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Synthesis of Derivatives of Di-butyldithiocarbamates

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The sodium salt of dithiocarbamate (**1a**) is synthesized by reaction of dibutylamine with carbon disulfide and sodium hydroxide. Phenacyl-dibutyl-dithiocarbamate (**1b**) is prepared by reaction of dibutylamine with carbon disulfide and alkylating agent. The (1-benzoyl-2,2-dibutylthio)vinyl dibutyl dithiocarbamates (**1c**) is prepared by dithiocarboxylation of (**1b**) under phase transfer conditions followed by butylation. All substance (**1a**), (**1b**) and (**1c**) are indentified by m.p., colour, ^{1}H NMR and IR spectra.

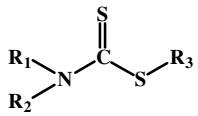
Key Words: Dithiocarbamates, Dibutylamine, Carbon disulfide, Fungicides, Herbicides.

INTRODUCTION

The dithiocarbamate family of chemicals is mainly used in agriculture and forms a large group of synthetic organic compounds that have been developed and used worldwide over the last 50 years. Dithiocarbamates are used as fungicides[1], a few have been used as herbicides and soil insecticides. In industry, they are used as slimicides in water-cooling system, in paper manufacturing and as vulcanization accelerators and antioxidants in rubber[2].

Exposure occurs mainly by inhalation and percutaneous absorption under occupational conditions. The general population can be orally exposed *via* ingestion of residues from treated food[3-8].

The general formula of dithiocarbamates is:

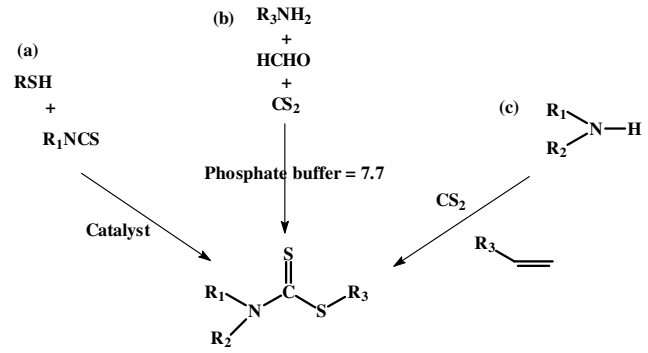


R_1,R_2 = H, alkyl, aryl, heteroaryl, alkylaryl
R_3 = Benzoyl, *o-p*-dichlorobenzoyl

Depending on the types of amines used (primary or secondary) in the reaction with the carbon disulfid, in the synthesis, mono-or dialkyldithiocarbamates are formed.

There are many salts of alkyl compounds dithiocarbamates known that result from the reaction of dithiocarbamates with metals or their salts which are uses in a wide variety of areas[9].

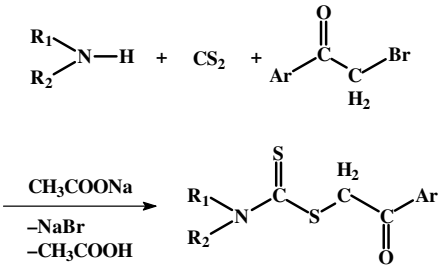
In spite of the growing interest in applications of dithiocarbamates, preparative methods available for their synthesis are still limited[10]. Well known routes for their synthesis (depicted in **Scheme-I**) include the reactions of (a) mercaptanes with isothiocyanates using suitable basic catalyst[11], (b) amines and carbon disulfide followed by treatment with formaldehyde and other amines in presence of phosphate buffer[12], (c) dialkyl amines, carbon disulfide, electron deficient olefin under one pot aqueous condition[13].



Scheme-I

However, all these synthetic methods are associated with one or the other limitations, such as low availability of starting material, or employment of harsh reaction conditions, high reaction temperature, long reaction times, low yields and two or more steps[14]. Due to the above mentioned facts and

reasons, the synthesis of the dithiocarbamates in one-pot reaction from dialkylamines, carbon disulfide, phenacylbromide in presence of anhydrous sodium acetate, because this method is safe, high yield, short time reaction, low reaction temperature and availability of raw material. **Scheme-II** shows the general reaction equation.



R_1, R_2 = C_4H_9; Ar = $-C_6H_5$, $-C_6H_3Cl_2$

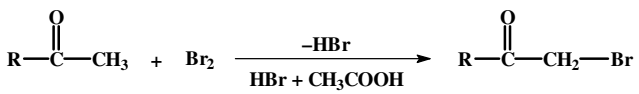
Scheme-II

In this paper, we reported the synthesis of N-dibutyl-dithiocarbamate, which contains the CH-acid group and electron accepting group such as sulfur group and then studied the reaction of these compounds with carbon disulfide in the liquid heterogeneous phase, to give derivatives of dibutyldithio-carbamate and sodium dithiocarbamate salt.

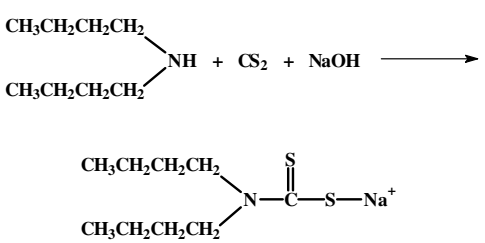
EXPERIMENTAL

Glassware were cleaned and dried in the dryer (Ecocell) at 100 ºC before use. Solvents were evaporated under reduced [9R-125-B:491(Büchi)] at temperature < 45 ºC. Thin layer chromatography (TLC) was performed using siliga gel 60F-254 plates with I_2 vapours as detecting agents followed by spraying with Draggendorff reagent. TMS was used as an internal standard in ^{1}H NMR in $CDCl_3$. Infrared spectra were recorded as KBr pellets by FT/IR-400 (Jasco) spectrometer. Melting points were determined on a melting point apparatus. Unless chemicals were obtained with high purity from (Merck, Panreac, Sep) and were used without further purification.

General procedure for the preperation of phenacyl-bromide: Into a 500 mL three-necked flask with stirrer, reflux condenser, dropper funnel dropwise and calcium chloride tube was added to a solution of 0.5 mol acetophenone in 100 mL glacial acetic acid with a few drops of hydrogen bromide/ glacial acetic acid and dropped 0.5 mol of bromine to be increased so that the temperature maintained at *ca.* 20 ºC (at first reaction can occur in transition). When it is cooled in ice water. If no one is crystallizing, it poured into ice water. The solid compounds extracted and washed with 50 % alcohol until they are colourless. It crystallized from alcohol to pure crys-talline compound.

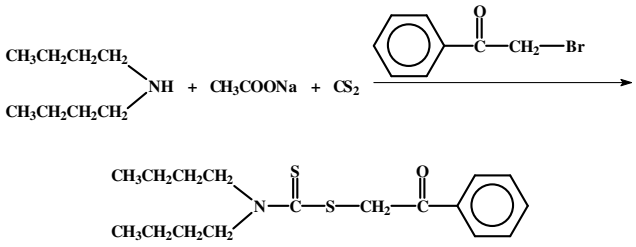


Preparation of di butyl-dithiocarbamates sodium salts ($C_9H_{18}NS_2Na$) (1a): Into a 250 mL two-necked flask with stirrer, dropwise is added of 100 mmol (12.9 g) di-butylamine, 100 mmol sodium hydroxide (4 g) in 175 mL pure methanol and is added dropwise 100 mmol of carbon disulfide (7.6 g, 6.022 mL) to the stirred reaction mixture at room temperature. After finished adding CS_2 stirring is continued for 1 h. Then the reaction mixture is or was left to the next day and then is evaporated. The di butyl- dithiocarbamates sodium salts is formed.



Spectral data of compound 1a: As yellow solid, yield 80 %, m.p. 50 °C, Ms 227 g/mol; IR (KBr, ν_{max}, cm^{-1}): 3100, 2850, 1464, 1367,1250, 924, 543. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.98 (m, 2(-CH_3) of C_4H_9), 1.26-1.58 (m, 2(-CH_2-) near of-CH_3), 1.62-1.68 (m, 2(-CH_2-)), 4.28 (s, 2 (-CH_2-) near of N) ppm.

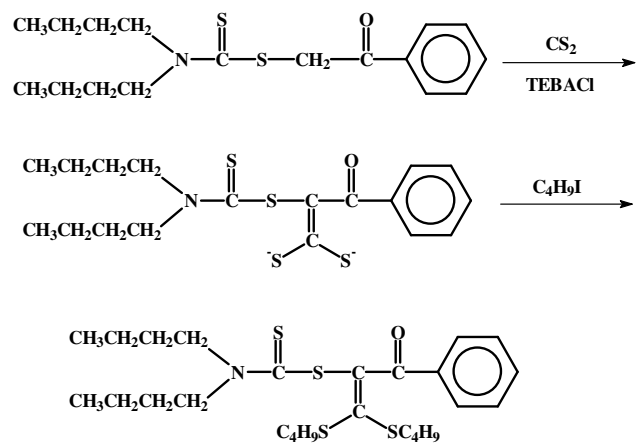
Preparation of phenacyl-dibutyl-dithiocarbamates ($C_{17}H_{25}NOS_2$) (1b): To a solution of 103 mmol (8.45 g) anhydrous sodium acetate, 103 mmol (13.287 g, 17.529 mL) dibutyl amine as the secondary amine and 103 mmol (10.18 g) carbon disulfide in 175 mL of absolute methanol was added dropwise 103 mmol (20.5 g) of an alkylating agent as phenacylbromide in 50 mL of absolute methanol. The solution left overnight at room temperature. Wherein the phenacyl-dialkyl-dithiocarba-mates precipitate.The precipitate was filtered off and washed several times with a little water to separate sodium halide.



Spectral data of compound 1b: As blancsale solid, yield 81.7 %, m.p. 49.2 ºC, Ms 323 g/mol; IR (KBr, ν_{max}, cm^{-1}): 3050, 2850, 1750, 1600, 1484, 1351, 1207, 1100, 744. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.98 (m, 2(-CH_3) of C_4H_9), 1.43-1.9 (m, 4(-CH_2-) of C_4H_9), 3.7-3.9 (m, 2(-CH_2-) near of N), 4.88 (s,(-CH_2-)), 7.2-8.07 (m,-C_6H_5) ppm.

Preparation of (1-benzoyl-2,2-dibutylthio)vinyl-dibutyldithiocarbamates ($C_{26}H_{41}NOS_4$) (1c): To a solution of 5 mmol (1.48 g) (**1b**) in 5 mL carbon disulfide and 5 mL chloroform is added with efficient stirring a mixture of 20 mmol (1.12 g) potassium hydroxide and 10 mmol (2.3 g) triethylbenzyl ammonium chloride (TEBA chloride) in 10 mL water. After 10 min at room temperature 15 mmol (2.5 mL) butyl iodide is added dropwise and stirring is continued for 1 h. The phases are separated and the organic layer is washed with water and dried over anhydrous calcium chloride. The

residue obtained by evaporation of the solvent is recrystallized from diethyl ether.



Spectral data of compound 1c: As white solid, yield 77.3 %, m.p. 55 ºC, Ms 511 g/mol; IR (KBr, ν_{max}, cm^{-1}): 3080, 2850, 1750, 1650, 1629, 1464, 1407, 1207, 1110, 739. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.24-1.27 (m, 4 (-CH_3) of 4-C_4H_9), 1.302-1.94 (m, 8 (-CH_2-) of C_4H_9), 3.64-3.69 (m, 2(-CH_2-) near of S), 3.914-3.996 (m, 2 (-CH_2-) near of N), 7.285 (-C_6H_5) ppm.

REFERENCES

1. R.K. Mishra, R.K. Tewari, S.K. Srivastava and S.C. Bahel, *Asian J. Chem.*, **4**, 412 (1992).
2. A.N. Pudovik, V.K. Khairullin, A.V. Il'yasov, M.A. Vasyanina, I.A. Aleksandrova, I.E. Ismayev and V.I. Ovcharov, *Polym. Sci. U.S.S.R.*, **30**, 475 (1988).
3. Environmental Health Criteria 142, Permethrin, Geneva, World Health Organization (1992).
4. Environmental Health Criteria 97, Deltamethrin, Geneva, World Health Organization (1990).
5. Environmental Health Criteria 95, Fenvalerate, Geneva, World Health Organization (1990).
6. H. Kidd and D.R. James, The Agrochemicals Handbook, Surrey, The Royal Society of Chemistry, edn. 3 (1991).
7. C.R. Worthing and R.J. Hance, The Pesticide Manual, Surrey, British Crop Protection Council, edn. 9 (1991).
8. F. He, J. Sun, K. Han, Y. Wu, P. Yao, S. Wang and L. Liu, *Br. J. Ind. Med.*, **45**, 548 (1988).
9. Alain Pelfrene Associated Consultants (APAC), A.F. Pelfrene, 5 Avenue Louis Momet F-69260 Charbonniers France: Chapter 3. Biological Monitoring of Selected Pesticides, pp. 123-165.
10. Y. Nishiyama, K. Tokunaga, H. Kawamatsu and N. Sonoda, *Tetrahedron Lett.*, **43**, 1507 (2002).
11. H. Ulirich, B. Tucker and A.A.R. Sayigh, *J. Org. Chem.*, **32**, 3938 (1967).
12. D. Katiyar, V.K. Tiwari, R.P. Tripathi, A.K. Srivastava, V. Chaturvedi, R. Srivastava and B.S. Srivastava, *Bio. Org. Med. Chem.*, **11**, 4369 (2003).
13. N. Azizi, F. Aryanasab, L. Torkiyan, A. Ziyaei and M.R. Saidi, *J. Org. Chem.*, **71**, 3634 (2006).
14. V.K. Tiwari, A. Singh, H.A. Hussain, B.B. Mishra and V. Tripathi, *Monatsh. Chem.*, **138**, 653 (2007).