaction of nitroalkanes does not occur in the absence of catalyst or solvent [23]. It has been shown, however, that it can take place in water depending on their solubility and acidity, although the reactivity is relatively limited [12,23-25]. To this respect, heterogeneous catalysis emerges as an excellent method to enhance the reactivity [3,26-31]. Numerous reactions have been studied in heterogeneous catalytic conditions improving noticeably selectivity. This has been the case for reactions involving nitroalkanes and α,β-unsaturated carbonyl compounds [13-16,32,33]. Ballini and Bosica [12] investigated such reactions in aqueous media and in the presence of sodium hydroxide and a catalytic amount of a phase transfer agent such as cetyltrimethyl ammonium chloride. In this context, Ballini and al. [34] have reported that Michael addition of nitroalkanes to several electrophilic alkenes work well with short reactions times, mild reaction conditions using a catalytic amount of cetyltrimethylammonium hydroxide (CTAOH), at room temperature in the presence of a minimum of water.

This paper describes a comparative study of several Michael additions of nitroalkanes to alkenes activated by electroattracting groups in the presence of various basic systems. We also examined the activation by phase transfer catalysts in water and water-dichloromethane mixtures.

RESULTS AND DISCUSSION

The Michael addition between nitroalkanes and alkenes activated by electroattracting groups proceeds as follows:



$$R^1R^2CH{-}NO_2 + H_2C{=}CH{-}EWG \longrightarrow R^2{-}C(R^1)(NO_2){-}CH_2{-}CH_2{-}EWG$$

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[*] corresponding author, e-mail: ridha.bensalem@voila.fr ; tel: (216) 74 276 400 ; fax: (216) 74 274 437

The reactions between nitromethane or nitroethane and methylvinylketone could not proceed without a base in methanol, ethanol, chloroform or water.
The table I. presents the results obtained in the presence of various basic systems.

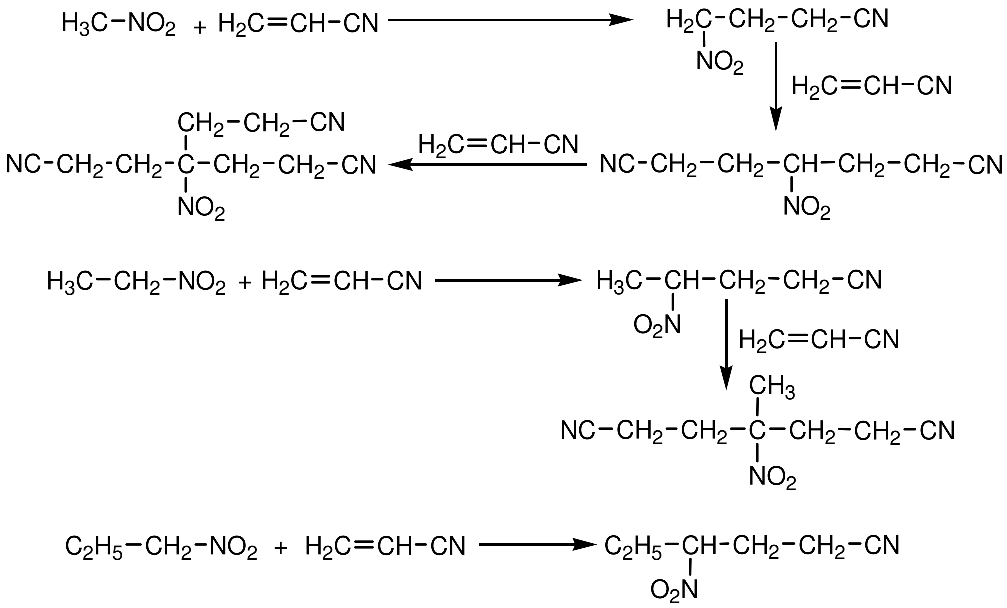
Table I. Effect of the medium on the yield in the Michael reaction involving nitroalkanes and α,β-unsaturated compounds.

R^1	R^2	EWG	Product	Medium	Yield %
H	H	CN	**1**	**A**	38
				B	50
				C	48
				D	48
CH_3	H	CN	**2**	**A**	40
				B	46
				C	42
				D	44
H	H	CO_2Me	**3**	**A**	18
				B	32
				C	66
				D	19
H	H	COMe	**4**	**A**	43
				B	63
				C	58
				D	60
CH_3	H	CO_2Me	**5**	**A**	19
				B	39
				C	60
				D	40
CH_3	H	COMe	**6**	**A**	46
				B	68
				C	64
				D	63
C_2H_5	H	CN	**7**	**A**	52
		CO_2Me	**8**	**A**	26
		COMe	**9**	**A**	57

A : NaOH (0.025M) ; **B :** $EtO^-/EtOH$; **C :** $MeO^-/MeOH$; **D :** NaOH/EtOH

In water the reactivity is enhanced with increasing chain length of the nitroalkane. The selectivity follows the same trend due to a lower solubility of the Michael adduct formed with a subsequent lower tendency to react further according to a second Michael addition. As an example, nitropropane gives only the expected Michael monoadduct whereas a second addition product is formed in the corresponding nitroethane reaction. In the case of nitromethane, three products are formed resulting from subsequent Michael additions. Scheme 1 summarizes the products obtained in the addition of nitroalkanes to acrylonitrile.

In the case of methyl acrylate, the Michael adduct is obtained in low yield compared to the acrylonitrile or methylvinylketone reaction. This is ascribed to hydrolysis and transesterification in the presence of alkoxide ions. Better yields are obtained in methanol with sodium methoxide.



Scheme 1. Michael reactions between acrylonitrile and nitroalkanes.

The low yields in water are certainly connected to the limited solubility of nitroalkanes in water. Thus, using a biphasic system (water-dichloromethane) improves the yields whereas the subsequent Michael additions are partly inhibited. Once formed, the Michael adduct migrates to the organic phase, the interactions between acidic hydrogen and hydroxide ions are less frequent. The results are presented in the table II.

Table II. Michael reactions in biphasic medium (water-dichloromethane).

EWG	R^2	R^1	Product	Yield % (**E**)
CN	H	H	**1**	50
		CH_3	**2**	57
		C_2H_5	**7**	63
	CH_3	CH_3	**10**	62
CO_2Me	H	H	**3**	36
		CH_3	**5**	39
		C_2H_5	**8**	45
	CH_3	CH_3	**11**	47
COMe	H	H	**4**	41
		CH_3	**6**	40
		C_2H_5	**9**	50
	CH_3	CH_3	**12**	50

E : NaOH (0.025M) + CH_2Cl_2, 1h ;

However, the yields are not satisfactory even if the liquid-liquid biphasic system is a fair compromise. To improve the yields we thought of interest to examine the effect of phase transfer catalysts (Table III.).

Table III. Effect of phase transfer catalysts.

EWG	R^2	R^1	Product	Yield %			
				A-1	**A-2**	**B-1**	**B-2**
CN	H	H	**1**	80	81	80	80
		CH_3	**2**	85	86	87	86
		C_2H_5	**7**	80	80	85	86
	CH_3	CH_3	**10**	74	77	80	78
CO_2Me	H	H	**3**	72	74	74	70
		CH_3	**5**	70	74	72	73
		C_2H_5	**8**	76	79	78	80
	CH_3	CH_3	**11**	70	74	75	74
COMe	H	H	**4**	81	84	85	83
		CH_3	**6**	87	88	90	88
		C_2H_5	**9**	78	80	84	85
	CH_3	CH_3	**12**	75	80	80	80

A-1 : NaOH (0.025M) + TBAB, 1h ; **A-2** : NaOH (0.025M) + TBACl, 0.5h.
B-1 : NaOH (0.025M) + CH_2Cl_2 + TBAB, 1h ; **B-2** : NaOH (0.025M) + CH_2Cl_2 + TBACl, 0.5h.

Comparison between Tables I and III reveals that the Michael reaction is essentially promoted by the use of phase transfer catalysts. In the absence of a transfer agent the hydroxide ions attack the carbon of the carbonyl group rather than the acidic hydrogen of the nitroalkane, particularly in the case of methyl acrylate. To this respect, the saponification of the ester group would be profitable. The result may be interpreted as an interaction of the Na^+ ion with the carbonyl group which weakens the C=O bond and promotes, therefore, the nucleophilic attack.

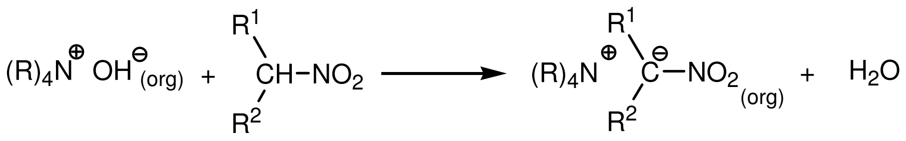
In the presence of Bu_4N^+ Br^- or Bu_4N^+ Cl^-, the active base is likely to be Bu_4N^+ OH^- [35]. The cation cannot easily be associated with the carbonyl and hence the OH^- ions remove the acidic hydrogen of the nitroalkane. We have observed that the reactivity depends on the nature of the anion associated with the ammonium cation. The chloride is more efficient than the bromide. Similar results were obtained by D'Incan in his study describing the effect of the phase transfer agent in the Horner-Emmons reaction between benzaldehyde and 1-cyanoethyl diethylphosphonate [36].

The liquid-liquid phase transfer used in our reactions can be schematized as follows:

- The first step consists of a transfer of the hydroxide ion from the aqueous to the organic phase by the ammonium cation through the equilibrium

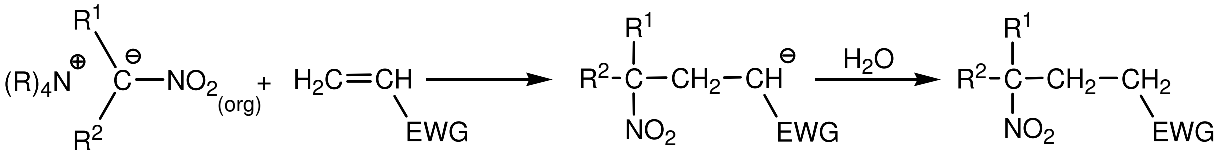
$$(R)_4N^{\oplus}\ X^{\ominus}_{(org)} + OH^{\ominus}_{(aq)} \rightleftharpoons (R)_4N^{\oplus}\ OH^{\ominus}_{(org)} + X^{\ominus}_{(aq)}$$

- The second step is the deprotonation of the nitroalkane to form a carbanion



$$(R)_4N^{\oplus}\,OH^{\ominus}_{(org)} + \underset{R^2}{\overset{R^1}{CH}}{-}NO_2 \longrightarrow (R)_4N^{\oplus}\ \underset{R^2}{\overset{R^1}{C}}{}^{\ominus}{-}NO_{2\,(org)} + H_2O$$

- The carbanion then condenses with unsaturated compound to form an intermediate which by re-protonation affords the Michael adduct.



$$(R)_4N^{\oplus}\ \underset{R^2}{\overset{R^1}{C}}{}^{\ominus}{-}NO_{2\,(org)} + H_2C{=}\underset{EWG}{CH} \longrightarrow R^2{-}\underset{NO_2}{\overset{R^1}{C}}{-}CH_2{-}\underset{EWG}{CH^{\ominus}} \xrightarrow{H_2O} R^2{-}\underset{NO_2}{\overset{R^1}{C}}{-}CH_2{-}\underset{EWG}{CH_2}$$

In conclusion, the Michael reaction involving nitroalkanes cannot occur in the absence of a base. In water and in the presence of sodium hydroxide, the low yields are due to the limited solubility of nitroalkanes. When using a biphasic medium (water-dichloromethane), the reactivity is increased as well as the selectivity with a lesser tendency of subsequent Michael additions on the primary product. The reactions reported in this paper are particularly favoured by addition of a phase transfer agent. Tetrabutylammonium chloride is more efficient than the corresponding bromide salt.

EXPERIMENTAL

- **Method A:** The nitroalkane (30mmol) and the acrylic compound (20mmol) are added to a 0.025M NaOH (50mL). After stirring at room temperature for 1 hour, the mixture is saturated with NaCl, the organic phase extracted with ether, dried on sodium sulfate and concentrated in *vacuo*. The reaction product is purified on a silicagel column with hexane/ether (9/1, 8/2, 7/3, 5/5) as eluent.
- **Method B:** A solution of sodium ethylate (0.85g, 1.25mmol), nitroalkane (30 mmol) and the acrylic compound (20mmol) in 50 mL ethanol is stirred for one hour. The solution is concentrated and the product purified on a silicagel column with hexane/ether (9/1, 8/2, 7/3, 5/5) as eluent.
- **Method C:** As method B replacing sodium ethoxide by sodium methoxide and ethanol by methanol.
- **Method D:** As method B replacing sodium ethoxide by sodium hydroxide
- **Method A-1:** As method A with additional tetrabutylammonium bromide (2mmol).
- **Method A-2:** As method A with additional tetrabutylammonium chloride (2mmol) for 0.5 h.
- **Method E:** The nitroalkane (30mmol) and the acrylic compound (20mmol) in 50mL of dichloromethane are added to a 0.025M NaOH (50mL). After stirring at room temperature for 1 hour, the mixture is saturated with NaCl, the organic phase extracted, dried on sodium sulfate and concentrated in *vacuo*. The reaction product is purified on a silicagel column with hexane/ether (9/1, 8/2, 7/3, 5/5) as eluent.
- **Method B-1:** As method E with additional tetrabutylammonium bromide (2mmol).
- **Method B-2:** As method A with additional tetrabutylammonium chloride (2mmol) for 0.5 h.

NMR Spectra: ^1H (300 MHz) and ^{13}C (75MHz) NMR spectra are recorded on a AC 300 Brüker spectrometer in $CDCl_3$ using tetramethylsilane (TMS) as internal reference. All chemical shifts (δ) were reported in ppm from internal TMS.

IR spectra are recorded on a JASCO FT–IR-420 device in KBr pellets.

Microanalyses were performed using a C, H, N Analyzer Model 185 from Hewlett-Packard; C ±0.20, H ±0.19.

4-Nitro-butyronitrile (1): ^1H-NMR ($CDCl_3$) (δ/ppm) 2.23-2.36 (m, 2H), 2.50 (t, 2H, J = 7.2 Hz), 4.57 (t, 2H, J = 7.2 Hz). ^{13}C-NMR ($CDCl_3$) (δ/ppm) 17.50, 23.54, 81.52, 118.47. Analysis (% Calculated/found) for $C_4H_6N_2O_2$ C: 42.10/42.32, H: 5.30/5.41, N: 24.55/24.77.

4-Nitro-pentanenitrile (2): Oil. Spectroscopic data corresponds to that reported in the literature [37,38]. ^1H-NMR ($CDCl_3$) (δ/ppm) 1.83 (d, 3H, J = 7.2 Hz), 2.24-2.35 (m, 2H), 2.49 (t, 2H, J = 7.2 Hz), 4.13-4.29 (m, 1H). ^{13}C-NMR ($CDCl_3$) (δ/ppm)14.70, 16.10, 30.18, 84.25, 118.40. Analysis (% Calculated/found) for $C_5H_8N_2O_2$ C: 46.87/46.94, H: 6.29/6.18, N: 21.86/21.97.

4-Nitro-butyric acid methyl ester (3): Spectroscopic data corresponds to that reported in the literature [39]. ^1H-NMR ($CDCl_3$) (δ/ppm) 2.27 (t, 2H, 7.2 Hz), 2.30-2.40 (m, 2H), 3.75 (s, 3H), 4.53 (t, 2H, J = 7.2 Hz). ^{13}C-NMR ($CDCl_3$) (δ/ppm) 23.40, 32.92, 53.24, 80.50, 174.02.

5-Nitro-pentan-2-one (4): I.R. $\nu_{C=O}$ = 1717 cm^{-1} ; $\nu_{C\text{-}NO_2}$ = 1548 cm^{-1}. ^1H-NMR ($CDCl_3$) (δ/ppm) 2.18 (s, 3H), 2.08-2.20 (m, 2H), 2.45 (t, 2H, J = 7.2 Hz), 4.46 (t, 2H, J = 7.2 Hz). ^{13}C-NMR ($CDCl_3$) (δ/ppm) 18.96, 25.49, 40.18, 83.06, 208.50. Analysis (% Calculated/found) for $C_5H_9NO_3$ C: 45.79/46.98, H: 6.91/6.89, N: 10.68/10.86.

4-Nitro-pentanoic acid methyl ester (5): Yellow oil. Spectroscopic data corresponds to that reported in the literature [32,40,41]. I.R. $\nu_{C=O}$ = 1735 cm^{-1} ; $\nu_{C\text{-}NO_2}$ = 1545 cm^{-1}. ^{1}H-NMR ($CDCl_3$) (δ/ppm) 1.55 (d, 3H, *J* = 6.9 Hz), 2.00-2.50 (m, 4H), 3.70 (s, 3H), 4.35-4.80 (m, 1H). ^{13}C-NMR ($CDCl_3$) (δ/ppm) 16.20, 28.50, 29.00, 52.04, 84.50, 173.00. Analysis (% Calculated/found) for $C_6H_{11}NO_4$ C: 44.71/44.93, H: 6.87/6.91, N: 8.69/8.65.

5-Nitro-hexan-2-one (6): Spectroscopic data corresponds to that reported in the literature [12,14,40,41]. I.R. $\nu_{C=O}$ = 1700 cm^{-1} $\nu_{C\text{-}NO_2}$ = 1535 cm^{-1}. ^{1}H-NMR ($CDCl_3$) (δ/ppm) 1.55 (d, 3H, *J* = 6.9 Hz), 2.19 (s, 3H), 2.05-2.17 (m, 2H), 2.57 (t, 2H, *J* = 6.9 Hz), 4.56-4.63 (m, 1H). Analysis (% Calculated/found) for $C_6H_{11}NO_3$ C: 49.64/49.79, H: 7.63/7.78, N: 9.64/9.58.

4-Nitro-hexanenitrile (7): Oil. Spectroscopic data corresponds to that reported in the literature [37]. ^{1}H-NMR ($CDCl_3$) (δ/ppm) 1.05 (t, 3H, *J* = 7.2 Hz), 1.89-2.01 (m, 2H), 2.21-2.33 (m, 2H), 2.51(t, 2H, *J* = 7.2 Hz), 4.08-4.19 (m, 1H). ^{13}C-NMR ($CDCl_3$) (δ/ppm) 12.16, 14.71, 24.00, 28.52, 87.60, 117.87. Analysis (% Calculated/found) for $C_6H_{10}N_2O_2$ C: 50.69/50.77, H: 7.09/6.98, N: 19.70/19.58.

4-Nitro-hexanoic acid methyl ester (8): I.R. $\nu_{C=O}$ = 1735 cm^{-1} ; $\nu_{C\text{-}NO_2}$ = 1545 cm^{-1}. ^{1}H-NMR ($CDCl_3$) (δ/ppm) 0.95 (t, 3H, *J* = 7.2 Hz), 1.90-2.42 (m, 6H), 3.72 (s, 3H), 4.52-4.65 (m, 1H). Analysis (% Calculated/found) for $C_7H_{13}NO_4$ C: 47.99/48.12, H: 7.47/7.57, N: 7.99/7.40.

5-Nitro-heptan-2-one (9): Spectroscopic data corresponds to that reported in the literature [12,14]. I.R. $\nu_{C=O}$ = 1700 cm^{-1}; $\nu_{C\text{-}NO_2}$ = 1535 cm^{-1}. ^{1}H-NMR ($CDCl_3$) (δ/ppm) 0.96 (t, 3H, *J* = 7.5 Hz), 1.68-2.15 (m, 4H), 2.16 (s, 3H), 2.50 (t, 2H, *J* = 7.2 Hz), 4.38-4.52 (m, 1H). Analysis (% Calculated/found) for $C_7H_{13}NO_3$ C: 52.81/52.98, H: 8.23/8.38, N: 8.79/8.59.

4-Methyl-4-nitro-pentanenitrile (10): ^{1}H-NMR ($CDCl_3$) (δ/ppm) 1.87 (s, 6H), 2.25 (t, 2H, *J* = 7.2 Hz), 2.53 (t, 2H, *J* = 7.2 Hz). ^{13}C-NMR ($CDCl_3$) (δ/ppm) 13.93, 24.35, 37.24, 86.75, 117.80. Analysis (% Calculated/found) for $C_6H_{10}N_2O_2$ C: 50.69/50.80, H: 7.09/6.91, N: 19.70/19.82.

4-Methyl-4-nitro-pentanoic acid methyl ester (11): Spectroscopic data corresponds to that reported in the literature [37]. I.R. $\nu_{C=O}$ = 1740 cm^{-1} ; $\nu_{C\text{-}NO_2}$ = 1554 cm^{-1}. ^{1}H-NMR ($CDCl_3$) (δ/ppm) 1.58 (s, 6H), 2.12-2.41 (m, 4H), 3.72 (s, 3H). Analysis (% Calculated/found) for $C_7H_{13}NO_4$ C: 47.99/48.07, H: 7.47/7.57, N: 7.99/7.86.

5-Methyl-5-nitro-hexan-2-one (12): Spectroscopic data corresponds to that reported in the literature [14]. ^{1}H-NMR ($CDCl_3$) (δ/ppm) 1.45 (s, 6H), 2.04 (s, 3H), 2.05 (t, 2H, *J* = 7.5 Hz), 2.34 (t, 2H, *J* = 7.5 Hz). ^{13}C-NMR ($CDCl_3$) (δ/ppm) 23.80, 25.75, 33.88, 38.05, 87.37, 206.49. Analysis (% Calculated/found) for $C_7H_{13}NO_3$ C: 52.81/52.69, H: 8.23/8.41, N: 8.79/9.00.

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