Pergamon

Tetrahedron Letters, Vol. 38, No. 43, pp. 7563-7564, 1997
© 1997 Elsevier Science Ltd
All rights reserved. Printed in Great Britain
0040-4039/97 $17.00 + 0.00

PII: S0040-4039(97)10035-1

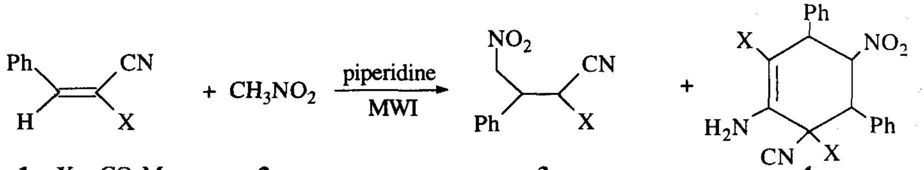
Michael Monoaddition of Nitromethane on Gem-Diactivated Alkenes in Dry Media Coupled with Microwave Irradiation.

David Michaud, Françoise Texier-Boullet* and Jack Hamelin

Laboratoire de Synthèse et Electrosynthèse Organiques 3, CNRS Université Rennes I, Campus de Beaulieu, 35042 Rennes France.

Abstract : Nitromethane reacts readily and selectively with a variety of electrophilic alkenes activated by cyano, ester or amide group to give the corresponding Michael monoadduct within a few minutes, in good yields over alumina without solvent and under focused microwaves. © 1997 Elsevier Science Ltd.

Michael addition of nitroalkanes has been largely reviewed[1]. Coupling dry media and microwave irradiation[2] is one of the main research area in our laboratory[3] and recently, we reported a novel pathway leading to functionalized cyclohexenes from nitromethane and electron - deficient alkenes activated by nitrile and ester group. These unexpected cyclohexenes were formed via a double and diastereoselective Michael addition which took place under solvent-free conditions coupled with microwave irradiation (MWI)[4]. The challenge was to isolate Michael monoadducts **3**, most of them being unknown in the literature. We shown that piperidine (3% towards alkene **1a**) was able to catalyze the formation of the monoadduct when nitromethane was used in excess (3 eq.) but in this case, 10% of cyclohexene **4a** were still formed making hard the purification of the adduct.



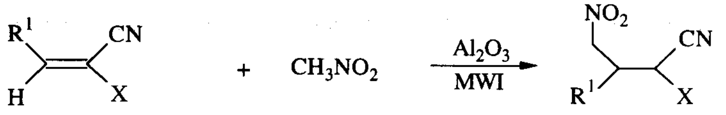
1a $X = CO_2Me$ **2a** **3a** **4a**

Scheme 1

When alumina was used as catalyst without solvent, the reaction led selectively to Michael adduct **3a**. Two recent reports [5] on Michael addition in presence of alumina under microwave irradiation prompt us to disclose our own results. A typical procedure for obtention of **3a** is as follows : the mixture of 5 mmoles of benzylidene methylcyanoacetate **1a** [6] and 15 mmoles of nitromethane adsorbed over alumina was placed in a quartz tube and introduced into Synthewave 402® microwave reactor with a temperature monitored at 90°C obtained after 3 and maintained 9 minutes. The mixture was cooled down and extracted with CH_2Cl_2. After filtration of Al_2O_3 and removal of the solvent the pure product **3a** (two diastereoisomers A/B : 50/50) was isolated by crystallization from cold ether[8].

* fax : 0299286374; e.mail : Francoise.Texier@univ-rennes1.fr

The monoaddition of nitromethane was successfully extended to electrophilic alkenes **1a-k**. Extension to nitroethane has been investigated : for example **1b**, **1c**, **1g** after 40 mn of irradiation at 80°C gave quantitative yields of adducts (estimated by ^{1}H NMR). All compounds were characterized by NMR and mass spectra.



1a-h **2** **3a** (A and B)

1a-e : X=CO_2Me ; R_1=C_6H_5, $pClC_6H_4$, $oBrC_6H_4$, oFC_6H_4, mFC_6H_4 ; **1f** : R^1=isoBu ; X=CO_2Et ; **1g** : R^1=C_6H_5, X=CN ; **1h** : R^1=C_6H_5, X=$CONH_2$.

3a : 70% ; **3b** : 72% ; **3c** : 83% ; **3d**: 100% (NMR); **3e** : 72% ; **3f** : 70% ; **3g** : 100% (NMR); **3h** : 68%.

Acknowledgements : We thank Prolabo SA, France for providing the Synthewave 402, Dr Perrocheau J. for helpfull discussions about NMR data and Artus D. for efficient collaboration.

References and notes

1. Baer, H.H.; Urbas, L. in *The Chemistry of the Nitro and Nitroso Groups. H. Feuer*, Ed, **1970**, Interscience Publishers, New York, **1970**, part 2, p. 130-149.
2. a- Bram, G.; Loupy, A.; Villemin, D. In *Solid Supports and Catalysts in Organic Synthesis* ; Smith, K.; Ed Ellis Horwood and Prentice Hall ; **1992**, chap.12, p.302. b- Caddick, S. *Tetrahedron*, **1995**, *51*, 10403-10432. c- Madjoub, M.; Loupy, A.; Petit, A.; Roudesli, S. *Tetrahedron*, **1996**, *52*, 617-628.
3. Jacquault, P.; Texier-Boullet, F.; Bazureau, J.P.; Hamelin, J. *International Chemical Congress of Pacific Basin Societies*, Honolulu HI; American Chemical Society; 17-22 December 1995, Book of Abstracts, Part II, 599.
4. Michaud, D.; Abdallah-El Ayoubi, S.; Dozias, M.J.; Toupet, L.; Texier-Boullet, F.; Hamelin, J. *J. Chem. Soc., Chem. Commun.*, **1997**, in press.
5. a- Boruah, A.; Baruah, M.; Prajapati, D.; Sandhu, J.S. *Chem. Lett.*, **1996**, 965-966. b- Ranu, B.C.; Saha, M.; Bhar, S.,*Synthetic Comm.*, **1997**, 24, 621-623.
6. a- Texier-Boullet, F.; Foucaud, A. *Tetrahedron Lett.*, **1982**, *23*, 4927-4928. b- Abdallah-El Ayoubi, S.; Texier-Boullet, F.; Hamelin, J. *Synthesis*, **1994**, 258-266.
7. Commarmot, R.; Didenot, R. and Gardais, J.F. *Fr. Demande*, 2 560 529 (Cl.B01J19/12), 06 Sep. 1985, Appl. 84/3,496, 02 Mar 1984 (*Chem. Abstr.*, **1986**, *105*, 17442e). Temperature measured by an IR captor : Prolabo, *Fr. Pat.* 62241D, 14669Fr, 23 Dec. **1991**.
8. Data for **3a** : C_6H_5-CH(1)-CH_2NO_2-CH(2)-(CN)(CO_2CH_3) follow : RMN ^{1}H ($CDCl_3$) δ : 3.67 (s, 3H, O-$C\underline{H}_3$, dia A) ; 3.75 (s, 3H, O-$C\underline{H}_3$, dia B) ; 3.96 (d, 1H, $C\underline{H}^1$, ^3J= 5.5 Hz, dia A) ; 4.15 (d, 1H, $C\underline{H}^1$, ^3J= 5.8 Hz, dia B) ; 4.09-4.27 (m, 1H, $C\underline{H}^2$) ; 4.79-5.03 (m, 2H, $C\underline{H}_2$) ; 7.23-7.39 (m, 5H, ArH). RMN ^{13}C ($CDCl_3$) δ : 41.51 (dm, CH^1, ^1J = 137 Hz, dia A) ; 41.60 (dm, CH^1, ^1J = 137 Hz, dia B) ; 42.72 (dm, CH^2, ^1J = 139 Hz, dia A) ; 42.99 (dm, CH^2, ^1J = 136 Hz, dia B) ; 53.83 (q, OCH_3, ^1J = 149 Hz, dia A) ; 54.03 (q, OCH_3, ^1J = 149 Hz, dia B) ; 75.86 (tm, CH_2NO_2, ^1J = 147.9 Hz, dia A) ; 76.26 (tm, CH_2NO_2, ^1J = 147.9 Hz, dia B) ; 114.27 (m, CN, dia A) ; 114.42 (m, CN, dia B) ; 127.5-134.5 (m, Ar) ; 164.54 (m, C=O, dia A) ; 164.37 (m, C=O, dia B).High-resolution mass spectrometry (HMRS) M^+ - HNO_2: calcd 201.0789. Found 201.083.

(*Received in France* 16 *July* 1997; *accepted* 3 *September* 1997)