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

Solid-Liquid Phase Transfer Catalytic Synthesis. XI. The Convenient and Efficient Alkylation of Ethyl Phenylmercapto-Acetate in the Presence of Quaternary Ammonium Salts Under Microwave Irradiation

Runhua Deng [a] , Yuliang Wang [a] & Yaozhong Jiang [a]
[a] Chengdu Institute of Organic Chemistry, Academia Sinica , Chengdu, 610041, P. R. China

To cite this article: Runhua Deng , Yuliang Wang & Yaozhong Jiang (1994) Solid-Liquid Phase Transfer Catalytic Synthesis. XI. The Convenient and Efficient Alkylation of Ethyl Phenylmercapto-Acetate in the Presence of Quaternary Ammonium Salts Under Microwave Irradiation, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 24:13, 1917-1921, DOI: 10.1080/00397919408010199

To link to this article: http://dx.doi.org/10.1080/00397919408010199

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

Downloaded by [UQ Library] at 22:19 02 February 2015

SYNTHETIC COMMUNICATIONS, 24(13), 1917-1921 (1994)

SOLID–LIQUID PHASE TRANSFER CATALYTIC SYNTHESIS XI: THE CONVENIENT AND EFFICIENT ALKYLATION OF ETHYL PHENYLMERCAPTO–ACETATE IN THE PRESENCE OF QUATERNARY AMMONIUM SALTS UNDER MICROWAVE IRRADIATION

Deng, Runhua; Wang, Yuliang; Jiang, Yaozhong*

Chengdu Institute of Organic Chemistry, Academia Sinica; Chengdu 610041, P. R. China.

ABSTRACT: The rapid alkylation of ethyl phenylmercapto–acetate with a series of halides was performed in 650W domestic microwave oven to yield the alkylated products in 58 to 83%.

Recently the rapid heating capability of microwave oven has been used in the organic synthesis. [1–4] In previous papers [5–8] we have reported rapid alkylations under microwave irradiation, a new and convenient alkylation synthetic method. Here we would like to describe the procedure to perform rapid and efficient alkylation of ethyl phenylmercapto–acetate in the absence of solvent in microwave oven, using TBAC (tetra–butyl ammonium chloride) as phase transfer catalysis.

---

* To whom correspondence should be addressed.

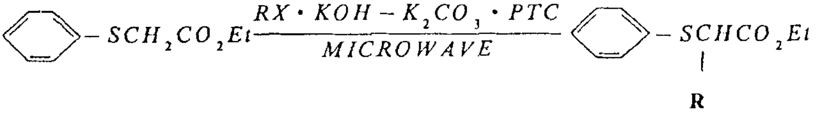
Table 1: Alkylation of ethyl phenylmercapto–acetate

alkyl halide	mol. ratio (RX:Subst.)	power level^a	irradiation time(min.)	isolated yield
Ph–CH_2Cl	1:1	3	4.5	83
$CH_2=CHCH_2Br$	1:1	2	3.5	67
p–$ClC_6H_4CH_2Br^b$	2:1	5	4	61
$CH_3(CH_2)_3Br$	1:1	8	4.5	59
m–$CH_3OC_6H_4CH_2Cl$	1:1	6	4.5	58

a. maximum power 650W, power scale 1–10.

b. add 1 mL toluene, dialkylated product.

The synthetic route is as follows:



(1) (2)

The alkylation of **(1)** was simply achieved by microwave irradiation of the mixture of ethyl phenylmercapto–acetate, alkyl halide, potassium hydroxide–potassium carbonate (1:2) and PTC (tetra–butyl ammonium chloride) for 3.5–4.5 min. The alkylated ethyl phenylmercapto–acetate was isolated after purification in 58–83% yield. The microwave power and the irradiation time were changed according to the activity of alkyl halides (Table 1).

When p–chlorobenzyl bromide was used, we fail to mix it with substrate well, so we added 1 mL toluene in order to solve this problem. In this reaction we obtained the dialkylated product (Table 1).

All the products were characterised by IR, ^1H–NMR and MS (Table 2).

Experimental

General considerations: IR spectra were recorded on a Beckman 620 infrared spectrometer; ^1H–NMR spectra were measured on a Varian

Table 2: Analytical date of compounds

products	IR (cm^{-1})	^{1}H−NMR(DCCl$_3$) δ.J(Hz).	MS m / z(%)
2a	1730,1580 1380,1260 740.	7.35−7.05 〔10H,m,(Ar−H)〕 ; 4.45(2H,d.J = 6Hz);3.45 (3H,m.);1.2(3H,t,J = 7Hz).	286(M^+100)
2b	1725,1640 1380, 920 700.	7.65−7.15(5H,m,Ar−H);6.1−4.9 (3H,m,−CH = CH_2);4.1(2H,d,J = 6Hz); 3.6(1H,t,J = 7Hz);2.55(2H, d,J = 7Hz);1.2(3H,t,J = 7Hz).	236(M^+83.45) 161(100)
2c	1730,1600 1490,1100 700.	7.1−6.75(13H,m,Ar−H);3.9 (2H,q,J = 7Hz);3(4H,s); 1.1(3H,t,J = 7Hz).	444(M^+29.14) 110(100)
2d	1730,1580 1380, 690	7.5−7.0(5H,m,Ar−H);4.05 (2H,q,J = 7Hz);3.6(1H,t,J = 7Hz); 1.75(2H,q,J = 6Hz);1.65−0.75(4H.m); 1.2(3H,t,J = 7Hz);0.85(3H,t,J = 6Hz).	252(M^+42.56) 224(100)
2e	1730,1600 1380,1270 700.	7.40−6.75(9H,m,Ar−H);4.5 (2H,d,J = 6Hz);3.85(3H,S,) 3.55(3H,m.);1.2 (3H,t,J = 7Hz).	316(M^+12.09) 122(100)

FT−80A instrument using TMS as an internal standard; MS date were obtained at 70eV using a HP−5988A instrument; K_2CO_3 was grounded and dried at 500℃ for 4h, then KOH was ground and mixed with the cooled K_2CO_3 powder.

General procedure for the alkylation of ethyl phenylmercapto−acetate: Ethyl phenylmercapto−acetate 0.98g (5.0mmol), benzyl chloride 0.65g (5.0mmol), KOH−K_2CO_3 (1:2) 4.0g (13mmol) and tetra−butyl ammonium chloride 0.15g (0.50mmol) was added into an open container and mixed well. The mixture was introduced into a 650W domestic microwave oven and irradiation was carried out for 4.5 min. (at power level 3). Then 50mL ether was poured into cooled mixture, filtration, concentration and followed by purification through column chromotography (silica gel 100−200 mesh; eluent: petroleum ether: ether 6:1) to give ethyl α−phenylmercapto−phenylpropionate. yield: (83%).

Acknowledgement: We are grateful to the support of the National Natural Science Foundation of China.

References:

1. Gedye, R.; Smith, F., Westaway, K.; Ali, H.; Baldisera, L.; Laberge, L.; Rousell, J.; Tetrahedron Lett., 1986, 73(3), 279−82.
2. Giguere, R. J.; Namen, A. M.; Lopez, B. O.; Arepally, A.; Ramos, D. E.; Tetrahedron Lett., 1987, 28(52), 6553−6.
3. Gutierrez, E.; Loupy, A.; Bram, G.; Ruiz−hitzky, E.; Tetrahedron Lett., 1989, 30, 945.
4. Bram, G.; Loupy, A.; Majdoub, M.; Synth. Commun., 1990, 20(1), 125−9.
5. Wang, Yuliang; Jiang, Yaozhong; Synth, Commun., 1992, 22 (15), 2287.
6. Deng, Runhua; Jiang, Yaozhong; Chinese Journal of Synth. Chem., 1993, 1(1), 85.
7. Deng, Runhua; Mi, Aiqiao; Jiang, Yaozhong; Chinese Chemical Letters, 1993, 4, 381−4.

8. Deng, Runhua; Mi, Aiqiao; Jiang, Yaozhong; Chinese journal of Applied Chem., 1993, 10(5): 108–109.

(Received in the USA 13 December 1993)