# Triton-B catalyzed, efficient one-pot synthesis of cyclic dithiocarbamates from primary amines, $CS_2$, and 2-(1-oxoacenaphthylen-2(1H)-ylidene)malononitrile

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**Abstract:** A highly efficient one-pot, solvent-free method for the synthesis of cyclic dithiocarbamates was developed through the reaction of corresponding primary amines, carbon disulfide and 2-(1-oxoacenaphthylen-2(1H)-ylidene)malononitrile employing in the presence of catalytic amount of Triton-B (Benzyl trimethyl ammonium hydroxide). The reaction conditions are milder with extremely simple work-up procedures than the reported methods, afforded the title compounds in high yields (82-98%) of desired product.

**Keywords:** 2-(1-oxoacenaphthylen-2(1H)-ylidene)malononitrile; Dithiocarbamate; Primary amines; Carbon disulfide; Triton-B.

## 1. Introduction

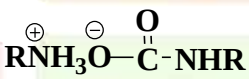
Organic dithiocarbamates have extensively been used as agrochemicals,[1] pharmaceuticals,[2] intermediates in organic synthesis,[3] protection of amino groups in peptide chemistry,[4] linkers in solid phase organic synthesis,[5] radical precursors in free-redical chemistry,[6] and synthesis of ionic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

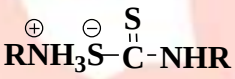
synthetic protocols for the syntheses of dithiocarbamates. Our group has been engaged from past several years for the development of new methodologies for the preparation of carbamates, dithiocarbamates and related compounds using cheap, abundantly available and safe reagents like carbon dioxide and carbon disulfide 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 of dithiocarbamates starting from their corresponding 2-(1-oxoacenaphthylen-2(1H)-ylidene) malononitrile and amines employing Triton B/$CS_2$ system

**Results and discussion**

In connection with our ongoing interest pertaining to the use of Triton-B 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 of dithiocarbamates, through the nucleophilic attack of S- ion of monoalkylammonium alkyl dithiocarbamate ion (MAAADC) **2** (Formulae 1) upon the carbocation generated from the electrophilic carbon of the corresponding alcoholic tosylates. 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 alkyl dithiocarbamate (MAAADC) ion **2** should be obtained through reaction of two molar equivalents of amine with $CS_2$ (Formulae 1). Since $CS_2$ is more reactive than $CO_2$, therefore the



**1**



**2**

**Formulae**

-reaction was tried at room temperature. It has been observed that the nucleophilicity of S- of MAAADC ion **2** could be increased by using basic phase transfer catalyst (PTC) like Triton-B. The nucleophilic attack of S- of MAAADC ion **2** to the electrophilic carbon of the corresponding.

Alkyl halide may led to afford the corresponding.

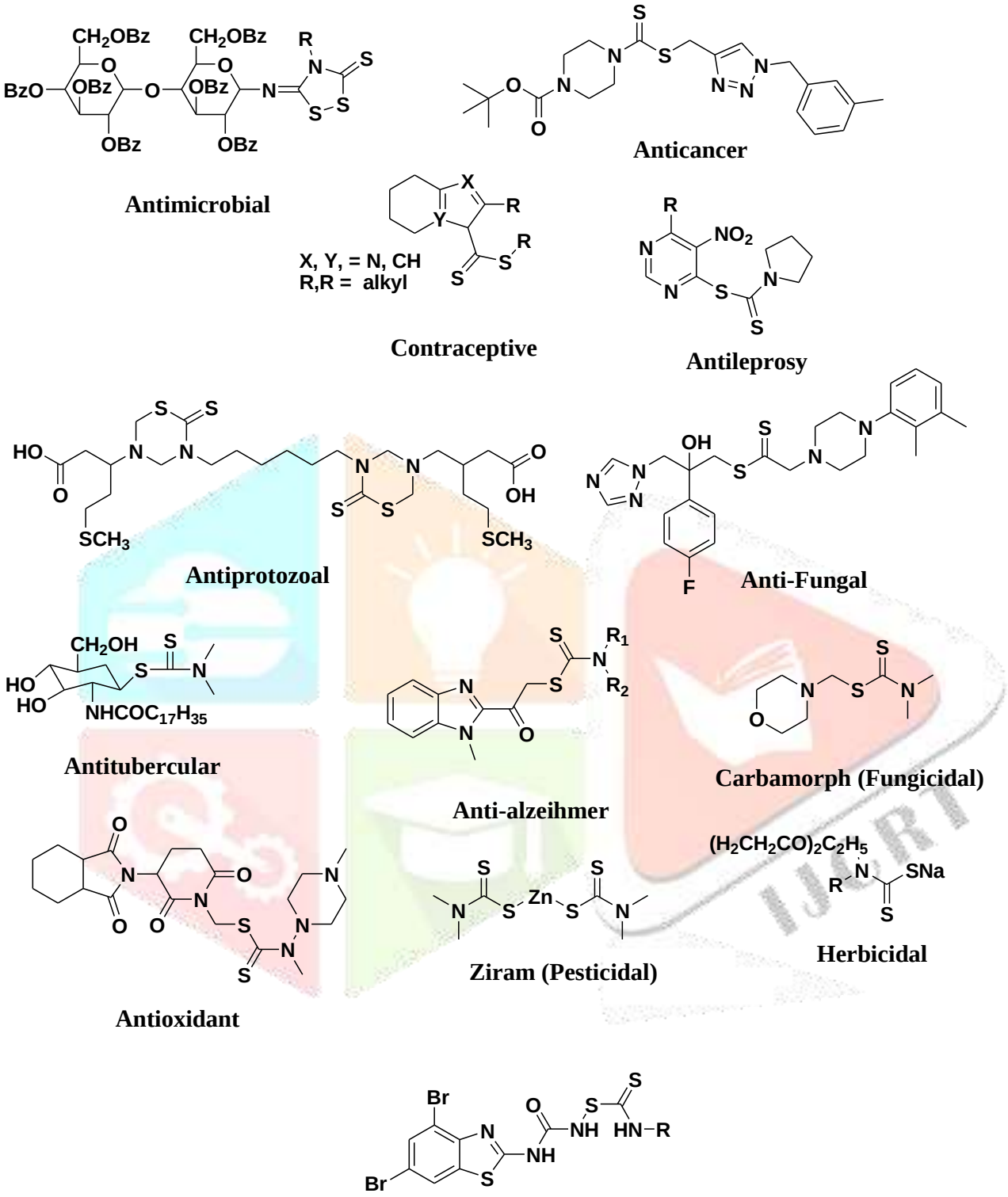



**Figure 1:** Various kinds of structurally diverse biologically potent dithiocarbamates

dithiocarbamate. The confirmation of product was made based on 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 MAAADC ion **2.** Therefore, this

reaction could not be successful for the dithiocarbamates from primary amines which do not have at least one hydrogen atom.

In order to study the effects of various phase transfer catalysts (CTC) on the yield of the reaction, a reaction of 2-(1-oxoacenaphthylen-2(1H) ylidene) malononitrile with primary amine employing various phase transfer catalysts (CTC) 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 **that Triton-B was found to best in achieving** the high yields of the desired dithiocarbamates (Table 1).

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

| S. No. | Name of PTC | Time (hr.) | Yield (%) |
|---|---|---|---|
| 1 | TBAI | 3 | 80 |
| 2 | TBAB | 3 | 85 |
| 3 | TBAC | 3.5 | 86 |
| 4 | TBAHS | 3.5 | 79 |
| 5 | TBAHC | 2 | 81 |
| 6 | Triton-B | 1 | 95 |

Comparing the catalytic activity of Triton-B with some reported catalysts such as $H_2O$, $K_3PO_4$ for the synthesis dithiocarbamates under solvent-free conditions, it was found that Triton-B was superior, achieving high yields of the desired products in shorter reaction times (Table 2).

| S. No. | Name of PTC | Time (hr.) | Yield (%) |
|---|---|---|---|
| 1 | $H_2O$ | 12 | 80 |
| 2 | $K_3PO_4$ | 3 | 85 |
| 3 | Triton-B | 1.5 | 96 |

The scope of this reaction was further explored with a primary aliphatic and aromatic amines having electron-releasing and electron-withdrawing function groups. Best yields of the products were obtained when an electron-releasing group was present at the aliphatic and aromatic amines.

After optimizing the reaction conditions, this reaction was employed to a variety of primary amine, 2-(1-oxoacenaphthylen-2(1H)-ylidene)malononitrile and aliphatic, alicyclic, heterocyclic, aromatic amines employing Triton-B/ $CS_2$ system at room temperature (Table 3).

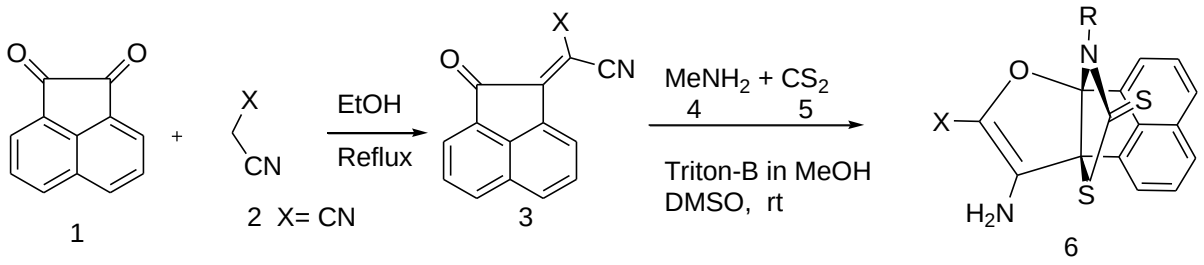



**Table-3 (Scheme-I)**

| S. No. | X | R | Product | Isolated Yield[b] % | Time (h) |
|---|---|---|---|---|---|
| 1 | CN | Me | 6a | 85 | 1.5 |
| 2 | CN | Et | 6b | 90 | 2.0 |
| 3 | CN | Pr | 6c | 86 | 1.0 |
| 4 | CN | Bu | 6d | 92 | 2 |
| 5 | CN | Bn | 6e | 93 | 1.5 |
| 6 | CN | 4-Cl-$C_6H_4$-$CH_2$ | 6f | 88 | 2.5 |
| 7 | CN | 2,4-$Cl_2$-$C_6H_3$-$CH_2$ | 6g | 89 | 2 |
| 8 | CN | Ph | 6h | 85 | 1.2 |
| 9 | CN | 4-MeO-$C_6H_4$ | 6i | 93 | 3 |
| 10 | CN | 4-Me-$C_6H_4$ | 6j | 87 | 3 |

In conclusion, the reaction of primary alkyl amines with $CS_2$ in the presence of 2-(1-oxoacenaphthylen-2(1H)-ylidene)malononitrile led to thioxo-9a,6b-(epithiomethanoimino) acenaphtho[1,2 b]furan-9-carbonitrile in excellent yields.

## Experimental Section

Chemicals were procured from Merck, Aldrich, alfa-Aesar, 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-400F, NMR (400 MHz), instrument using $CDCl_3$ and some other deutrated solvents and TMS and internal standard. Elemental analysis were conducted by means of a Carlo-Erba EA 1110-CNNO-S analyzer and agreed favourably with calculated values.

## Conclusion

In conclusion, we have developed highly efficient solvent-free one-pot approach three-components coupling various amines with 2-(1-oxoacenaphthylen-2(1H)-ylidene)malononitrile via $CS_2$ bridge using Triton-B. 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 formation of carbon-sulfur bonds essential to numerous organic synthesis.

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**Typical procedure for the preparation of cyclic dithiocarbamates**

**Synthesis of 2-(1-oxoacenaphthylen-2(1H)-ylidene)malononitrile (3):**

A solution of acenaphthylene-1,2-dione (1.0 mmol) in Ethanol and malononitrile (1.1 mmol). Reaction mass was reflux at 80$^{o}$C for 2.0 hr. The reaction mass was monitored by TLC and concentrate under reduce pressure get crude. Crude was used for next step.

**6. Synthesis of thioxo-9a,6b-(epithiomethanoimino)acenaphtho[1,2 b]furan9carbonitrile (6a):**

To a stirred solution of amine (2 mmol) in $CS_2$ (10 mmol), was stirred at room temperature for 15 min. Then Triton-B (1.0 mmol) was added and again stirred for 15 more minutes. Then 2-(1-oxoacenaphthylen-2(1H)-ylidene) malononitrile (1 mmol) was added at RT. The reaction mixture was than stirred for 2h. The progress of reaction was monitored by TLC. After completion the reaction mass was quenched with water (50 mL) and extracted with ethyl acetate (3x20 mL). The combined organic layer was separated washed with saturated brine solution (2x20 mL). The organic layer was dried over anhydrous $Na_2SO_4$ and concentrated under reduced pressure to give crude product. This crude product was further purified by silica gel (100-200 mesh) column chromatography by using eluent 20% (EtOAc : Hexane) to afford pure product.

### *5.2. 8-Amino-12-methyl-11-thioxo-9a,6b-(epithiomethanoimino)acenaphtho[1,2 b]furan9carbonitrile 6a*

Violet solid (0.25 g, 71%). mp: 254–258°C. $^1$H NMR (500 MHz, DMSO-$d_6$): 3.54(s, 3H), 7.57 (d, *J* =7.0 Hz, 1H), 7.69(t, *J* =7.5 Hz, 1H), 7.76 (t, *J* = 8.0 Hz, 1H), 7.93(d, *J* = 8.0 Hz, 1H), 7.99 (s, 2H), 8.02 (d, *J* = 7.0 Hz, 1H), 8.09 (d, *J* = 8.0 Hz, 1H). $^{13}$C NMR (125 MHz, DMSO-$d_6$): 34.3 (Me), 58.9 (C-S), 73.4 (CCN), 117.7 (CN), 119.2 (OCN), 119.8 (CH), 122.3 (CH), 126.0 (CH), 129.0 (CH), 129.9 (CH), 130.5 (CH), 132.5 (C), 134.6 (C), 135.5 (C), 143.0 (C), 166.5 (CNH2), 196.6 (C=S). IR (KBr) (Vmax, cm$^{-1}$): 3325 and 3272 (NH2), 2194 (CN), 1656 (OC=C), 1593, 1429 (C=CAr), 1345 (C=S). EI-MS: m/z (%) = 337 ($M^+$, 30), 322(100), 280 (20), 256(56), 229(40), 178(10), 154(15), 127(9). Anal.Calc. for $C_{17}H_{11}N_3OS_2$ (337.42): C, 60.52; H, 3.29; N, 12.45. Found: C, 60.82; H, 3.32; N, 12.53%.

### *5.3. 8-Amino-12-ethyl-11-thioxo-9a,6b-(epithiomethanoimino)acenaphtho[1,2-b]furan-9-carbonitrile 6b*

Cream color solid (0.27 g, 74%). mp: 257–260°C. $^1$H NMR (500 MHz, DMSO-$d_6$): 1.28 (t, J = 7.0 Hz, 3H), 4.12–4.26 (m, 2 H) 7.55 (d, J =7.0 Hz, 1H), 7.68 (t, J =7.5 Hz, 1H), 7.76 (t, J= 7.7 Hz, 1H), 7.93 (d, J= 8.3 Hz, 1H), 7.99 (s, 2H), 8.09 (t, J= 7.5 Hz, 2H). 13C NMR (125 MHz, DMSO-$d_6$): 13.5 (Me), 42.3 (CH2), 58.4 (C-S), 73.2 (CCN), 117.1 (CN), 119.2 (OCN), 119.8 (CH), 121.7 (CH), 125.8 (CH), 128.3 (CH), 129.4 (CH), 130.5 (CH), 131.8 (C), 134.1 (C), 135.5 (C), 142.5 (C), 165.8 (CNH2), 196.2 (C=S). IR (KBr) (Vmax, cm$^{-1}$): 3275 and 3196 (NH2), 2197 (CN), 1657 (OC=C), 1596, 1434 (C=CAr), 1384 (C=S). EI-MS: m/z (%) = 351 ($M^+$, 28), 323(100), 291(23), 267(60), 240(23), 189(15), 165(13). Anal.Calc. for $C_{18}H_{13}N_3OS_2$ (351.44): C, 61.52; H, 3.73; N, 11.96. Found: C, 61.80; H, 3.81; N, 12.00%.

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