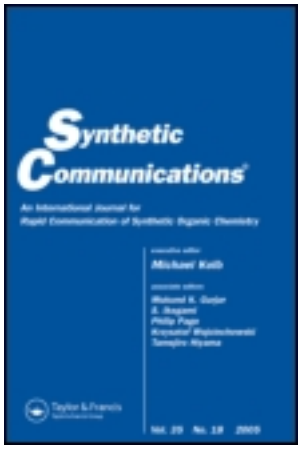


Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

SH-Methylation of SH-Containing Heterocycles with Dimethyl Carbonate via Phase-Transfer Catalytic Reaction

Jian-Gang Xie [a b], Jing Quan [a], Shu-Bai Li [a], Yan Zheng [a] & Li-Min Zhu [a]

[a] College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai, China

[b] Department of Chemistry, Zhengzhou Teachers College, Zhengzhou, China

Version of record first published: 25 Feb 2011.

To cite this article: Jian-Gang Xie, Jing Quan, Shu-Bai Li, Yan Zheng & Li-Min Zhu (2011): SH-Methylation of SH-Containing Heterocycles with Dimethyl Carbonate via Phase-Transfer Catalytic Reaction, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 41:6, 871-878

To link to this article: http://dx.doi.org/10.1080/00397911003707048

Synthetic Communications®, 41: 871–878, 2011

ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397911003707048

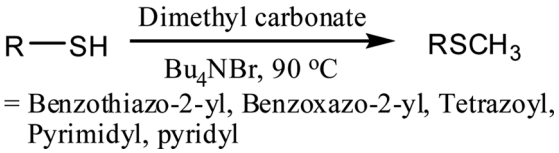
Taylor & Francis
Taylor & Francis Group

SH-METHYLATION OF SH-CONTAINING HETEROCYCLES WITH DIMETHYL CARBONATE VIA PHASE-TRANSFER CATALYTIC REACTION

Jian-Gang Xie,[1,2] Jing Quan,[1] Shu-Bai Li,[1] Yan Zheng,[1] and Li-Min Zhu[1]

[1]*College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai, China*
[2]*Department of Chemistry, Zhengzhou Teachers College, Zhengzhou, China*

GRAPHICAL ABSTRACT



Abstract *A reaction of SH-containing heterocycles with dimethyl carbonate (DMC) in the presence of K_2CO_3 and tetrabutylammonium bromide (Bu_4NBr) gave heteroaryl methyl thioethers in 44–93% yields. The reaction was carried out under mild conditions. This method provided a useful synthetic method for preparation of various heteroaryl methyl thioethers without the use of toxic methylic halides or dimethyl sulfate.*

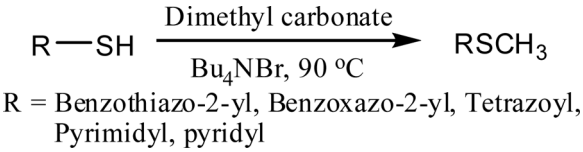
Keywords Dimethyl carbonate; methylation; phase-transfer catalyst; SH-containing heterocycle; thioether

INTRODUCTION

S-Methylation of thiols is a useful reaction in organic synthesis because of its wide applications. The SH-group can be protected as methyl thioether, or after oxidation as disulfate, from which it can be regenerated by reduction.[1] At present, the most commonly used method for the preparation of methyl thioethers is the methylation with methylic halides[2–4] or dimethyl sulfate.[5,6] However, substrate dependency and operational practicality have limited the use of these strategies in methyl thioether synthesis because of the highly toxic reagents and generation of stoichiometric amounts of salt for disposal. For these reasons, dimethyl carbonate (DMC) has emerged as a suitable alternative green methylating agent that is nontoxic and has less negative environmental impact in methylation.[7–10] Its various

Received May 24, 2009.

Address correspondence to Li-Min Zhu, College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai 201620, China. E-mail: lzhu@dhu.edu.cn



Scheme 1. The route of SH-methylation of heterocyles with DMC promoted by Bu_4NBr.

reactivity has given it great potential as a reagent for the methylation of several O-,[11] N-,[12] and S-nucleophiles.[13] For the SH-methylation of SH-containing heterocycles, there are few reports on the preparation of heteroaryl methyl thioethers by reaction of thiols with DMC using a phase-transfer catalyst (PTC) with the exception of the reaction of 2-mercaptopyridine with DMC in the presence of K_2CO_3 and 18-crown-6, reported by Lissel et al.[13b] Moreover, it should be noted that crown ethers are expensive and toxic. In conjunction with our interest in readily accessing diversified sulfoxide and sulfone, there is a need to develop a simple and efficient method for the construction of heteroaryl methyl thioethers.

In this communication, we report a simple, rapid, efficient, and environmentally friendly method for the synthesis of heteroaryl methyl thioethers (Scheme 1). Simple stirring of a mixture of various SH-containing heterocycles compounds, tetrabutylammonium bromide (Bu_4NBr), and K_2CO_3 in the presence of excess DMC for 1–6 h gave the desired heteroaryl methyl thioethers in excellent yields. The products were characterized by ^1H NMR, ^{13}C NMR, mass spectroscopy (MS), and melting points, which were consistent with the literature data.

RESULTS AND DISCUSSION

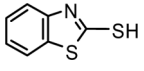
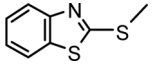
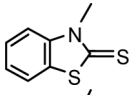
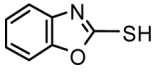
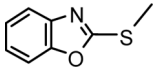
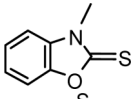
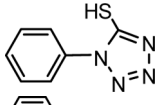
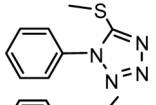
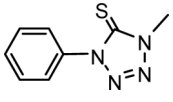
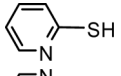
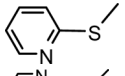
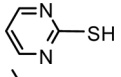
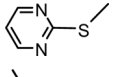
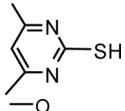
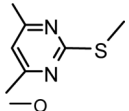
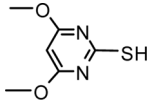
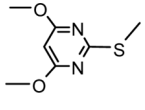
To investigate the catalytic activity of quaternary ammonium salts and the effect of base, the reaction of 2-mercaptobenzothiazole (MBT) with DMC was selected as a

Table 1. SH-Methylation of 2-mercaptobenzothiazole under different reaction conditions[a]

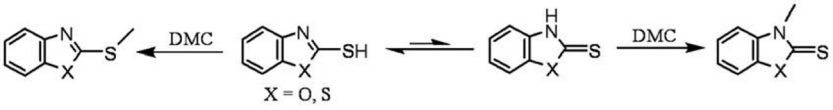
Entry	Catalyst[b]	Base[c]	Time (h)	Yield[d] (%)
1	None	None	20	—
2	None	K_2CO_3	20	<5
3	Bu_4NBr	None	20	<5
4	Bu_4NBr	K_2CO_3	18	72[e]
5	Bu_4NBr	K_2CO_3	3	76
6	Bu_4NBr	NaOH	3	63
7	Bu_4NBr	KOH	3	68
8	Et_4NOH	K_2CO_3	3	54
9	Et_4NBr	K_2CO_3	3	72
10	$Et_3(PhCH_2)NCl$	K_2CO_3	3	30
11	$(CH_3)_4NBr$	K_2CO_3	3	44
12	$(CH_3)_4NCl$	K_2CO_3	3	47

[a]Reaction conditions: 2-mercaptobenzothiazole = 10 mmol, DMC = 180 mmol, temperature = 90 °C.
[b]Ammonium quaternary salt = 2 mmol.
[c]Base = 15 mmol.
[d]Isolated yields based on 2-mercaptobenzothiazole after column chromatography.
[e]Temperature = 70 °C.

Table 2. Effect of reaction conditions on yield of the reaction of SH-containing heterocyclic compounds with DMC[a]

Entry	Substrates	Product		Time (h)	Yield[b] (%)		Mp (lit.) (°C)	
		S-Methyl	N-Methyl		S-Methyl	N-Methyl	S-Methyl	N-Methyl
1				3	76	11	45–47 (48)[2]	91–93 (92–94)[14]
2				4	62	7	Oil	131–133 (133)[15]
3				5	59	Trace	81–82 (82)[16]	45–47 (47)[17]
4			—	2	89	—	Oil	—
5			—	2.5	91	—	Oil	—
6			—	1	93	—	Oil	—
7			—	6	44	—	54–56	—

[a]Reaction conditions: substrates = 10 mmol, DMC = 180 mmol, Bu_4NBr = 2 mmol, base = 15 mmol, temperature = 90 °C.
[b]Isolated yields after column chromatography.



Scheme 2. Possible mechanism of the reaction of 2-mercaptobenzothia(xa)zole with DMC.

model reaction. The reaction was carried out at 90 °C, and the results are shown in Table 1. When the mixture of DMC and MBT was heated to 90 °C in the absence of base and catalyst, no products were detected. Similarly, the reaction was very slow without the base or catalyst at the same condition, and only trace amounts of products were detected after 20 h. This problem was overcome by using the base in conjunction with the catalyst. However, the amount of SH-methylation can be altered by changing the reaction conditions. To optimize the reaction conditions, we examined the reaction by changing the temperature, the base, and the catalyst (entries 4–12). From Table 1, we found that K_2CO_3–Bu_4NBr was the most efficient catalyst system and gave the greatest yield of 2-methylthiobenzothiazole (76%).

On the basis of the results in Table 1, we focused our studies on the application of K_2CO_3 and Bu_4NBr to SH-methylation of different SH-containing heterocycles with DMC. The results are summarized in Table 2. In some cases, heteroaryl methyl thioethers were obtained in good yields (entries 4–6).

The reaction of MBT with DMC within 3 h gave a mixture of SH-methylated and N-methylated products. Along with 76% of 2-(methylthio)benzothiazole, an N-methylated by-product, 3-methyl-2(3H)-benzothiazolethione, was also produced in 11% yield. Under the same reaction conditions, 62% of the desired product, 2-(methylthio)benzoxazole, was obtained within 4 h. N-methylated by-product, 3-methyl-2(3H)-benzoxazolethione, was also produced in 7% yield. The 5-methylthio-1-phenyltetrazole yield of 59% was obtained in 5 h, when 5-mercapto-1-phenyltetrazole was used as substrate. The N-methylated by-product, 4-methyl-1-phenyltetrazolethione, was also produced in trace amounts. A possible mechanism of this reaction is shown in Scheme 2.[18]

2-Mercaptopyridine, 2-mercaptopyrimidine, and 4,6-dimethyl-2-mercaptopyrimidine can be converted into their corresponding thioethers with good selectivity and yields, and no N-methylation products were obtained. 2-(Methylthio)pyridine was obtained in 89% yield within 2 h, and 91% of the desired product, 2-(methylthio) pyrimidine, was obtained within 2.5 h. Sulfides containing electron-donating groups, such as 4,6-dimethyl-2-mercaptopyrimidine, gave fast reaction rates with reaction times from 1 h. 4,6-Dimethyl-2-(methylthio)pyrimidine was obtained in 93% yield. However, the reaction of 4,6-dimethoxy-2-mercaptopyrimidine with DMC was slow, and it took 6 h to convert 4,6-dimethoxy-2-mercaptopyrimidine to the desired products. To our surprise, 4,6-dimethoxy-2-(methylthio)pyrimidine was obtained in 44% yield, possibly because of side reactions.

CONCLUSION

The SH-methylation of some kinds of SH-containing heterocycles with DMC was studied in the presence of K_2CO_3 and Bu_4NBr. Methylation with DMC has been

found to be a convenient method to prepare heteroaryl methyl thioethers. The reactions were carried out at 90 °C under atmospheric pressure. K_2CO_3–Bu_4NBr showed high catalytic activity for SH-methylating types of mercapto groups on heterocyclic rings. SH-Containing heterocycles can be converted into their corresponding thioethers with good selectivity and yields. Therefore, it provides an alternative clean and easy route to SH-methylated reaction of SH-containing heterocycles.

EXPERIMENTAL

All materials are commercially available and were used without further purification. Melting points were determined on a digital melting-point apparatus and were not corrected. The structures of products were determined by ^1H NMR and ^{13}C NMR (Bruker DRX 400-MHz NMR spectrometer, Germany) at 400 and 100 MHz, respectively. $CDCl_3$ was used as solvent. Chemical shifts were given in parts per million (ppm) relative to tetramethylsilane (TMS) as internal standard. The electrospray ionization–mass spectra (ESI-MS) were recorded on a Shimadzu LCMS-QP 2010 spectrometer.

General Procedure for the Reaction

MBT (10 mmol), Bu_4NBr (2 mmol), and K_2CO_3 (15 mmol) were added in DMC (180 mmol). The reaction mixture was stirred for 3 h at 90 °C under atmospheric pressure. Reaction was monitored by thin-layer chromatography (TLC). After the reaction, K_2CO_3 was recovered simply by filtration. The resulting mixture was washed with water (2×10 mL). The Bu_4NBr recovered in the aqueous phase can be regenerated.[11c,19] The aqueous phase was extracted with Et_2O (2×10 mL). The combined organic layers were dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure to give the crude product, which was purified by preparative column chromatography (silica gel). The other syntheses were performed under identical reaction conditions.

Selected Spectral Data

2-(Methylthio)benzothiazole. ^1H NMR (400 MHz, $CDCl_3$): δ 2.77 (s, 3H), 7.24–7.28 (m, 1H), 7.37–7.41 (m, 1H), 7.74 (d, 1H), 7.87 (d, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.9, 119.9, 120.3, 123.0, 125.0, 134.1, 152.3, 167.0; MS: m/z, 181 [M^+], 148, 136, 108, 69, 45.

3-Methyl-2(3h)-benzothiazolethione. ^1H NMR (400 MHz, $CDCl_3$): δ 3.86 (s, 3H), 7.19–7.32 (m, 2H), 7.40–7.49 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 32.1, 111.3, 120.2, 123.8, 125.9, 126.5, 141.0, 188.4; MS: m/z, 181 [M^+], 148, 136, 104.

2-(Methylthio)benzoxazole. ^1H NMR (400 MHz, $CDCl_3$): δ 2.85 (s, 3H), 7.30–7.39 (m, 2H), 7.53 (d, 1H), 7.71–7.73 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.8, 112.1, 120.6, 126.0, 126.5, 144.2, 154.2, 167.9; MS: m/z, 165 [M^+], 150, 132, 122, 97, 83, 70, 57.

3-Methyl-2(3h)-benzoxazolethione. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.87 (s, 3H), 7.27 (d, 2H), 7.27–7.51 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 31.9, 109.2, 110.3, 124.3, 124.9, 132.4, 147.1, 180.6; MS: m/z, 165 [M^+], 132, 122, 77.

5-Methylthio-1-phenyltetrazole. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.98 (s, 3H), 7.69–7.73 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.4, 123.7, 129.8, 130.1, 133.6, 154.9; MS: m/z, 192 [M^+], 164, 117, 91, 77, 65, 51.

2-(Methylthio)pyridine. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.54 (s, 3H), 6.92–6.95 (m, 1H), 7.16 (d, 1H), 7.42–7.46 (m, 1H), 8.41–8.42 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.1, 118.0, 120.3, 134.6, 148.3, 158.9; MS: m/z, 125 [M^+], 79, 57, 52, 39.

2-(Methylthio)pyrimidine. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.55 (s, 3H), 6.94–6.98 (m, 1H), 8.49–8.51 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.2, 118.5, 159.3, 175.0; MS: m/z, 126 [M^+], 80, 68, 53, 40.

4,6-Dimethyl-2-(methylthio)pyrimidine. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.39 (s, 6H), 2.55 (s, 3H), 6.67 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.8, 22.6, 114.3, 165.6, 170.4; MS: m/z, 154 [M^+], 108, 93, 81, 67, 45, 40.

4,6-Dimethoxy-2-(methylthio)pyrimidine. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.54 (s, 3H), 3.92 (s, 6H), 5.72 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.1, 53.1, 84.5, 165.6, 170.0, 170.2; MS: m/z, 186 [M^+], 171, 140, 125, 69, 55.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (50773009) and by the Program for Changjiang Scholars and Innovative Research Team in University (IRT0526).

REFERENCES

1. Shah, S. T. A.; Khan, K. M.; Martinez Heinrich, A.; Voelter, W. An alternative approach towards the syntheses of thioethers and thioesters using CsF-celite in acetonitrile. *Tetrahedron Lett.* **2002**, *43*, 8281–8283.
2. Narkhede, H. P.; More, U. B.; Dalal, D. S.; Pawar, N. S.; More, D. H.; Mahulikar, P. P. Fly-ash-supported synthesis of 2-mercaptobenzothiazole derivatives under microwave irradiation. *Synth. Commun.* **2007**, *37*, 573–577.
3. Mauleón, P.; Alonso, I.; Rodríguez Rivero, M.; Carretero, J. C. Enantioselective synthesis of chiral sulfones by Rh-catalyzed asymmetric addition of boronic acids to α,β-unsaturated 2-pyridyl sulfones. *J. Org. Chem.* **2007**, *72*, 9924–9935.
4. Hu, Y.; Chen, Z. C.; Le, Z. G.; Zheng, Q. G. Organic reactions in ionic liquids: An efficient method for selective S-alkylation of 2-mercaptobenzothia(xa)zole with alkyl halides. *Synth. Commun.* **2004**, *34*, 2039–2046.
5. Vlassa, M.; Kezdi, M.; Goia, I. Application of phase-transfer catalysis in the acridine series I:S-Alkylation and S-acylation of thioacridone and of some halogenated thioacridone derivatives. *Synthesis* **1980**, *10*, 850–851.
6. Heravi, M. M.; Ahari, N. Z.; Oskooie, H. A.; Ghassemzadeh, M. Solid state S-methylation of thiols and O-methylation of phenols and naphthols with dimethyl

sulfate under microwave irradiation. *Phosphorus, Sulfur Silicon Relat. Elem.* **2005**, *180*, 1701–1712.
7. Shaikh, A. A.; Sivaram, S. Organic carbonates. *Chem. Rev.* **1996**, *96*, 951–976.
8. Ono, Y. Catalysis in the production and reactions of dimethyl carbonate, an environmentally benign building block. *Appl. Catal. A.* **1997**, *155*, 133–166.
9. Tundo, P. New developments in dimethyl carbonate chemistry. *Pure Appl. Chem.* **2001**, *73*, 1117–1124.
10. Tundo, P.; Selva, M. The chemistry of dimethyl carbonate. *Acc. Chem. Res.* **2002**, *35*, 706–716.
11. (a) Janin, Y. L.; Chiki, J.; Legraverend, M.; Huel, C.; Bisagni, E. On the methylation of 3-cyano-6-hydroxypyridin-2(1H)-ones. *Tetrahedron* **1999**, *55*, 12797–12804; (b) Jyothi, T. M.; Raja, T.; Talawar, M. B.; Rao, B. S. Selective O-methylation of catechol using dimethyl carbonate over calcined Mg-Al hydrotalcites. *Appl. Catal. A.* **2001**, *211*, 41–46; (c) Ouk, S.; Thiébaud, S.; Borredon, E.; Legars, P.; Lecomte, L. O-Methylation of phenolic compounds with dimethyl carbonate in solid/liquid phase transfer systems. *Tetrahedron Lett.* **2002**, *43*, 2661–2663; (d) Ouk, S.; Thiébaud, S.; Borredon, E.; Legars, P. High-performance method for O-methylation of phenol with dimethyl carbonate. *Appl. Catal. A.* **2003**, *241*, 227–233; (e) Romero, M. D.; Ovejero, G.; Rodriguez, A.; Gomez, J. M.; Agueda, I. O-Methylation of phenol in liquid phase over basic zeolites. *Ind. Eng. Chem. Res.* **2004**, *43*, 8194–8199; (f) Shen, Z. L.; Jiang, X. Z.; Mo, W. M.; Hu, B. X.; Sun, N. Catalytic O-methylation of phenols with dimethyl carbonate to aryl methyl ethers using [BMIm]Cl. *Green Chem.* **2005**, *7*, 97–99; (g) Luque, R.; Campelo, J. M.; Conesa, T. D.; Luna, D.; Marinas, J. M.; Romero, A. A. Catechol O-methylation with dimethyl carbonate over different acid–base catalysts. *New J. Chem.* **2006**, *30*, 1228–1234; (h) Wu, G. D.; Wang, X. L.; Chen, B.; Li, J. P.; Zhao, N.; Wei, W.; Sun, Y. H. Fluorine-modified mesoporous Mg-Al mixed oxides: Mild and stable base catalysts for O-methylation of phenol with dimethyl carbonate. *Appl. Catal. A.* **2007**, *329*, 106–111.
12. (a) Jiang, X. L.; Tiwari, A.; Thompson, M.; Chen, Z. H.; Cleary, T. P.; Lee, T. B. K. A practical method for N-methylation of indoles using dimethyl carbonate. *Org. Proc. Res. Dev.* **2001**, *5*, 604–608; (b) Shieh, W. C.; Dell, S.; Repič, O. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) and microwave-accelerated green chemistry in methylation of phenols, indoles, and benzimidazoles with dimethyl carbonate. *Org. Lett.* **2001**, *3*, 4279–4281; (c) Selva, M.; Tundo, P.; Perosa, A. Reaction of functionalized anilines with dimethyl carbonate over NaY faujasite, 3: Chemoselectivity toward mono-N-methylation. *J. Org. Chem.* **2003**, *68*, 7374–7378; (d) Ouk, S.; Thiébaud, S.; Borredon, E.; Chabaud, B. N-Methylation of nitrogen-containing heterocycles with dimethyl carbonate. *Synth. Commun.* **2005**, *35*, 3021–3026; (e) Selva, M.; Perosa, A. Green chemistry metrics: A comparative evaluation of dimethyl carbonate, methyl iodide, dimethyl sulfate, and methanol as methylating agents. *Green Chem.* **2008**, *10*, 457–464; (f) Juárez, R.; Padilla, A.; Corma, A.; García, H. Organocatalysts for the reaction of dimethyl carbonate with 2,4-diaminotoluene. *Ind. Eng. Chem. Res.* **2008**, *47*, 8043–8047.
13. (a) Stanovnik, B.; Tišler, M.; Hribar, A.; Barlin, G. B.; Brown, D. J. Methylation of heterocyclic compounds containing imino, mercapto, and/or hydroxy groups by means of N,N-dimethylformamide dimethyl acetal. *Aust. J. Chem.* **1981**, *34*, 1729–1738; (b) Lissel, M.; Schmidt, S.; Neumann, B. Use of dimethyl carbonate as a methylating agent under phase-transfer-catalyzed conditions. *Synthesis* **1986**, 382–383; (c) Tundo, P.; Trotta, F.; Moraglio, G.; Ligorati, F. Continuous-flow processes under gas–liquid phase-transfer catalysis (GL-PTC) conditions: The reaction of dialkyl carbonates with phenols, alcohols, and mercaptans. *Ind. Eng. Chem. Res.* **1988**, *27*, 1565–1571; (d) Selva, M.; Tundo, P. Highly chemoselective methylation and esterification reactions with dimethyl carbonate in the presence of NaY faujasite: The case of mercaptophenols,

mercaptobenzoic acids, and carboxylic acids bearing OH substituents. *J. Org. Chem.* **2006**, *71*, 1464–1470.
14. Akiba, K.; Shiraishi, H.; Inamoto, N. Direct synthesis of 2,2-diaryl-3-methyl-2,3-dihydrobenzothiazoles from 3-methyl-2,3-dihydrobenzothiazole-2-thione and some mechanistic aspects. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 156–159.
15. Shridhar, D. R.; Jogibhukta, M.; Rao, P. S.; Handa, V. K. An improved method for the synthesis of 2-thioxo-2,3-dihydro-1,3-benzoxazoles [2(3H)-benzoxazolethiones]. *Synthesis.* **1983**, 936–937.
16. Quast, H.; Fuss, A.; Nahr, U. Photochemical formation of methylenecyclopropane analogs, 11: Photochemical elimination of nitrogen from phenyl-substituted 1,4-dihydro-5-imino-5H-tetrazoles: Products of phenyl-substituted tris(imino)methane diradicals. *Chem. Ber.* **1985**, *118*, 2164–2185.
17. Tochtermann, W.; Gustmann, H.; Wolff, C. Carbon-13 NMR spectra of heterocycles, 1: Nitrogen heterocycles, 1: The reaction of bis(5-tetrazolyl) disulfides with diazoalkanes. *Chem. Ber.* **1978**, *111*, 566–573.
18. Harizi, A.; Romdhane, A.; Mighri, Z. Synthesis and reactivity of benzoxa(thia)zol-2-thiones: new route to 2-alkylthiobenzoxa(thia)zoles. *Tetrahedron Lett.* **2000**, *41*, 5833–5835.
19. Berris, B. C. Recovery of quaternary ammonium salts from aqueous solution. U.S. Patent 5030757; *Chem. Abstr*. **1991**, *115*, 114015g.