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# Synthesis Of New Heteroannulated [2,4]Benzothiazepinones

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## ABSTRACT

Benzimidazole-2-thione **(2a)** was converted to a new derivative of [1,3] benzimidazo[2,1-c] [2,4]benzothiazepin-12(7H)-one **(3a)** but naphtho[2,3-d]imidazol-2-thione **(2b)** and perimidin-2-thione **(2c)** were each converted to a derivative of the novel heterocyclic ring systems, naphtha [2',3':4,5] imidazo[2,1-c][2,4]benzothiazepin-15 (5H) -one **(3b)** and [2,4] benzothia zepino[4,3-a] perimidin-14(9H)-one **(3c)**. 

## KEYWORDS

Benzimidazole-2-thione;
Fused 2;
4-Benzothiazepinone;
Naphtho[2,3-d]
imidazole-2-thione;
Perimidin-2-thione.

## INTRODUCTION

As part of our continuing interest in the synthesis of polyheterocyclic compounds[1-4] we have synthesized a new derivative of [1,3]benzimidazo[2,1-c][2,4]benzothiazepin-12(7H)-one**(3a)** and derivatives of two novel heterocyclic systems, naphtho [2',3':4,5]imidazo[2,1-c][2,4] benzothiazepin-15(5H)-one**(3b)** and [2,4]benzothiazepino[4,3-a]perimidin-14(9H)-one**(3c)**. In each instance the thiazepine ring was constructed from the readily available heterocyclic-2-thione precursors, compounds**(2a)**[5], **(2b)**[6] and**(2c)**[7] (SCHEME 1).

## RESULTS AND DISCUSSION

Using our previously described procedure[1] the thiones**(2a-c)** were reacted with 2-chloromethyl-benzoyl chloride**(1)** in boiling acetonitrile in the presence of triethylamine to obtain the desired new heterocyclic compounds**(3a-c)**. The utility of 2-chloromethylbenzoyl chloride as a bifunctional electrophilic reagent for the formation of carbon-carbon and carbon-sulfur bonds through nucleophilic substitution reactions with thioamide functionality and the regioselectivity of the reactions, by now been well established[1,8,9] in a typical example sequentional

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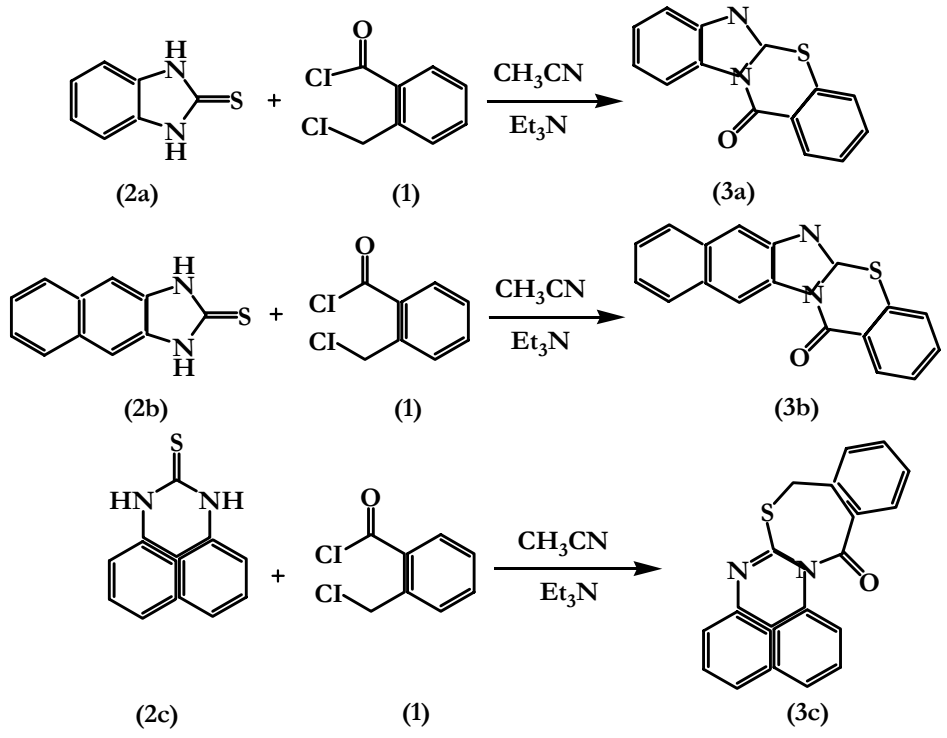


SCHEME 1

addition of 2-chloromethylbenzoyl chloride and triethylamine to the boiling mixture of benzimidazole-2-thione**(1a)** in acetonitrile gave a mixture which was heated at reflux for 5 hours. The reaction was monitored by TLC and after work up the reaction mixture; the crude product was purified by column chromatography using $CHCl_3$:MeOH(95:5) as the eluent to get the desired product**(3a)** in 65% yield. The structure of this compound was established on the basis of its spectral and microanalytical data. The IR spectrum shows an absorption band at 1675 $cm^{-1}$ assignable to an amide carbonyl group. The $^1$HNMR spectrum which was recorded in deuterated chloroform exhibits a singlet at δ 4.16 ppm attributed to S-$CH_2$ protons and three multiplets at δ 7.2-7.8 ppm, 7.9-8.2 ppm and 8.4-8.6 ppm due to eight aromatic protons. The mass spectrum of this compound showed the molecular ion peak at 266 which is in agreement with the proposed structure. All these data plus the microanalytical data clearly indicate the formation of compound**(3a)**.

In summary we have synthesized a new derivative of [1,3]benzimidazo[2,1-c][2,4] benzothiazepin-12(7H)-one**(3a)** and derivatives of two novel hetero cyclic systems, naphtho[2',3':4,5]imidazo [2,1-c][2,4] benzothiazepin-15(5H)-one**(3b)** and [2,4]benzothiazepino[4,3-a]perimidin-14(9H)-one**(3c)** through the reaction of heterocyclic thiones with 2-chloromethylbenzoyl chloride.

## EXPERIMENTAL

Melting points were recorded on an electrothermal type 9100 melting point apparatus. The IR spectra were obtained on a 4300 Shimadzu spectrometer. The $^1$HNMR (100 MHz) spectra were recorded on a Bruker AC l00 spectrometer. The mass spectra were scanned on a Varian Mat CH-7 instrument at 70ev. Elemental analysis was performed on a thermofinnigan flash EA microanalyzer.

### General procedure for preparation of hetero-annulated [2, 4]benzothiazepinones(3a-c)

2-chloromethylbenzoyl chloride**(1)** (1.32g, 7mmol) was added drop wise to the boiling mixture of heterocyclic-2-thione(5mmol) in boiling acetonitrile(40mL). To this mixture an equimolar of triethylamine(5mmol) was added. The reaction was

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monitored by TLC. Heating was continued for 5 hours, then the reaction mixture, while hot, was filtered off, water was added to the point of precipitation and the crude product was separated and purified by column chromatography using $CHCl_3$:MeOH 95:5 as the eluent.After evaporation of the solvent, the desired product was obtained.

**[1,3] Benzimidazo[2,1-c][2,4]benzothiazepin-12(7H)-one (3a)**

This compound was obtained as white crystal (0.87g, 65%), m.p. 178-180ºC. $^1$HNMR: δ($CDCl_3$), 4.16(s, 2H, $CH_2$), 7.2-8.6(m, 8H, aromatic rings). IR(KBr disc): $\upsilon_{C=O}$ 1675 $cm^{-1}$. MS: m/z 266 ($M^+$); Anal:Calcd. for $C_{15}H_{10}N_2OS$: C, 67.65; H, 3.78; N, 10.52; S, 12.04. Found: C, 67.33; H, 4.04; N, 10.67; S, 11.86%.

**Naphtho[2',3':4,5]imidazo[2,1-c][2,4]benzothiazepin-15(5H)-one (3b)**

This compound was obtained as yellow crystal (1.11g, 70%), m.p. 280-282ºC. $^1$HNMR: δ($CDCl_3$), 4.22(s, 2H, $CH_2$), 7.2-8.2(m, 10H, aromatic rings). IR(KBr disc): $\upsilon_{C=O}$ 1670$cm^{-1}$. MS:m/z 316($M^+$); Anal: Calcd. for $C_{19}H_{12}N_2OS$: C, 72.13; H, 3.82; N, 8.85; S, 10.14. Found: C, 71.92; H, 3.96; N, 8.71; S, 10.31%.

**[2,4]Benzothiazepino[4,3-a]perimidin-14(9H)-one (3c):**

This compound was obtained as yellow crystal (0.98g, 62%), m.p. 265-267ºC. $^1$HNMR: δ($CDCl_3$), 5.1(s, 2H, $CH_2$), 6.5-8.2(m, 10H, aromatic rings). IR(KBr disc): $\upsilon_{C=O}$ 1665 $cm^{-1}$. MS:m/z 316($M^+$); Anal: Calcd. for $C_{19}H_{12}N_2OS$: C, 72.13; H, 3.82; N, 8.85; S, 10.14. Found: C, 72.29; H, 4.01; N, 8.67; S, 9.98%.

## REFERENCES


[1] M.Bakavoli, A.Davoodnia, M.Rahimizadeh, M.M.Heravi, M.Ghassemzadeh; J.Chem.Res.(S)., 178 **(2002)**.

[2] M.Bakavoli, A.Davoodnia, M.Rahimizadeh, M.M. Heravi; Phosphorous, Sulfur, Silicon, **177**, 2303 **(2002)**.

[3] M.Bakavoli, A.Davoodnia, M.Rahimizadeh, M.M. Heravi; Mendeleev Commun., **16(1)**, 29 **(2006)**.

[4] A.Davoodnia, M.Bakavoli, A.Vahedinia, M. Rahimizadeh, M.Roshani; Heterocycles, **68(4)**, 801 **(2006)**.

[5] H.E.Album, R.L.Fenichel, F.G.Gregory, P.H.L.Wei; U.S., 4, 214, 069, Chem.Abs., **94**, 4018a **(1980)**.

[6] D.J.Brown; J.Chem.Soc., 1974-7 **(1958)**.

[7] Liu.Kang Chien, Chen.Hsiu Ho, Lin.Yueh O; Arch.Pharm., (Weinheim. Ger), **316**, 728; Chem.Abs., **99**, 122412a **(1983)**.

[8] Y.Sato, H.Fujita; Chem.Abs., **84**, P105670f **(1976)**.

[9] H.Fujita, Y.Sato; Chem.Pharm.Bull, **23**, 1764 **(1975)**.