Chinese Chemical Letters Vol. 14, No. 4, pp 333 – 334, 2003
http://www.imm.ac.cn/journal/ccl.html

A New Solvent-free Synthesis of α, α′-Dibenzylidenecycloalkanones from Acetals with Cycloalkanones under Microwave Irradiation

Dan Feng HUANG, Jin Xian WANG*, Yu Lai HU

College of Chemistry & Chemical Engineering, Northwest Normal University, Lanzhou 730070

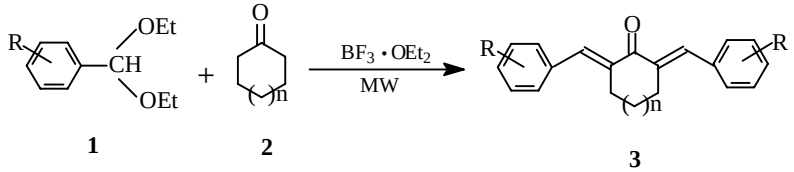
Abstract: A new rapid synthetic method is described for synthesis of α, α′-dibenzylidene-cycloalkanones by the reaction of acetals and cycloalkanones without solvent using $BF_3{\cdot}Et_2O$ as catalyst under microwave irradiation.

Keywords: Cycloalkanone, acetal, Lewis acid, microwave irradiation.

α, α′-Dibenzylidenecycloalkanones are very important intermediates for synthesis of bioactive pyrimidine derivatives[1]. Usually, their preparation is achieved by the cross-aldol condensation, which has low yield and too many by-products[2]. The methods with catalyst such as $RuCl_3$[3a], $TiCl_3(SO_3CF_3)$[3b], $InCl_3 \cdot 4H_2O$[3c] or BMPTO [d] require expensive catalysts and long reaction times and give more by-products. Acetals have been successfully applied as a protective group in organic synthesis[4], and some acetalation reactions have been carried out under microwave irradiation conditions[5]. However, there is no report on the synthesis of α, α′-dibenzylidenecycloalkanones from acetals and cycloalkanones.

In the previous paper[6], we have reported the reaction of aryl ketones with acetals catalyzed by Lewis acid under microwave irradiation to give chalcons. Here we wish to report the method for synthesis of α, α′-dibenzylidenecycloalkanones by the reaction of acetals **1** with ketones **2** using $BF_3{\cdot}Et_2O$ as the catalyst in microwave irradiation condition without solvent (**Scheme 1**). In this reaction no any self-condensation products were formed from ketones. The reaction has following advantages: short reaction time, simple work-up procedures, moderate yields and easy availability of catalyst. Thus, it is an efficient method for the preparation of α, α′-dibenzylidenecycloalkanones.

Scheme 1



1 **2** **3**

*E-mail: Wangjx@nwnu.edu.cn

Table 1 The cross-condensation of cycloalkanones with acetals catalyzed by $BF_3 \cdot Et_2O$ under microwave irridiation

3	n	R	Yield(%) [a]	Mp (lit)/°C
a	0	H	73	190-192(189)[7]
b	0	*p*-CH_3O	77	214-216(216)[8]
c	0	*o*-Cl	71	158-160(163)[9]
d	1	H	76	119-121(118)[10]
e	1	*p*-CH_3O	75	162-163(157-162)[10]
f	1	*o*-Cl	81	108-110(104-110)[9]

a: Isolated yield

All reactions finished within 1 min. di-condensation products were obtained even if the ratio of cycloalkanones to acetals changed. This result can be explained by its reaction mechanism[6]. General procedure: $BF_3 \cdot Et_2O$ (0.4 mmol) was added to a mixture of aryl acetal (10 mmol) and cyclohexanone (10 mmol). The color of the reaction mixture changed from colorless to red-brown immediately. The reaction mixture was irradiated at 375 W for 1 min. Et_2O (15 mL), H_2O (15 mL) were added. The organic layer was separated and dried over $MgSO_4$. The product was separated by chromatography on silica gel using petroleum ether:ethyl acetate (10:1) as an eluent**.**

Acknowledgments

The work was supported by the National Natural Science Foundation of China (NO. 20272047) and the Northwest Normal University Science and Technology Development Foundation of China.

References

1. J. Deli, T. Lorand, D. Szabo, A. Foldesi, *Pharmazi.* **1984**, *39*, 539.
2. a) B. A. Hathaway, *J. Chem. Educ.* **1987**, *64*, 367; b) T. Nakano, S. Irifune, S. Vmano, A. Inada, Y. Ishii, M. Ogawa, *J. Org. Chem.*, **1987**, *52*, 2239.
3. a) N. Iranpoor, F. Kazemi, *Tetrahedron*, **1998**, *54*, 9475; b) N. Iranpoor, B. Zeynizadeh, A. Aghapoun, *J. Chem. Research (S)*, **1999** ,554; c) G. Deng, T. Ren, *Chin. Chem. Lett*., **2001**, *12*, 859; d) M. Zheng, L. Wang, J. Shao, Q. Zhong, *Synth. Commun*., **1997**, *27*, 351.
4. T. W. Greene, P. G. M, Wuts, *Protective Groups in Organic Synthesis*, John Wiley and Sons, Inc.: New York, **1991**, 188.
5. T. Beregszászi, Á. Molnár, *Synth. Commun*., **1997**, *27*, 3705; b) B. Pério, M. J. Dozias, P. Jacquault, J. Hamelin, *Tetrahedron Lett*., **1997,** *38*, 7867.
6. D. F. Huang, J. X. Wang, Y. L. Hu, *Synth. Commun*., **2002**, *32*,971.
7. M. Zheng, L. Wang, J. Shao, Q. Zhong, *Synth. Commun.*, **1997**, *27*, 351.
8. R. mayer, B.Gebhardt, *Chem.Ber.*, **1960**, *93*, 1212.
9. CH. B. Rao, P. V. N. Raju, *Indian J. Chem. Sect. B*, **1984**, *23*, 321.
10. R. Gupta, A. K. Gupta &P. L. Kachroo, *India J. Chem. Sect. B*, **1995** ,61.

Received 7 March, 2002