This article was downloaded by: [Michigan State University] On: 08 March 2015, At: 11:31 Publisher: Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK





Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/gpss20

An Efficient and Straightforward Access to Symmetrical Dialkyl Trithiocarbonates Using a Basic Task-Specific Ionic Liquid and Carbon Disulfide

Soheil Sayyahi^a, Saeid Moonesi^b & Mehdi Fallah-Mehrjardi^c ^a Department of Chemistry, Mahshahr Branch, Islamic Azad University, Mahshahr, Iran

^b Department of Chemistry, Omidieh Branch, Islamic Azad University, Omidieh, Iran

^c Department of Marine Chemistry, Khoramshahr University of Marine Science and Technology, Khoramshahr, Iran Accepted author version posted online: 30 Apr 2014.Published online: 21 Oct 2014.

To cite this article: Soheil Sayyahi, Saeid Moonesi & Mehdi Fallah-Mehrjardi (2014) An Efficient and Straightforward Access to Symmetrical Dialkyl Trithiocarbonates Using a Basic Task-Specific Ionic Liquid and Carbon Disulfide, Phosphorus, Sulfur, and Silicon and the Related Elements, 189:11, 1718-1722, DOI: <u>10.1080/10426507.2014.887078</u>

To link to this article: <u>http://dx.doi.org/10.1080/10426507.2014.887078</u>

PLEASE SCROLL DOWN FOR ARTICLE

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 <u>http://www.tandfonline.com/page/terms-and-conditions</u>





AN EFFICIENT AND STRAIGHTFORWARD ACCESS TO SYMMETRICAL DIALKYL TRITHIOCARBONATES USING A BASIC TASK-SPECIFIC IONIC LIQUID AND CARBON DISULFIDE

Soheil Sayyahi,¹ Saeid Moonesi,² and Mehdi Fallah-Mehrjardi³

¹Department of Chemistry, Mahshahr Branch, Islamic Azad University, Mahshahr, Iran

²Department of Chemistry, Omidieh Branch, Islamic Azad University, Omidieh, Iran

³Department of Marine Chemistry, Khoramshahr University of Marine Science and Technology, Khoramshahr, Iran

GRAPHICAL ABSTRACT



Abstract We report an efficient one-pot route for the synthesis of symmetrical dialkyl trithiocarbonates from alkyl halides using carbon disulfide and a basic ionic liquid 1,1'-bis-methyl-3, 3-methylene-bisimidazolium dihydroxide as a reagent and phase-transfer catalyst.

Keywords Trithiocarbonate; basic ionic liquid; alkyl halides; carbon disulfide

INTRODUCTION

Since the introduction of the term "task-specific ionic liquids" (TSILs) by Professor J. H. Davis to describe a functionalized ionic liquid, this has been an area of rapid interest in the chemical literature.^{1–3} Different TSILs are synthesized with a particular application in mind and employed as a catalyst, reagent, and/or solvent in organic reactions.^{4,5} Among the three main classes of TSILs, acidic, neutral, and basic, much less attention has been paid to the basic ionic liquids in organic chemistry. Otherwise, it has been noted that replacing traditional bases (NaOH, KOH, NaHCO₃) with basic ionic liquids has advantages such as stability in water and air, easy separation, and high catalytic efficiency.⁶ They are flexible, nonvolatile, noncorrosive, and immiscible with many organic solvents.⁷

Received 21 October 2013; accepted 21 January 2014.

Address correspondence to Soheil Sayyahi, Department of Chemistry, Mahshahr Branch, Islamic Azad University, Mahshahr, Iran. E-mail: sayyahi.soheil@gmail.com

Trithiocarbonates are an important class of organic compounds that have found a wide range of application in industrial and medical chemistry. They have been employed as key precursors, intermediates, or a protection for thiol functionality in organic synthesis.^{8–14}

From several routes for the synthesis of trithiocarbonates, the dialkylation of in situ generated trithiocarbonate anion (CS_3^{2-}) with alkyl halide is most convenient.^{15,16} The reaction is carried out in the presence of carbon disulfide and under basic conditions, such as amberlyst A-26 (OH⁻),¹⁷ Cs₂CO₃/polar aprotic solvents,¹⁸ KF/Al₂O₃,¹⁶ *n*Bu₄NOH (20% in H₂O),¹⁹ basic Al₂O₃,²⁰ K₃PO₄,²¹ KOH/TBAB/Al₂O₃,²² Also, a phase-transfer catalyst has often been used to increase the yield and the reaction rate.²³

In the present study, we have discovered that a task-specific dicationic ionic liquid (TSDIL) 1,1'-bis-methyl-3, 3-methylenebisimidazolium dihydroxide (2) can act as a basic reagent and PTC and efficiently promotes the synthesis of trithiocarbonates from alkyl halides.

Dicationic imidazolium-based ionic liquids have been shown to possess superior physical properties in terms of thermal stability and volatility compared to traditional ionic liquids. They are able to dissolve all manner of polar and nonpolar molecules, including some proteins, peptides, polymers, and simple organic molecules.²⁴

RESULTS AND DISCUSSION

The ionic liquid was readily prepared by treatment of 1,1'-bis-methyl-3, 3-methylenebisimidazolium dichloride $(1)^{25,26}$ with KOH in dry dichloromethane for 12 h at room temperature (Scheme 1). The IR and ¹H NMR spectra of **2** exhibited the characteristic absorption at 3444 cm⁻¹ and resonance at $\delta = 4.71$ ppm corresponding to the hydroxide functionality.



Scheme 1 Preparation of 1,1'-bis-methyl-3, 3-methylenebisimidazolium dihydroxide.

Then, benzyl chloride was selected as a model alkyl halide to optimize the reaction condition by screening different amounts of the ionic liquid as catalyst and basic reagent. The best result was obtained when 2.0 mmol benzyl chloride reacted with a mixture of 1.5 mmol of the TSDIL in 3 mL CS_2 at 50°C under reflux conditions (Table 1). It was

Table 1Trithiocarbonation of benzyl chloride: effect of the basic ionic liquid 2^a

Conversion	Temperature	Time (min)	Catalyst (mmol)	Entry
N.R	50°C	120	_	1
Trace	50°C	120	0.25	2
Completed	50°C	75	1.0	3
Completed	50°C	35	1.5	4
Not completed	r.t.	120	1.5	5

^aBenzyl chloride (2 mmol), CS₂ (3 mL).



Scheme 2 Synthesis of trithiocarbonates using 1,1'-bis-methyl-3, 3-methylenebisimidazolium dihydroxide.

observed that adding some drops of water increased the reaction rate and conversion to the desire compounds according to thin layer chromatography analysis. This may be due to the addition of water causes to the decrease in the viscosity of the ionic liquid, which increases the solubility of the alkyl halides in CS_2 .

Under these conditions, different alkyl and benzyl halides afford symmetrical trithiocarbonates in good to excellent yields (Scheme 2 and Table 2).

Interestingly, the reaction of 1,2-dichloroethane gave 1,3-dithiolane-2-thione as a cyclic trithiocarbonate without the formation of any polymeric by-product (Entry 13). Since nucleophilic substitution of trithiocarbonate anion occurs under $S_N 2$ conditions,²² a low yield was obtained in the case of secondary alkyl halide and no product was isolated for the tertiary halide (Entries 14 and 15).

In all cases, the structure of products was established by comparison of their spectroscopic analyses with authentic samples.^{21,22} The compounds displayed a characteristic FTIR vibration bands of C = S at approximately 1050 to 1070 cm⁻¹. Also, the ¹³C NMR resonances at 222 to 227 ppm can be attributed to carbon of CS₃ group.

	2 R—X I.L (1.5 mmol), CS ₂ (3	mL) S	R
	50 °C		
Entry	Alkyl halide	Time (min)	Yield (%) ^a
1	C ₆ H ₅ CH ₂ Cl	35	92 ^{16,22}
2	$C_6H_5CH_2Br$	30	9016,22
3	C ₆ H ₅ CH ₂ CH ₂ Br	60	90 ²²
4	4-BrC ₆ H ₄ CH ₂ Cl	40	91 ²²
5	2,4-Cl ₂ C ₆ H ₃ CH ₂ Cl	75	92 ²²
6	2-FC ₆ H ₄ CH ₂ Cl	45	90 ²²
7	2-ClC ₆ H ₄ CH ₂ Cl	25	91 ²²
8	C ₁₀ H ₇ CH ₂ Cl	60	87 ²²
9	CH ₃ I	20	64 ¹⁶
10	<i>n</i> -BuCl	90	75 ¹⁷
11	$CH_2 = CHCH_2Cl$	45	77 ^{17,21}
12	$CH_2 = CHCH_2Br$	40	8217,21
13	ClCH ₂ CH ₂ Cl	60	60 ¹⁶
14	$(C_6H_5)_2CHBr$	90	55 ²²
15	C ₆ H ₅ C(CH ₃) ₂ Br	120	_

 Table 2 Conversion of various alkyl halides into corresponding trithiocarbonates

^aYields refer to isolated products.

Entry	Substrate, catalyst, condition	Time (min)	Yield (%)	
1	BnCl, basic Al ₂ O ₃ /CS ₂ , reflux ²⁰	240	85	
2	BnBr, K_3PO_4/CS_2 , DMF ²¹	600	92	
3	BnCl, TBAH/CS ₂ , $50^{\circ}C^{19}$	240	92	
4	BnBr, A-26 (OH ⁻)/CS ₂ , reflux ¹⁶	90	96	
5	BnCl, basic IL/CS ₂ , 50°C ^a	35	92	
6	BnBr, basic IL/CS ₂ , 50°C ^a	30	90	

Table 3 Comparison of the efficiency of 1,1'-bis-methyl-3, 3-methylenebisimidazolium dihydroxide with other reported catalysts in the synthesis of dibenzyl trithiocarbonate

^aThis work

The superiority of using 1,1'-bis-methyl-3, 3-methylenebisimidazolium dihydroxide as reagent and catalyst for the synthesis of a target product (dibenzyl trithiocarbonate) is shown by comparing with those of the previously reported methods (Table 3).

CONCLUSION

We have introduced a novel TSDIL (1,1'-bis-methyl-3, 3-methylenebisimidazolium dihydroxide) as a highly efficient basic reagent as well as a phase-transfer catalyst for the straightforward access to symmetrical dialkyl trithiocarbonates form alkyl halides. The reaction is simple, rapid and gives high product yields.

EXPERIMENTAL

All compounds were purchased from the supplier and used as received without further purification. Progress of the reaction was monitored by TLC on Merck DC-Alufolien plates precoated with silica gel F_{254} . Nuclear magnetic resonance spectra were recorded in CDCl₃ on a Bruker Avance DPX 400 MHz instrument spectrometer using TMS as internal standard. IR spectra were recorded on a Perkin-Elmer RX1 FTIR spectrometer.

General Procedure

A round-bottomed flask (25 mL) was charged with 1,1'-bis-methyl-3, 3-methylenebisimidazolium dihydroxide (0.318 g, 1.5 mmol) in carbon disulfide (3 mL) and the mixture was stirred vigorously for 15 min. To increase the solubility, 10 drops of water were used. Then, alkyl halide (2 mmol) was added and the suspension was stirred under reflux conditions (50°C) for the time as shown in Table 1. TLC analysis [*n*-hexane/ethyl acetate (10:1)] indicated the completion of the reaction. Next, the remaining CS₂ was evaporated, product was extracted with EtOAc (15 mL), and the organic phase was washed with water (3 × 5 mL), dried over Na₂SO₄ and then concentrated under reduced pressure to give the desired trithiocarbonate.

FUNDING

The financial support of this work by the Mahshahr Branch, Islamic Azad University, Iran is greatly appreciated. Also, the author, S. Moonesi, acknowledges the funding support received for part of this project from the Omidieh Branch Research Council, Islamic Azad University, Iran.

REFERENCES

- 1. Giernoth, R. Angew. Chem., Int. Ed. 2010, 49, 2834-2839.
- 2. Yue, C.; Fang, D.; Liu, L.; Yi, T.-F. J. Mol. Liq. 2011, 163, 99-121.
- 3. Davis, J. H. Chem. Lett. 2004, 33, 1072-1077.
- 4. Olivier-Bourbigou, H.; Magna, L.; Morvan, D. Appl. Catal., A. 2010, 373, 1-56.
- Ignat'ev, N. V.; Schulte, M.; Koppe, K.; Barthen, P.; Zlotin, S. G.; Makhova, N. N.; Sheremetev, A. B.; Valente, A. A. *Phosphorus, Sulfur Silicon Relat. Elem.* 2011, 186, 1205-1216.
- 6. Hajipour, A. R.; Rafiee, F. JICS. 2009, 6, 647-678.
- Abello, S.; Medina, F.; Rodriguez, X.; Cesteros, Y.; Salagre, P.; Sueiras, J. E.; Tichit, D.; Coq, B. Chem. Commun. 2004, 1096-1097.
- Chaturvedi, D.; Mishra, N.; Chaturvedi, A. K.; Mishra, V. Monatshefte f
 ür Chemie Chemical Monthly 2008, 139, 1467-1470.
- 9. Gholinejad, M. Eur. J. Org. Chem. 2013, 2013, 257-259.
- 10. Keddie, D. J.; Moad, G.; Rizzardo, E.; Thang, S. H. Macromolecules 2012, 45, 5321-5342.
- Dehmel, F.; Weinbrenner, S.; Julius, H.; Ciossek, T.; Maier, T.; Stengel, T.; Fettis, K.; Burkhardt, C.; Wieland, H.; Beckers, T. J. Med. Chem. 2008, 51, 3985-4001.
- 12. Carta, F.; Akdemir, A.; Scozzafava, A.; Masini, E.; Supuran, C. T. J. Med. Chem. 2013, 56, 4691-4700.
- 13. Wood, M. R.; Duncalf, D. J.; Rannard, S. P.; Perrier, S. Org. Lett. 2006, 8, 553-556.
- 14. Soleiman-Beigi, M.; Izadi, A. J. Chem. 2013, 2013, 1-5.
- 15. Godt, H. C.; Wann, R. E. J. Org. Chem. 1961, 26, 4047-4051.
- 16. Movassagh, B.; Soleiman-Beigi, M.; Nazari, M. Chem. Lett. 2008, 37, 22-23.
- 17. Tamami, B.; Kiasat, A. R. J. Chem. Res., Synop. 1998, 454-455.
- 18. Aoyagi, N.; Ochiai, B.; Mori, H.; Endo, T. Synlett 2006, 2006, 0636-0638.
- 19. Soleiman-Beigi, M.; Arzehgar, Z.; Movassagh, B. Synthesis 2010, 2010, 392-394.
- 20. Kiasat, A. R.; Kazemi, F.; Savari, A. Synth. Commun. 2008, 38, 1057-1063.
- 21. Movassagh, B.; Alapour, S. J. Sulfur Chem. 2012, 34, 222-226.
- 22. Kiasat, A. R.; Fallah-Mehrjardi, M. J. Chin. Chem. Soc. 2008, 55, 639-642.
- Sugawara, A.; Hasegawa, K.; Suzuki, K.-I.; Takahashi, Y.; Sato, R. Bull. Chem. Soc. Jpn. 1987, 60, 435-437.
- Payagala, T.; Huang, J.; Breitbach, Z. S.; Sharma, P. S.; Armstrong, D. W. Chem. Mater. 2007, 19, 5848-5850.
- 25. Sayyahi, S.; Rezaee, H. M.; Khalfabadi, F. S.; Gorjizadeh, M. J. Chem. Res. 2012, 36, 396-397.
- 26. Ahrens, S.; Strassner, T. Inorg. Chim. Acta 2006, 359, 4789-4796.