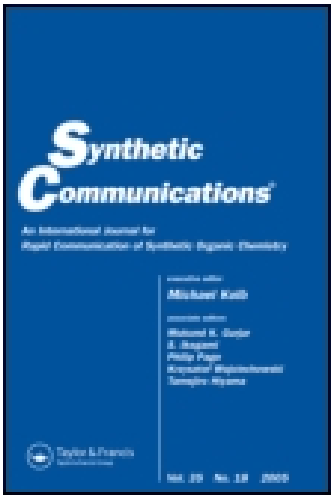


Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Solvent-Free Microwave Michael Addition Between EMME and Various Nucleophiles

André Loupy [a] , Suk Jin Song [b] , Seong Jin Cho [b] , Dong Kyu Park [b] & Tae Woo Kwon [b]

[a] Laboratoire des Réactions Sélectives sur Supports, associé au CNRS, UMR 8615-ICMMO , Université Paris-Sud , Batiment, Orsay Cédex, France

[b] College of Science , Kyungsung University , Daeyoen-dong, Busan, 608-736, Korea

Published online: 05 Aug 2006.

To cite this article: André Loupy , Suk Jin Song , Seong Jin Cho , Dong Kyu Park & Tae Woo Kwon (2005) Solvent-Free Microwave Michael Addition Between EMME and Various Nucleophiles, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 35:1, 79-87, DOI: 10.1081/SCC-200046503

To link to this article: http://dx.doi.org/10.1081/SCC-200046503

Synthetic Communications®, 35: 79–87, 2005

ISSN 0039-7911 print/1532-2432 online
DOI: 10.1081/SCC-200046503

Solvent-Free Microwave Michael Addition Between EMME and Various Nucleophiles

André Loupy
Laboratoire des Réactions Sélectives sur Supports, associé au CNRS,
UMR 8615-ICMMO, Université Paris-Sud, Batiment,
Orsay Cédex, France

Suk Jin Song, Seong Jin Cho, Dong Kyu Park, and Tae Woo Kwon
College of Science, Kyungsung University, Busan, Korea

Abstract: Michael addition reaction between EMME and various O, S, N nucleophiles were investigated in the presence of catalysts such as KF, KOH, or $K(OCCH_3)_3$ under solvent-free conditions either neat or on alumina as solid support. Compared to low reactivity of alcohols (40 to 80% yields according to aliphatic chain), aniline or thiophenol gave good to excellent yields (90–99%).

Keywords: Alumina, Michael addition, microwave irradiation, solvent-free reactions, specific microwave effects

INTRODUCTION

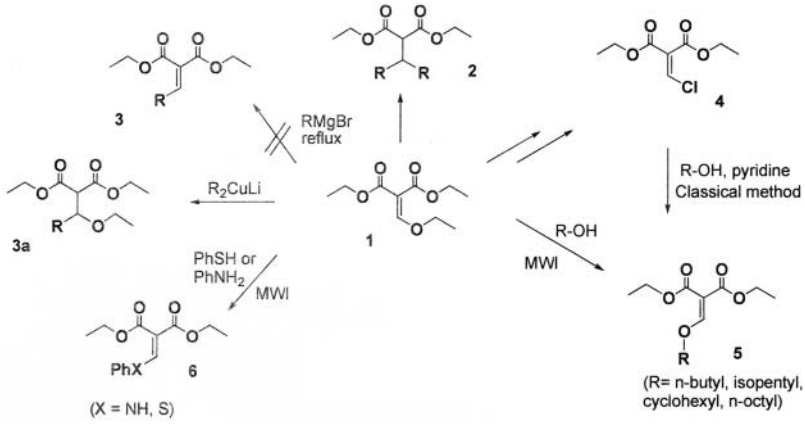
The electron-deficient alkenes such as commercially available diethyl ethoxymethylenemalonate (EMME) **1** are valuable intermediates for the synthesis of biologically important materials[1–4] and attractive acceptors for a variety of Michael addition donors.[5–7] The applications of microwave irradiation in organic chemistry have increased very rapidly. Intra- or intermolecular addition of a variety of primary[8,9] and secondary amines,[10,11]

Received in Japan August 18, 2004
Address correspondence to Tae Woo Kwon, College of Science, Kyungsung University, Daeyoen-dong, Busan 608-736, Korea. E-mail: aloupy@icmo.u-psud.fr or twkwon@star.ks.ac.kr

enamines,[12] imidazole,[13] and active carbon anions[14,15] have been used in the microwave activated Michael additions. In a previous paper, we reported that **1** may be unexpectedly converted into symmetrical dialkyl and diarylmethyl malonated derivatives **2** using Grignard reagent (RMgBr/reflux) (2a). No α-β unsaturated products **3** were isolated. Addition of organocuprates (R_2CuLi) to **1** gave ethoxy substituted Michael adduct **3a**. However, it was not facile to introduce oxygen atoms in electro-deficient alkenes backbone. For example, it required two or more steps to obtain **5** via unstable chlorinated intermediate **4** in the presence of highly toxic thionyl chloride and pyridine reagents.[16] In the hope that this troublesome step[16–18] can be replaced by microwave irradiation (MWI) technique under mild conditions, we focused on the environmentally benign Michael addition between various O, S, and N nucleophiles leading to **5** (R = *n*-butyl, isopentyl, cyclohexyl, *n*-octyl alcohols) and **6** (X = S or NH) and EMME for carbon-heteroatom bond formation under MWI in the absence of solvent or toxic species (Scheme 1).

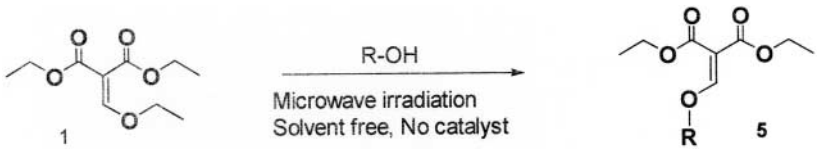
First we check the stability of **1** under microwave irradiation. EMME **1** was irradiated for 5 min in the absence of any nucleophile or catalyst and was recovered as 99.9%. Then we examined the time and yields relationship between EMME and various alcohols under MWI conditions in the absence of catalyst.

When *n*-butyl alcohol was irradiated for 1 min, reaction did not take place and only EMME was recovered (Table 1, entry 1). The best results were obtained when the mixtures were irradiated for 10 min with all the aliphatic alcohols examined affording the desired product as the major one within 40, 41, 57, and 80% yields, respectively, with R = *n*-Bu, *i*-Pent, Cyclohexyl and *n*-Oct (Table 1, entries 3, 6, 8, and 13). The specific (non-purely thermal) microwave effects were clearly observed after accurate comparaisons



Scheme 1.

Table 1. Optimization of the reaction time in the solvent-free Michael Addition between neat EMME and various alcohols ROH under MWI or conventional heating in a thermostated oil bath under similar sets of conditions. (Scale = 5.55 mmol, mole ratio of **1** : **ROH** = 1 : 3)



Entry	R	Time (min)	Temperature[a] (°C)	Yield 5 (%)	Recovered EMME (%)
1 (**5a**)	*n*-Butyl	1	—	0	99
2 (**5a**)	*n*-Butyl	5	—	17	82
3 (**5a**)	*n*-Butyl	10	—	**40**	59
4 (**5a**)	*n*-Butyl	20	101	40	57
5 (**5b**)	*i*-Pentyl	1	—	5	93
6 (**5b**)	*i*-Pentyl	10	—	**41**	45
7 (**5b**)	*i*-Pentyl	30	—	52	42
8 (**5c**)	Cyclohexyl	10	142	**57 (MW)**	40
9 (**5c**)	Cyclohexyl	10	142	29 (Δ^b)	65
10 (**5c**)	Cyclohexyl	30	—	54	37
11 (**5c**)	Cyclohexyl	40	—	51	34
12 (**5c**)	Cyclohexyl	50	—	50	33
13 (**5d**)	*n*-Octyl	10	—	**80**	16
14 (**5e**)	Phenyl	22	—	0	**99**

[a]Temperature of the reaction mixture was recorded with a digital thermometer just at the end of MWI.

[b]Conventional heating at the same temperature but using a thermostated oil bath.

between MWI and conventional heating under similar conditions (vessels, reaction time, and temperature) (entries 8 vs. 9). Extension of reaction times up to more than 10 min did not enhance the formation of the desired Michael addition adduct (entries 10–12). Under these conditions, PhOH was not a successful nucleophile toward **1** and did not give the desired coupling product (Table 1, entry 14).

Within 10 min of MWI, the sequence of yields we obtained is tightly connected to the boiling point of the alcohol involved (Table 2).

The effect of R group can be understood by considering the addition-elimination mechanism of ROH on EMME (Scheme 2). The competitive pathways **a** and **b** can be either driven by the relative leaving group ability (EtOH should be surely close to ROH) or better by ROH volatility. Pathway **a** will be therefore favored when a high boiling point ROH is

Table 2. Yields of reaction between EMME and ROH as a function of R and of their boiling points

R	*n*-Butyl	*i*-Pentyl	Cyclohexyl	*n*-Octyl
Yield of **5** (%)	40	41	57	80
Boiling point of ROH (°C)	116–118	118–119	160–161	196

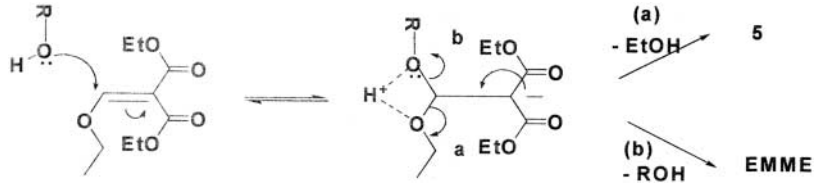
involved. This consideration leads to the same sequence as for observed yields.

We have next studied the effects of different basic species generally used under solvent-free conditions: a supported base on solid mineral support (KF/alumina) and a phase transfer catalysis system (KOH + TBAB).

The main results are given in Table 3. In all cases, as reaction time increased in the presence of KF/Al_2O_3 the yields were enhanced but remained rather limited (entries 1–4 and 5–8). No base addition effect was observed in the case of cyclohexyl alcohol (Table 3, entry 7 vs. Table 1 entry 8). Nonactivated phenol was totally inert (entries 11–12). This fact can be explained by considering that phenol is a better leaving group than ethanol. However, on another hand, the phenoxy compound was obtained easily by reacting phenol with the diethyl chloromethylenemalonate **4** (Scheme 3).

The reactions between EMME and other nucleophiles were also investigated (Table 4). In the case of aniline, the best yield (90%) was obtained without using catalyst (entry 8). From the reaction between **1** and aniline, only a small difference between microwave and thermal effect was observed (entry 8 vs. 9). The presence of base or support did not significantly increase the yields (entries 1, 3 and 6, 8).

In sharp contrast of low reactivity of phenol (Table 1, entry 14), treatment of **1** with thiophenol under similar conditions afforded excellent yields of **8** (quantitative yield; 99%, entry 15). In this case, no solid support effects were detectable (entries 11 vs. 12). The yield was significantly increased in the presence of KF (entries 12 vs. 15, from 24 to 99% within 2 min).



Scheme 2. Addition-elimination mechanism of ROH to EMME.

Table 3. Use of different basic systems for the solvent-free reaction between **1** and **ROH** under MWI

Entry	R	Basic system	Time (min)	Yield(%) (Microwave)	Recovered EMME yield(%)
1	*n*-butyl	KF/Al_2O_3	1	8	90
2	*n*-butyl	KF/Al_2O_3	5	26	65
3	*n*-butyl	KF/Al_2O_3	10	**30**	58
4	*n*-butyl	KF/Al_2O_3	20	30	56
5	Cyclohexyl	KF/Al_2O_3	1	4	93
6	Cyclohexyl	KF/Al_2O_3	6	27	67
7	Cyclohexyl	KF/Al_2O_3	10	**50**	43
8	Cyclohexyl	KF/Al_2O_3	20	50	39
9	Cyclohexyl	KOH/TBAB[b]	1	20	70
10	Cyclohexyl	KOH/TBAB	2	22	65
11	Phenyl	KF/Al_2O_3	3 (89°C)[a]	0 (NR)[c]	85
12	Phenyl	KOH/TBAB	3	0 (NR)[c]	32

[a]Temperature of the reaction mixture was evaluated by a digital thermometer just at the end of MWI.

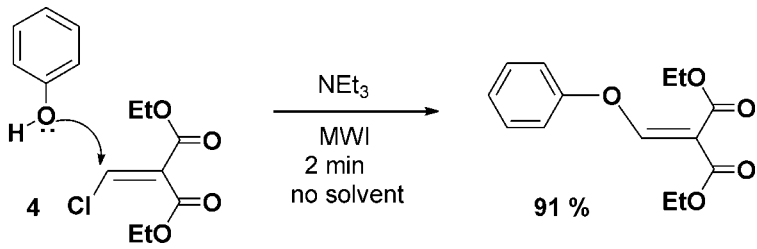
[b]Tetrabutylammonium bromide.

[c]NR = no reaction.

A significant microwave effect was observed. When the reaction between **1** and PhSH was carried using classical heating in the absence of microwave irradiation, the yield was only 7% (entry 16) when compared to 99% under MWI (entry 15).

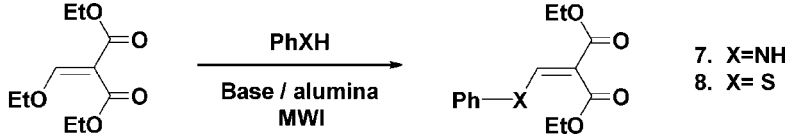
In summary, aniline and thiophenol gave good to excellent yields of nucleophilic addition toward EMME. The order of nucleophilicity under microwave irradiation without using any catalyst or solid support is aniline > thiol > aliphatic alcohols ≫ phenol. In the case of the reaction between PhSH and EMME, a supported base such as KF/alumina increased the yield.

The most important microwave effect was observed in the case of thiophenol and was also rather significant with aliphatic alcohols that gave



Scheme 3. Solvent-free preparation of phenoxymethylenemalonate.

Table 4. Solvent-free Michael addition of other nucleophiles ($PhNH_2$, PhSH) under MWI (ratio of 7: $PhNH_2 = 1:1.2$, 7 : PhSH = 1 : 1.2)



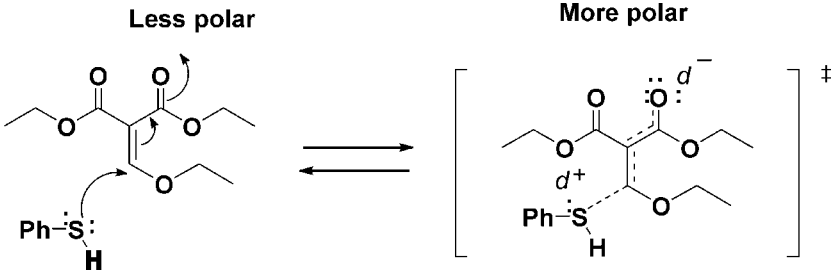
Entry	X	Base	Support	Time (min)	Temp. (°C)	Yield (%)	Recovered EMME (%)
1	NH	none	none	2	70	MW 86	3
2	NH	none	none	2	70	Δ 73	—
3	NH	K_2CO_3	none	2	—	89	—
4	NH	K_2CO_3	Al_2O_3	2	—	67	—
5	NH	KF	Al_2O_3	1	—	79	6
6	NH	KF	Al_2O_3	2	—	86	—
7	NH	none	Al_2O_3	1	—	82	2
8	NH	none	Al_2O_3	2	55	**MW 90**	—
9	NH	none	Al_2O_3	2	55	Δ 79	—
10	NH	none	bentonite	8	105	65	24
11	S	none	none	12	—	25	52
12	S	none	Al_2O_3	2	—	24	30
13	S	none	Al_2O_3	7	—	52	6
14	S	KF	Al_2O_3	1	—	90	—
15	S	KF	Al_2O_3	2	62	**MW 99**	—
16	S	KF	Al_2O_3	2	62	Δ 7	—

moderate yields but were strongly dependent on the chain length. Unfortunately, no nucleophilic addition between inactivated PhOH toward **1** was successful in our various MWI conditions.

The important specific MW effects observed here are consistent with the consideration of mechanisms and with the assumption that the MW effects are increased when the polarity of a system is enhanced. The rate-determining step consists of the addition of nucleophile on the double bond of EMME. The transition state is therefore more polar than ground state and consequently more prone to electrostatic interactions of dipole-dipole type with the electric field (Scheme 4). The more important stabilization of the transition state is therefore responsible of reactivity by a decrease of the activation energy.

EXPERIMENTAL

Typical microwave procedure for 2-cyclohexyloxymethylene-malonic acid diethyl ester, 5c (Table 1, entry 8) EMME (1.21 g, 5.55 mmol,



Scheme 4. Ground and transition states for the addition of thiophenol to EMME.

purchased from Aldrich) and cyclohexanol (1.68 g, 16.80 mmol, 3 eq.) were mixed with Al_2O_3 (5.78 g) in the absence of any organic solvent and then submitted for 10 min to microwave irradiation inside a domestic microwave oven (Sam Sung, RE-555 TCW). The reaction mixture was dissolved in ethyl acetate. Al_2O_3 was filtered off and the filtrate was concentrated by rotary evaporator. The crude product was purified using column chromatography to give 5c (0.86 g, 3.19 mmol, 57%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) 7.70 (1H, vinyl H, s), 4.23 (4H, two $O\underline{CH_2}$, q, J = 7.2 Hz), 4.01 (1H, cyclohexyl CH, quintet, J = 3.8 Hz), 2.01–1.59 (10H, m, cyclohexyl CH_2), 1.35(3H, $CH_2\underline{CH_3}$, t, J = 7.2 Hz), 1.31 (3H, $CH_2\underline{CH_3}$, t, J = 7.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) 164.5(C═O), 164.5(C═O), 163.2(Vinyl H), 106.3(>C═), 84.9 (cyclohexyl CH) 61.1(OCH_2), 61.0(OCH_2), 32.4(cyclohexyl CH_2), 25.4(cyclohexyl CH_2), 23.3 (cyclohexyl CH_2), 14.6(ethoxy CH_3), 14.5 (ethoxy CH_3), Anal. Calcd for $C_{14}H_{22}O_5$ = C62.20, H8.20; Found C61.17, H8.23.

2-Butoxymethylene-malonic acid diethyl ester, 5a. ^{1}H NMR (300 MHz, $CDCl_3$) 7.60(1H, vinyl H, s), 4.46 (2H, $O\underline{CH_2}$, q, J = 7.2 Hz), 4.20 (2H, $O\underline{CH_2}$ q, J = 7.2 Hz), 4.12 (2H, $O\underline{CH_2}CH_2$, t, J = 6.6 Hz), 1.71 (2H, quintet, $CH_2\underline{CH_2}CH_2$, J = 6.6 Hz), 1.45(2H, m, $CH_2\underline{CH_2}CH_3$), 1.31 (3H, $OCH_2\underline{CH_3}$, t, J = 7.2 Hz), 1.28 (3H, $OCH_2\underline{CH_3}$, t, J = 7.2 Hz), 0.92 (3H, t, $CH_2CH_2\underline{CH_3}$, J = 6.6 Hz), ^{13}C NMR (75 MHz, $CDCl_3$) 165.5(C═O), 164.6(C═O), 164.4(Vinyl H), 106.5(>C═), 61.3–61.0(three O CH_2), 32.1(butyl CH_2), 19.0 (butyl CH_2), 14.5–14.0 (three CH_3). IR(neat); 3050.4, 2928.2, 2850.8, 1734.8, 1712.7, 1640.9, 1187.8 cm^{-1}. Anal. Calcd for $C_{12}H_{20}O_5$ = C59.00, H8.25; Found C58.93, H8.29.

2-(3-Methyl-butoxymethylene)-malonic acid diethyl ester, 5b. ^{1}H NMR (300 MHz, $CDCl_3$) 7.59(1H, vinyl H, s), 4.31–4.20 (2H, $O\underline{CH_2}CH_3$, q, J = 7.1 Hz), 4.12(2H, $O\underline{CH_2}$, t, J = 6.7 Hz), 1.73(1H, $\underline{CH}(CH_3)_2$, m, J = 6.8 Hz), 1.62 (2H, q, $CH_2\underline{CH_2}CH$., J = 6.7 Hz), 1.30 (two, $OCH_2\underline{CH_3}$, t, J = 7.1 Hz), 0.94 (6H, d, $CH(\underline{CH_3})_2$, J = 6.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) 164.5(C═O), 165.4(C═O), 162.3(Vinyl H), 106.6(>C═),

61.3–61.1(three $O\underline{CH_2}$), 38.7($OCH_2\underline{CH_2}$), 25.1(isopropyl CH), 22.8(isopropyl CH_3), 14.5(3H, t, $OCH_2\underline{CH_3}$), 14.6(3H, t, $OCH_2\underline{CH_3}$) IR (neat); 3050.5, 2958.2, 1732.5, 1716.8, 1638.5, 1180.8 cm^{-1} Anal· Calcd for $C_{13}H_{22}O_5$ = C60.45, H8.58; Found C60.40, H8.59.

2-Octyloxymethylene-malonic acid diethyl ester, 5d. ^1H NMR (300 MHz, $CDCl_3$) 7.59(1H, vinyl H, s), 4.25 (4H, two, $O\underline{CH_2}$, q, J = 7.1 Hz), 4.11 (one $O\underline{CH_2}$, t, J = 6.7 Hz), 1.68 (2H, $OCH_2\underline{CH_2}$, quintet, J = 6.7 Hz), 1.35–1.26 (10H, octyl, $\underline{CH_2}$), 1.32(6H, $OCH_2\underline{CH_3}$, J = 7.1 Hz), 0.88(3H, octyl $\underline{CH_3}$, t, J = 6.9 Hz), ^{13}C NMR (75 MHz, $CDCl_3$) 165.4(C═O), 164.5(C═O), 164.4(Vinyl H), 106.5(>C═), 61.2–61.0(three O CH_2), 32.1(butyl CH_2),30.1(butyl CH_2), 29.5(butyl CH_2), 29.5(butyl CH_2), 25.8(butyl CH_2), 23,0(butyl CH_2), 14.6($OCH_2\underline{CH_3}$), 14.6($OCH_2\underline{CH_3}$), 14.4 (octyl CH_3). IR (neat); 3072.5, 2950.3, 2885.3, 1735.8, 1715.9, 1642.3, 1465.4, 1180.5 cm^{-1}. Anal. Calcd for $C_{16}H_{28}O_5$ = C63.97, H9.40; Found C63.91, H9.43.

Typical microwave procedure for 2-phenylaminomethylene-malonic acid diethyl ester, 13 (Table 4, entry 8) EMME (1.24, 5.73 mmol), aniline (1.63 g, 16.87 mmol) were mixed with Al_2O_3 (3.68 g) in the absence of any organic solvent and then submitted for 2 min to microwave irradiation inside a domestic microwave oven (Sam Sung, RE-555 TCW). The reaction mixture was dissolved in ethyl acetate. Al_2O_3 was filtered off and the filtrate was concentrated by rotary evaporator. The crude product was purified using column chromatography to give 13 (1.35 g, 5.15 mmol, 90%) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$) 10.90 (1H, d, NH, J = 13.4 Hz), 8,56 (1H, vinyl H, d, J = 13.7 Hz), 7.41(2H, aromatic ortho-H, m),7.15(3H, m, aromatic meta and para H), 4.28 (4H, two $O\underline{CH_2}$, q, J = 7.1 Hz), 1.40–1.30 (6H, two $\underline{CH_3}$, t, J = 7.1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) 169.5(C═O), 165.1(C═O), 152.3(vinyl H), 139.2(Ar), 130.2(Ar), 125.3(Ar), 117.6(>C═), 60.8(OCH_2), 60.5 (OCH_2), 14.8(CH_3), 14.7(CH_3). Anal. Calcd for $C_{14}H_{17}NO_4$═C63.87 H6.51; Found C63.81, H6.55.

Typical microwave procedure for 2-phenylsulfanylmethylene-malonic acid diethyl ester, 14. (Table 4, entry 15) EMME (1.10 g, 5.09 mmol), thiophenol (0.67 g, 6.10 mmol, 1.2 eq.) and KF (0.29 g, 5.09 mmole) were mixed with Al_2O_3 (4.12 g) in the absence of any organic solvent and then submitted for 2 min to microwave irradiation inside a domestic microwave oven (Sam Sung, RE-555 TCW). The product was isolated as described above and purified by column chromatography to give 14 (1.41 g, 5.03 mmol, 99 %) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$) 8.40 (1H, vinyl H, s), 7.47 (5H, aromatic H, m), 4.37 (2H, $O\underline{CH_2}$, q, J = 7.1 Hz), 4.23 (2H, $O\underline{CH_2}$, q, J = 7.1 Hz), 1.38 (3H, $\underline{CH_3}$, t, J = 7.1 Hz), 1.28 (3H, $\underline{CH_3}$, t, J = 7.1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) 163.7(C═O), 165.0(C═O), 160.8(vinyl H), 135.4(Ar), 131.7(Ar), 130.0(Ar), 129.4(Ar), 119.0(>C═), 61.8(OCH_2), 61.6 (OCH_2), 14.7(CH_3), 14.6 (CH_3). Anal. Calcd for $C_{14}H_{16}O_4S$ = C59.98,H5.75; Found C59.82, H5.79.

ACKNOWLEDGMENTS

This work was supported by grant from the Kyungsung University research foundation (2003) and Basic Research Program of the Korea Science & Engineering Foundation (KOSEF R05-2003-000-11732-0).

REFERENCES

1. Chung, S. K.; Sun, J. H. *Kor. J. Med. Chem.* **1992**, *5*, 38–42.
2. Deady, L. W.; Quazi, N. H. *J. Heterocyclic Chem.* **1994**, *31* (4), 793–796.
3. Siim, B. G.; Atwell, G. J.; Anderson, R. F.; Wardman, P.; Pullen, S. M.; Wilson, W. R.; Denny, W. A. *J. Med. Chem.* **1997**, *40* (9), 1381–1390.
4. Garcon, S.; Vassiliou, S.; Cavicchioli, M.; Hartmann, B.; Monteiro, N.; Balme, G. *J. Org. Chem.* **2001**, *66* (11), 4069–4073.
5. Michaud, D.; Abdallah-El, A. S.; Dozias, M. J.; Toupet, L.; Texier-Boullet, F.; Hamelin, J. *J. Chem. Soc., Chem. Commun.* **1997**, 1613.
6. Kim, Y. M.; Kwon, T. W.; Chung, S. K.; Smith, M. B. *Synthetic Commun.* **1999**, *29* (2), 343–350.
7. Vanden Eynde, J. J.; Hecq, N.; Kataeva, O.; Kappe, C. O. *Tetrahedron* **2001**, *57* (9), 1785–1791.
8. Romanova, N. N.; Gravis, A. G.; Shaidullina, G. M.; Leshcheva, I. F.; Bundel, Y. G. *Mendeleev Commun.* **1997**, *6*, 235–236.
9. Hakkou, H.; Vanden; Eynde, J.J.; Hamelin, J.; Bazureau, J. P. *Tetrahedron* **2004**, *60* (17), 3745–3753.
10. Romanova, N. N.; Gravis, A. G.; Leshcheva, I. F.; Bundel', Y. G. *Mendeleev Commun.* **1998**, *4*, 147–148.
11. Matloubi-Moghaddan, F. M.; Mohammadi, M.; Hosseinnia, A. *Syn. Commun.* **2000**, *20* (4), 643–650.
12. Sharma, U.; Bora, U.; Boruah, R. C.; Sandu, J. *Tetrahedron Lett.* **2002**, *43*, 143–145.
13. Martin-Aranda, R. M.; Vicente-Rodriguez, M. A.; Lopez-Pestana, J. M.; Lopez-Peinado, A. J.; Jerez, A.; Lopez-Gonzalez, J. D.; Banares-Munoz, M. A. *J. Mol. Catalysis A: Chemical* **1997**, *124*, 115–121.
14. Kaupp, G.; Naimi-Jamal, R.; Schmeyer, J. *Tetrahedron* **2003**, *59*, 3753–3760.
15. Michaud, D.; Hamelin, J.; Texier-Boullet, F. *Tetrahedron* **2003**, *59*, 3323–3331.
16. Egri, G.; Fogassy, E.; Novak, L.; Poppe, L. *Tetrahedron Asymm.* **1997**, *8*, 547–557.
17. Baldwin, J. E.; Thomas, R. C.; Kruse, L. I.; Silberman, L. *J. Org. Chem.* **1977**, *42*, 3846–3852.
18. Baldwin, J. E.; Cutting, W.; Dupont, L. I.; Kruse, L. I.; Silberman, L.; Thomas, R. C. *J. Chem. Soc. Chem. Commun.* **1976**, 736.