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Triton-B catalyzed, efficient and solvent-free approach for the synthesis of dithiocarbamates

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A novel one-pot, solvent-free method for the synthesis of dithiocarbamates was developed through the reaction of corresponding alkyl halides, amines and carbon disulfide employing catalytic amount of benzyl trimethyl ammonium hydroxide (Triton-B). The reaction conditions are milder with extremely simple work-up procedures than the reported methods, afforded high yields (82-98%) of the desired products.

1. Introduction

Organic dithiocarbamates have extensively been used as agrochemicals,[1] pharmaceuticals,[2]intermediates in organic synthesis,[3] protection of amino groups in peptide chemistry,[4] linkers in solid phase organic synthesis,[5] radical precursors in free-radical chemistry[6]and synthesis of ionic liquids.[7] Furthermore, different transition metal complexes of dithiocarbamates have been synthesized for various studies, primarily because of their applications as organic superconductors.[8]In recent years, dithiocarbamates have been emerged as a novel class of potential agrochemicals (e. g. pesticides,[9] herbicides,[10] insecticides,[11] fungicides [12]*etc.*) such as carbamorph, ziram, benzathiazole derivatives *etc.*(**Fig. 1**). As-pharmaceuticals, they have been used as drugs and prodrugs for the different type of biological activities such as anti-microbial,[13] anticancer,[14] antiprotozoal,[15] antileprosy,[16]antitubercular,[17] anti-fungal,[18] anti-alzheimer,[19] and contraceptive agents [20]*etc*. Furthermore, recently it has been realized through various published reports that by incorporating dithiocarbamate linkage into structurally diverse biologically potent synthetic/semisynthetic/natural

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molecules may lead to manifold increase in biological activities.[21]As a useful synthon, organic dithiocarbamates have been extensively used for the synthesis of structurally diverse biological potent scaffolds such as isothiocyanates,[22] thiourea,[23] cynamide,[24] dithiobenzophene,[25] glycosides,[26] amide,[27] dicarboxylates,[28] benzimidazole,[29] carbamate,[30] pyran,[31] flavonoids[32] *etc*. In view of their tremendous importance and wide applications, their syntheses have gained considerable attention, and therefore have become a focus of synthetic organic chemistry.

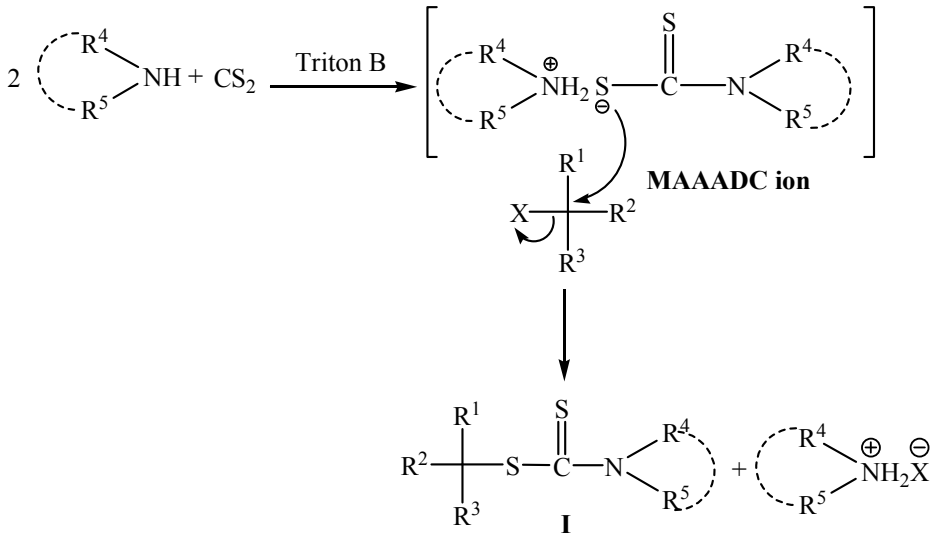
Traditional synthesis of organic dithiocarbamates involves use of phosgene[33] and its derivatives.[34] However, these methods are associated with several drawbacks like use of costly and toxic reagents such as thiophosgene and its derivatives, longer reaction time and lesser yield. Therefore, their syntheses has been changed from harmful reagents to abundantly available, cheap and safe reagent like carbon disulfide.[35] However, their formation using carbon disulfide employed harsh reaction conditions such a use of strong bases, higher reaction temperatures and longer reaction times.[36] Therefore, there is still need for the development of safer and efficient synthetic protocols for the syntheses of dithiocarbamates. Our group has been engaged from past several years for the development of new methodologies for the preparation of carbamates, dithiocarbamates and related compounds using cheap, abundantly available and safe reagents like carbon dioxide and carbon disulphide respectively.[37] In recent years, we found that Triton-B has emerged as a best catalyst for the synthesis of carbamates, dithiocarbamates, carbazates, dithiocarbazates, dithiocarbonates employing a variety of reagents and catalytic systems.[38] In the present communication, we report here an efficient and novel, one-pot, solvent-free synthesis ofdithiocarbamates starting from their corresponding alkyl halides, amines employing Triton B/CS_2 system.

2. Results and Discussion

In connection with our ongoing interest pertaining to the use of Triton-B (Fig. 1.) for the synthesis of carbamates, dithiocarbamates, carbazates, dithiocarbazates and dithiocarbonates (xanthates).[38] In the present paper, we wish to report a simple and effective one-pot procedure for the synthesis ofdithiocarbamates,through the nucleophilic attack of S^- ion of monoalkylammonium alkyl dithiocarbamate ion **2** (Figure 1.) upon the carbocation, generated from the electrophilic carbon of the corresponding alkyl halide (Scheme 1.). Thus, a mixture of amine and CS_2 were taken without any solvent and Triton-B was added into it with constant stirring at room temperature. It has been reported by our group that by reacting two molar ratio of amine with carbon dioxide afforded the corresponding monoalkylammonium alkyl carbamate (MAAAC) ion **1**, by adopting similar approach, monoalkylammonium alkyldithiocarbamate (MAAADC) ion **2** should be obtained through reaction of two molar equivalents of amine with CS_2 (**Fig. 1.**).

Fig. 1. Formation of MAAAC **1** & MAAADC **2** ions

CS_2 is more reactive than CO_2, therefore thereaction was tried at room temperature. It has been observed that the nucleophilicity of **2** could be increased by using basic phase transfer catalyst (PTC) like Triton-B. The nucleophilic attack of **2** to the electrophilic carbon of the corresponding alkyl halide may led to the corresponding dithiocarbamate (**Scheme 1**). The confirmation of product was made based on the spectroscopic and analytical data with our previously synthesized authentic dithiocarbamate. It is important to note here that amine used for this reaction should have at least one available hydrogen atom to help in the formation of **2**. Therefore, this reaction could not be successful for the dithiocarbamates synthesized from tertiary amines which do not have at least one hydrogen atom.



Scheme 1. Proposed mechanism of formation of dithiocarbamates of general formula **I**

In order to study the effects of various phase transfer catalysts (PTC) on the yield of the reaction, a reaction of phenyl ethyl chloride with *n*-butyl amine employing various phase transfer catalysts (PTC) such as tetra-*n*-butyl ammonium iodide (TBAI), tetra-*n*-butyl ammonium bromide (TBAB), tetra-*n*-butyl ammonium chloride (TBAC), tetra-*n*-butyl ammonium hydrogen sulfate (TBAHS), tetra-*n*-butyl ammonium hydrogen carbonate (TBAHC), and benzyl trimethyl ammonium hydroxide (Triton-B) etc. was tried. We found that Triton-B is the best in achieving high yields of the desired dithiocarbamates (**Table 1**).

Table 1. Effect of various phase transfer catalysts on the yield of dithiocarbamates

entry	Name of PTC	Time (hr.)	Yield (%)
1	TBAI	2	89
2	TBAB	2	88
3	TBAC	2.5	86
4	TBAHS	2.5	82
5	TBAHC	2	83
6	Triton B	1.5	91

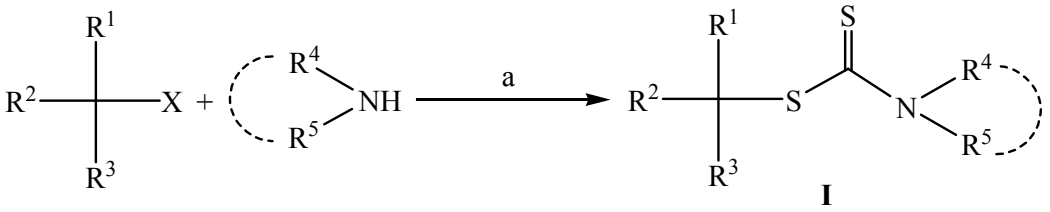
In order to study the effect of halide group (I, Cl, Br) of corresponding alkyl halide on the yield of the dithiocarbamates, we tried a reaction of each of 2-chloro/bromo/iodo ethyl benzene with *n*-butyl amine employing Triton-B/CS_2 system at room temperature, wherein we found that alkyl halide bearing iodide group gives best yields as compared to corresponding chloride and bromide compounds (**Table 2**).

Table 2. Effect of different alkyl halides in the formation of dithiocarbamates **I**

R^1	R^2	R^3	R^4	R^5	X	Time	Yield
Ph-CH_2	H	H	*n*-C_4H_9	H	I	1	92
Ph-CH_2	H	H	*n*-C_4H_9	H	Br	1.5	90
Ph-CH_2	H	H	*n*-C_4H_9	H	I	1.5	85

After optimizing the reaction conditions, this reaction was employed to a variety of primary, secondary, and *tert.* alkyl halides with various kinds of primary, secondary aliphatic, alicyclic, heterocyclic, aromatic amines employing Triton-B/CS_2 system at room temperature (**Table 3**). This reaction works well with primary alkyl halides in comparison to secondary and tertiary alkyl halides. Steric hindrance could be the reason for lesser yield of secondary or tertiary alkyl halides. It has also been observed that aromatic amines with electron releasing group (EWG) like *p*-anisidine and *p*-toluedine afforded high yields and lesser reaction time as compared to aromatic amine without EWG

like aniline. Also, dithiocarbamates of cyclic amines such as cyclohexyl amine was obtained in lesser yields as compared to aliphatic long chain amines. The spectral characterization of all the dithiocarbamates obtained from various amines and alkyl halides were confirmed through the data of authentic dithiocarbamates prepared in our Laboratory from various starting materials .[37f, 38b, 38d]



Scheme 1. Reagents and conditions: (a) Triton B, CS_2, rt, 1.5-2.5 hr., 82-98%

Table 3. Conversion of alkyl halides into dithiocarbamates of general formula **I**

Comp. No.	R^1	R^2	R^3	R^4	R^5	X	Time (hrs)	Yield	Refs.
1.	2-Naphthyloxypropyl	H	H	*n*-C_4H_9	H	Cl	1.5	96	38d
2.	2-Naphthyloxyethyl	H	H	*c*-C_6H_{13}	H	Cl	2	89	38d
3.	2-Naphthyloxyethyl	H	H	$R_4 = R_5$ = Morpholine		Cl	2	8	38d
4.	2-Naphthyloxyethyl	H	H	$R_4 = R_5$ = Pyrrolidine		Cl	2	86	38b
5.	2-Naphthyloxyethyl	H	H	*n*-C_3H_7	*n*-C_3H_7	Cl	2	85	38b
6.	*n*-C_3H_7	H	H	*n*-C_8H_{17}	H	I	2.5	87	38d
7.	$(CH_3)_2CH.CH_2$	H	H	*n*-C_8H_{17}	H	I	2	90	38d
8.	$CH_3(CH_2)_3$	H	H	*n*-C_4H_9	H	I	2	92	38d
9.	$CH_3(CH_2)_4$	H	H	*c*-C_6H_{11}	H	Cl	2.5	88	38d
10.	$CH_3(CH_2)_5$	H	H	$PhCH_2$	H	Cl	2	90	37f
11.	$CH_3(CH_2)_6$	H	H	4-MePh	H	Br	2	92	38d
12.	$CH_3(CH_2)_8$	H	H	*n*-C_6H_{13}	H	I	1.5	98	38d
13.	$PhCH_2$	H	H	*n*-C_4H_9	H	Cl	2	91	38d
14.	$PhCH_2.CH_2$	H	H	*n*-C_6H_{13}	H	Cl	2	94	38d
15.	$PhCH_2$	H	H	*i*-C_3H_7	i-C_3H_7	Cl	2	89	38d
16.	2-Naphthyloxyethyl	H	H	4-MeOPh	H	Cl	2	88	38d
17.	*n*-C_4H_9	*n*-C_4H_9	H	*n*-C_8H_{17}	H	Cl	2.5	84	38d
18.	*n*-C_4H_9	*n*-C_4H_9	*n*-C_4H_9	*n*-$C_{12}H_{25}$	H	Cl	2	94	38d
19.	*n*-C_6H_{11}	H	H	Ph	Br	I	2.5	82	37f
20.	*n*-C_5H_{11}	H	H	Cyclohexyl	H	Cl	2.5	83	38b
21.	*n*-C_4H_9	H	H	$PhCH_2CH_2$	H	I	2	89	38b
22.	*n*-C_5H_{11}	H	H	$Ph.CH_2.CH_2.CH_2$	H	Cl	2	92	38b

3. Conclusions

We have developed a convenient and efficient protocol for one-pot, solvent-free coupling of various primary and secondarysubstituted aliphatic, aromatic, alicyclic, heterocyclic amineswith a variety of primary, secondary and tertiary alkyl halides employing Triton-B/CS_2 system. This method generates the corresponding dithiocarbamates in good to excellent yields. Furthermore, this method exhibits substrate versatility, mild reaction conditions and experimental convenience. This synthetic protocol developed in our laboratory is believed to offer a more general method for the formation of carbon-oxygen bonds essential to numerous organic syntheses.

4. Experimental

Chemicals were procured from Merck, Aldrich, and Fluka chemical companies. Reactions were carried out under an atmosphere of Argon. Infra-Red (IR) spectra 4000-200 cm^{-1} were recorded on Bomem MB-104–FTIR spectrophotometer using neat technique, whereas NMRs were scanned on AC-300F, NMR (300 MHz), instrument using $CDCl_3$ and some other deutrated solvents and *TMS* as internal

standard. Elemental analysis were conducted by means of a Carlo-Erba EA 1110-CNNO-S analyser and agreed favourably with calculated values.

4.1 Typical experimental procedure for the synthesis of dithiocarbamates

An equimolar amount (6mmol) ofTriton-B and CS_2 was and was allowed to stir20 min at room temperature. Amine (5 mmol) was added and the reaction was continued at rt for 1 h. Now corresponding alkyl halide (2 m mol) compound were added. The reaction was further continued until completion (Table 1). The reaction mixture was poured into 50 cm^3 distilled H_2O and extracted with ethyl acetate thrice. The organic layer was separated, dried (Na_2SO_4), and concentrated to get the desired compound.

4.2 Data of selected compounds.

[4-(2-Naphthyloxy)but-1-yl] n-butyldithiocarbamate(1):(Table 2, entry 1)[38b]

M.p.106ºC. IR (KBr): ν = 670 (C–S), 1114 (C=S), 1474 (Ar), 1510 (Ar), 1609 (Ar), 2874 (CH), 2937(CH), 3418 (NH) cm^{-1};^{1}H NMR ($CDCl_3$): δ = 0.93–0.97 (t, CH_3,J = 7.1Hz), 1.30–1.34 (m, CH_2CH_3),1.53–1.56 (m, $CH_2CH_2CH_3$), 1.70–1.72 (m, naphthyl-O–CH_2CH_2,J = 6.5 Hz), 1.95–1.98 (m, S–CH_2CH_2), 2.0 (br, NH), 2.63–2.66 (m, $NHCH_2$,J = 7.2Hz), 2.84–2.88 (t, CH_2–S–C=S), 4.01–4.04 (t, CH_2–O-naphthyl), 6.97–7.64 (m, Ar–H) ppm. MS: m/z = 347.

3-(2-Naphthyloxy)prop-1-yl] n-hexyldithiocarbamate (2):(Table 2, entry 2)[38b]

M.p.129ºC; IR (KBr): ν = 664 (C–S), 1116 (C=S), 1474 (Ar), 1512 (Ar), 1601 (Ar), 2874 (CH), 2937 (CH), 3395 (NH) cm^{-1};^{1}H NMR ($CDCl_3$): δ = 0.92–0.96 (t, CH_3, J = 7.2 Hz), 1.27–1.29 (m, $CH_2CH_2CH_2CH_3$), 1.30–1.34 (m, CH_2CH_3), 1.53–1.56 (m, $CH_2CH_2CH_3$), 2.2 (br, NH), 2.36–2.40 (m, naphthyl-O–$CH_2CH_2CH_2$-, J = 6.5 Hz), 2.63–2.66 (m, $NHCH_2$,J = 7.2Hz), 2.83–2.87 (t, CH_2–S–C=S), 4.01–4.04 (t, CH_2–O-naphthyl),6.97–7.64 (m, Ar–H) ppm. MS: m/z = 361.

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References

1. (a) Lambert C. (**2004**) Sulphur chemistry in crop protection. *J. Sulphur Chem*., 25(1) 39-62; (b) Eng G., Song X., Duong Q., Strickman D., Glass J., May L. (**2003**) Synthesis, structure characterisation and insecticidal activity of some triorganotin dithiocarbamates. *Appl. Organomet. Chem*., 17 (4) 218-225; (c) Senkbeil S., Lafleur J. P., Jensen T. G., Kutter J. P. (**2012**) Gold nanoparticle-based fluorescent sensor for the analysis of dithiocarbamate pesticide in water. *Min. System Chem. Life Sci*., 1423-1425.
2. (a) Cao S. L., Feng Y. P., Jiang Y. Y., Liu S. Y., Ding G. Y., Li R. T. (**2005**) Synthesis and *in-vitro* antitumor activity of 4(3*H*)-quinazolinone derivatives with dithiocarbamate side chains. *Bioorg. Med. Chem. Lett.,* 15 (7) 1915-1917; (b) Cao S. L., Wang Y., Zhu L., Liao J., Guo Y. W., Chen L. L., Liu H. Q., Xu X. (**2010**) Synthesis and *in-vitro* antitumor activity of 4(3*H*)-quinazolinone derivatives with dithiocarbamate side chains. *Eur. J. Med. Chem.,* 45 (9) 3850-3857; (c) Cao S. L., Han Y., Yuan C. Z., Wang Y., Xiahou Z. K., Liao J., Gao R. T., Mao B. B., Zhao B. L., Li, Z. F., Xu X. (**2013**) Synthesis and antiproliferative activity of 4-substituted-piperazine-1-carbodithioate derivatives of 2,4-diaminoquinazoline. *Eur. J. Med. Chem.,* 64 401-409; (d) Cvek B., Dvorak Z. (**2007**) Targeting of nuclear factor-κB and proteasome by

dithiocarbamate complexes with metals. *Curr. Pharm. Design.,* 13 (30) 3155-3167; (e) Guzel O., Salman A. (**2006**) Synthesis, antimycobacterial and antitumor activities of new (1,1-dioxido-3-oxo-1,2-benzisothiazol-2(3*H*)-yl)methyl *N*,*N*-disubstituted dithiocarbamate/*O*-alkyldithiocarbonate derivatives. *Bioorg. Med. Chem.,* 14 (23) 7804-7815; (f) Qian Y., Ma G. Y., Yang Y., Cheng K., Zheng Q. Z., Mao W. J., Shi L., Zhao J., Zhu H. L. (**2010**) Synthesis, molecular modeling and biological evaluation of dithiocarbamates as novel antitubulin agents. *Bioorg. Med. Chem.,* 18 (12) 4310-4316.

3. Rudorf W. D. (**2007**) Reactions of carbon disulfide with N-nucleophiles. *J. Sulfur Chem.,* 28(3) 295-339; (b) Katrizky A. R., Singh S., Mahapatra P. P., Clemense N., Kirichenko K. (**2005**) Synthesis of functionalised dithiocarbamates *via N*-(1-benzotriazolylalkyl)dithiocarbamates. *.ARKIVOC,* IX , 63-79.
4. Greene T. W., Wuts P. G. M. (**1999**) *Protecting Groups in Organic Synthesis* 3rd Edition,
5. Gomez L., Wagner A., Mioskowski C. (**2000**) An efficient procedure for traceless solid-phase synthesis of N,N‘-substituted thioureas by thermolytic cleavage of resin-bound dithiocarbamates. *J. Comb. Chem.,* 2 (1) 75-79.
6. Crich D., Quintero L. (**1989**) Radical chemistry associated with the thiocarbonyl group. *Chem. Rev*., 89 (7) 1413-1432.
7. Zhang D., Chen J., Liang Y., Zhou H. (**2005**) Facile synthesis of novel ionic liquids containing dithiocarbamate. *Synth Commun.,* 35 (4) 521-526.
8. Alexander N., Ramalingam K., Rizzoli C. (**2011**) Supramolecularly linked linear polymers of thallium(I) dithiocarbamates: Steric influence on the supramolecular interactions of methyl and ethylcyclohexyl dithiocarbamates of thallium(I). *Inorg. Chim. Acta.* 365 (1) 480-483.
9. (a) Haendel M. A., Tilton F., Bailey G. S., Tanguay R. L. (**2004**) Developmental toxicity of the dithiocarbamate pesticide sodium metam in Zebrafish. *Toxicol. Sci*., 81 (2) 390-400; (b) Senkbeil S., Lafleur J. P., Jensen T.G., Kutter J. P. (**2012**) Gold nanoparticle-based fluorescent sensor for the analysis of dithiocarbamate pesticide in water. *Min. System Chem. Life Sci*., 1423-1425.
10. Rogachev I., Kampel V., Gusis V., Cohen N., Gressel J., Warshawsky A. (**1998**) Synthesis, properties and use of copper-chelating amphiphilic dithiocarbamate as synergist of oxidant-generating herbicide. *Pesticide Biochem & Physiol*., 60 (3) 133-145.
11. Eng G., Song X., Duong Q., Strickman D., Glass J., May L. (**2003**) Synthesis, structure characterisation and insecticidal activity of some triorganotin dithiocarbamates. *Appl. Organomet. Chem*., 17 (4) 218-225.
12. Lambert C. (**2004**) Sulphur chemistry in crop protection. *J. Sulphur Chem*., 25 (1) 39-62.
13. Byrne S. T., Gu P., Zhou J., Denkin S. M., Chong C., Sullivan D., Liu J. O., Zhang Y. (**2007**) Pyrrolidine dithiocarbamate and diethyldithiocarbamate are active against growing and nongrowing persister *Mycobacterium tuberculosis. Antimicrob. Agents Chemother*., 51 (12) 124495-124497.
14. Zheng Y. C., DuanY. C., Ma J. L., Xu R. M., Zi X., Lv W. L.,Wang M. M., Ye X. W., Zhu S., Mobley D., Zhu Y. Y., Wang J. W., Li J. F., Wang Z. R., Zhao W., Liu H. M. (**2013**) Triazole–dithiocarbamate based selective lysine specific demethylase 1 (LSD_1) inactivators inhibit gastric cancer cell growth, invasion, and migration. *J. Med. Chem*., 56 (21) 8543-8560.
15. Coro J., Atherton R., Little S., Wharton H., Yardley V., Alvarez A., Suarez M., Perez R., Rodriguez H. (**2006**) Alkyl-linked bis-THTT derivatives as potent *in-vitro* trypanocidal agents. *Bioorg. Med. Chem*., 16 (5) 1312-1315.
16. Marakov V., Riabova O. B., Yuschenko A., Urlyapova N., Daudova A., Ziplef P. F., Mollmann U. (**2006**) Synthesis and antileprosy activity of some dialkyldithiocarbamate. *J. Antimicrobial Chemother*., 57 (6) 1134-1138.
17. Guzel O., Salman A. (**2006**) Synthesis, antimycobacterial and antitumor activities of new (1,1-dioxido-3-oxo-1,2-benzisothiazol-2(3H)-yl)methyl N,N-disubstituted dithiocarbamate/ O-alkyldithiocarbonate derivatives. *Bioorg Med. Chem.,* 14 (23) 7804-7815.

18. Zou Y., Yu S., Li R., Zhao Q., Li X., Wu M., Huang T., Chai X., Hu H., Wu Q. (**2014**) Synthesis, antifungal activities and molecular docking studies of novel 2-(2,4-difluorophenyl)-2-hydroxy-3-(1*H*-1,2,4-triazol-1-yl)propyl dithiocarbamates. *Eur. J. Med. Chem.,* 74 366-374.
19. Mohsen U. A. (**2014**) Synthesis and biological evaluation of some new benzimidazole derivatives bearing dithiocarbamate moiety as potential cholinesterase inhibitors. *Cukurova Med. J*., 39 (4) 729-735.
20. Jangir S., Bala V., Lal N., Kumar L., Sarswat A., Kumar A., Hamidullah., Saini K. S., Sharma V., Verma V., Maikhuri J. P., Konwar R., Gupta G., Sharma V. L. (**2014**) Novel alkylphospholipid-DTC hybrids as promising agents against endocrine related cancers acting via modulation of Akt-pathway. *Eur. J. Med. Chem.,* 85 638-647.
21. Chauhan K., Sharma M., Singh P., Kumar V., Shukla P. K., Siddiqi M. I., Chauhan P. M. S. (**2012**) Discovery of a new class of dithiocarbamates and rhodanine scaffolds as potent antifungal agents: synthesis, biology and molecular docking. *Med. Chem. Comm*., 3 (9) 1104-1110.
22. Liu P., Li C., Zhang J., Xu X. (**2013**) Facile and versatile synthesis of alkyl and aryl isothiocyanates by using triphosgene and coolent. *Synth. Commun*., 43 (24) 3342-3351.
23. Halimjani A. Z., Pourshojaei Y., Saidi M. R. (**2009**) Highly efficient and catalyst-free synthesis of unsymmetrical thioureas under solvent-free conditions. *Tetrahedron Lett.* 50 (1) 32-34.
24. Jamir J., Sinha U. B., Nath J., Patel B. K. (**2012**) Environmentally benign one-pot synthesis of cyanamide from dithiocarbamates using I_2 and H_2O_2. *Synth. Commun*., 42 (7) 951-958.
25. Kienle M., Unsinn A., Knochel P. (**2010**) Synthesis of dithiobenzophenes and related class of heterocycles by using functionalized dithiocarbamates. *Angew. Chem. Int. Ed*., 49 (28) 4751-4754.
26. Aucagne V., Lorin C., Tatibouet A., Rollin P. (**2005**) Regioselective Michael-induced cyclisation of γ- and δ-hydroxy vinyl sulphides and vinyl dithiocarbamates. *Tetrahedron Lett*., 46 (25) 4349-4352.
27. Kumar N. K.; Sreeramamurthy, K.; Palle, S.; Mukkanti, K.; Das, P. (**2010**) Dithiocarbamate and DBU-promoted amide bond formation under microwave condition. *Tetrahedron Lett.,* 51 (6) 899-902.
28. Khalizadeh M. A., Hossaini Z., Baradarani M. A., Hassania A. (**2010**) A novel isocyanide-based three-component reaction: A facile synthesis of substituted 2*H*-pyran-3,4-dicarboxylates. *Tetrahedron*, 66 (43) 8464-8467.
29. Mohsin U. A. (**2014**) Synthesis and biological evaluation of some new benzimidazole derivatives bearing dithiocarbamate moiety as potential cholinesterase inhibitors. *Curkova Med. J*., 39 (4) 729-735.
30. Tandel S. K., Rajappa S., Pansare S. V. (**1993**) Conversion of thiocarbamates to carbamates. *Tetrahedron,* 49 (34) 7479-7486.
31. Charati F. R., Hossaini Z., Hajinasiri R. (**2012**) Solvent-free multicomponent reactions of dithiocarbamates, activated acetylenes and isocyanide. *J. Applied Chem. Res.,* 20 (1) 54-59.
32. Bahrin L. J., Jones P. J., Hopf H. (**2012**) Tricyclic flavonoids with 1,3-dithiolium substructure. *Beilstein J. Org. Chem*., 8 1999-2003.
33. Burke J. T. R., Bajwa B. S., Jacobsen A. E., Rice K. C., Streaty R. A., Klee W. A. (**1984**) Probes for narcotic receptor mediated phenomena: Synthesis and pharmacological properties of irreversible ligands specific for .mu. or .delta. opiate receptors. *J. Med. Chem*., 27 (12) 1570-1574.
34. Walter W., Bode K. D. (**1967**) Syntheses of Thiocarbamates. *Angew. Chem. Int. Ed*., 6 (4) 281-293.
35. Garin J., Melandz E., Merchain F. L., Tejero T., Urid S., Ajaysteron J. (**1991**)Palladium-catalyzed hetero-cope rearrangement of alkyl allyl *N*-aryldithiocarbonimidates. *Synthesis,* 147-149.
36. (a) Sharma S. (**1978**) Thiophosgene in organic synthesis. *Synthesis, (11),* 803–820; (b) Pascual R. M. (**2015**) Thiophosgene. *Synlett,* 26 (12) 1776-1777.
37. (a) Chaturvedi D., Kumar A., Ray S. (**2002**) An efficient one pot synthesis of carbamates esters through alcoholic tosylates. *Synth Commun.,* 32 (17) 2651-2655; (b) Chaturvedi D., Kumar A., Ray S. (**2003**) A high yielding, one-pot, novel synthesis of carbamate esters from alcohols using

Mitsunobu's reagent. *Tetrahedron Lett*., 44 (41) 7637-7639; (c) Chaturvedi D., Ray S. (**2005**) An efficient, one-pot, basic resin catalyzed novel synthesis of carbamate esters through alcoholic tosylates. *Lett. Org. Chem.,* 2 (8) 742-744; (d) Chaturvedi D., Ray S. (**2005**) An efficient, basic resin mediated, one-pot synthesis of dithiocarbamate esters through alcoholic tosylates. *J Sulfur Chem.,* 26 (4-5) 365-371; (e) Chaturvedi D., Ray S. (**2006**) An efficient, basic resin mediated, one-pot synthesis of O-alkyl-S-methyl dithiocarbonates from the corresponding alcohols. *J Sulfur Chem.,* 27 (3) 265-270; (f) Chaturvedi D., Ray S. (**2006**) An efficient, one-pot, synthesis of dithiocarbamate esters from alcohols using Mitsunobu's reagent. *Tetrahedron Lett.,* 47 (8) 1307-1309; (g) Chaturvedi D., Mishra N., Mishra V. (**2006**) *Chin. Chem. Lett*., 17 (10) 1309-1312; (h) Chaturvedi D., Ray S. (**2007**) A high yielding one-pot, synthesis of *O,S*-dialkyl dithiocarbonates from the alcohols using Mitsunobu's reagent. *Tetrahedron Lett.,* 48 (1) 149-151; (i) Chaturvedi D., Mishra N., Mishra V. (**2007**) A high yielding, one-pot synthesis of dialkyl carbonates from alcohols using Mitsunobu's reagent. *Tetrahedron Lett*., 48 (29) 5043-5045; (j) Chaturvedi D., Mishra N., Mishra V. (**2008**) An efficient, one-pot synthesis of *S*-alkyl thiocarbamates from the corresponding thiols using the Mitsunobu reagent. *Synthesis,* (3) 355-357; (k) Chaturvedi D., Chaturvedi A. K., Mishra N., Mishra V. (**2008**) An efficient, one-pot synthesis of trithiocarbonates from the corresponding thiols using the Mitsunobu reagent. *Tetrahedron Lett.,* 49 (33) 4886-4888; (l) Chaturvedi D., Chaturvedi A. K., Mishra N., Mishra V. (**2009**) Basic resin mediated efficient one-pot synthesis of carbazates from the corresponding alkyl halides. *J. Iran. Chem. Soc.,* 6 (3) 510-513; (m) Chaturvedi D., Mishra N., Chaturvedi A. K., Mishra V. (**2009**)An efficient, basic resin-mediated, one-pot synthesis of dithiocarbazates through alcoholic tosylates. *Phosphorus Sulfur and Silicon,* 184 (3) 550-558; (n) Chaturvedi A. K., Chaturvedi D., Mishra N., Mishra V. (**2010**) A high yielding, one-pot synthesis of *S,S*-dialkyl dithiocarbonates through the corresponding thiols using Mitsunobu's reagent. *J. Iran. Chem. Soc*., 7 (3) 702-706; (o) Chaturvedi A. K., Chaturvedi D., Mishra N., Mishra V. (**2011**)An efficient one-pot synthesis of carbazates and dithiocarbazates through the corresponding alcohols using Mitsunobu's reagent. *J. Iran. Chem. Soc*., 8 (2) 396-400; (p) Chaturvedi D., Zaidi S., Chaturvedi A. K., Vaid S., Saxena A. K. (**2016**) An efficient protocol for the synthesis of *β*-substituted ethyl dithiocarbamates: A novel class of anti-cancer agent. *Ind. J. Chem*. Sec. B, 55B (8) 1019-1025.

38. (a) Chaturvedi D., Ray S. (**2006**) A high yielding, one-pot, triton-B catalyzed, expeditious synthesis of carbamate esters by four component coupling methodology. *Monatsh Chem.,* 137 (2) 201-206; (b) Chaturvedi D., Ray, S. (**2006**) Triton-B catalyzed efficient one-pot synthesis of dithiocarbamate esters. *Monatsh. Chem.,* 137 (2) 311-317; (c) Chaturvedi D., Ray S. (**2006**) Triton-B catalyzed, efficient, one-pot synthesis of carbamate esters from alcoholic tosylates. *Monatsh. Chem*., 137 (4) 459-463; (d) Chaturvedi D., Ray S. (**2006**) A high yielding, one-pot, triton-B catalyzed synthesis of dithiocarbamates using alcoholic tosylates. *Monatsh. Chem.,* 137 (4) 465-469; (e) Chaturvedi D., Chaturvedi A. K., Mishra N., Mishra V. (**2008**) Triton-B catalyzed, efficient, one-pot synthesis of carbazates through alcoholic tosylates. *Synth. Commun.,* 38 (22) 4013-4022; (f) Chaturvedi D., Mishra N., Chaturvedi A. K., Mishra V. (**2009**) Triton-B catalyzed, efficient, one-pot synthesis of dithiocarbazates through alcoholic tosylates. *Synth. Commun*., 39 (7) 1273-1281.