

Mohd. Imran Ansari,^a Ravi Shankar,^a Mohd. Kamil Hussain,^a Ruchir Kant,^b Prakash R. Maulik,^b K. Ravi Kumar,^c and K. Hajela^{a,*}

^aMedicinal and Process Chemistry Division, Central Drug Research Institute, Lucknow 226001, UP, India

^bMolecular and Structural Biology Division, Central Drug Research Institute, Lucknow-226001, UP, India

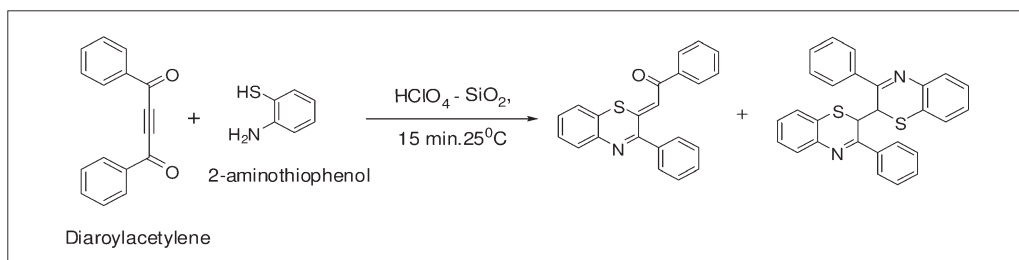
^cX-ray Crystallographic Division, Indian Institute of Chemical Technology, Hyderabad-500007, AP, India

*E-mail: kanchan_hajela@cdri.res.in

Received September 24, 2010

DOI 10.1002/jhet.795

Published online 18 August 2011 in Wiley Online Library (wileyonlinelibrary.com).



Mono- and bis-diaryl-2H-1,4-benzothiazines were obtained in quantitative yields through silica-supported perchloric acid catalyzed reaction cascade of double condensation and 1,4 addition of diarylacetylenes with 2-aminothiophenol at room temperature. The structures were confirmed by spectroscopic analyses and X-ray crystallographic studies.

J. Heterocyclic Chem., **48**, 1336 (2011)

INTRODUCTION

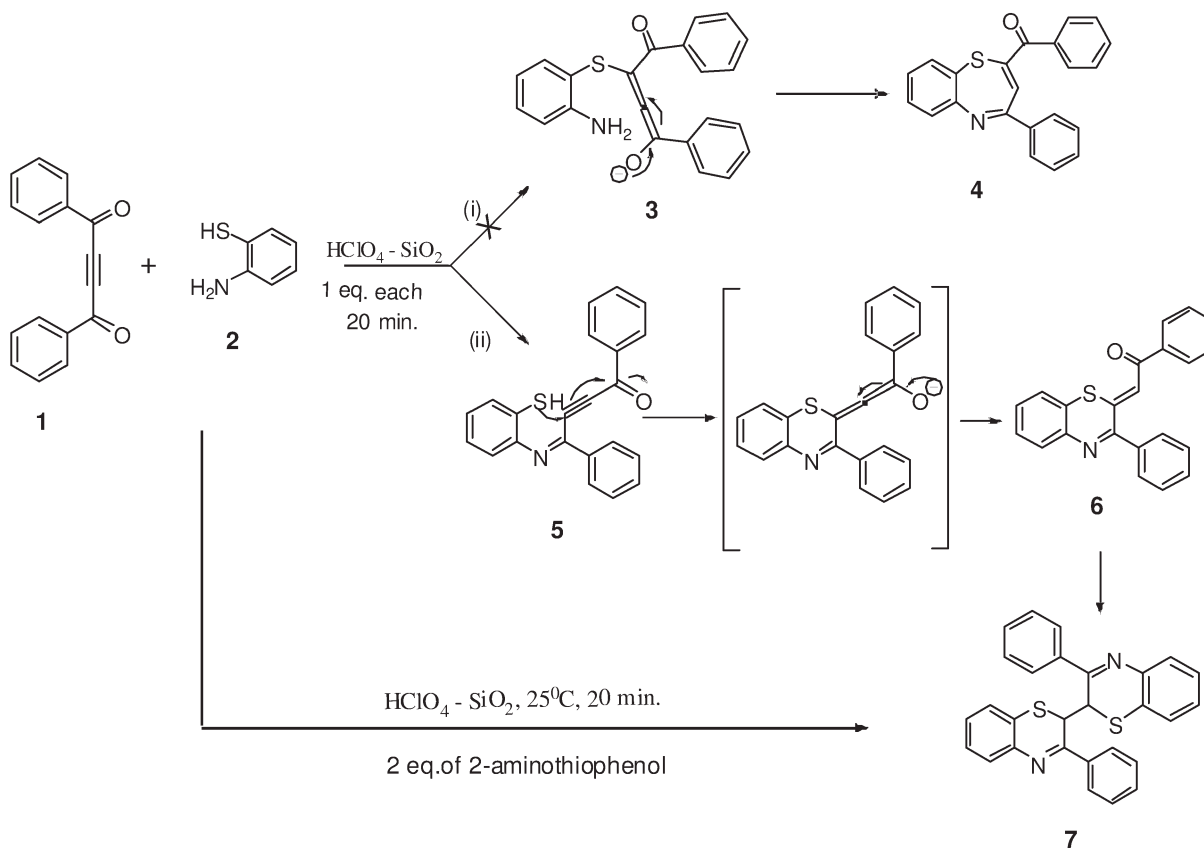
The leading contenders for eco-friendly processes are supported reagents [1a,b]. The good thermal and mechanical stabilities of such reagents make them easy to handle as free flowing powders, less toxic, noncorrosive, and their ease of separation and regeneration. Novel solid acid catalysts are being developed for use in organic synthesis. The newly introduced silica-supported perchloric acid ($\text{HClO}_4\text{-SiO}_2$) has emerged as a mild and a highly efficient, recyclable heterogenous catalyst system [2]. Its successful application as a versatile solid acid catalyst in a variety of multicomponent reactions/synthetic transformations [3–5] for the synthesis of diverse heterocyclic compounds led us to explore its utility in the condensation reactions of diarylacetylenes and diarylethylene with 2-aminothiophenol.

Benzothiazine ring system containing compounds are well known for their biological activities as antifungal, cytotoxic, anti-inflammatory, antiallergic, immunostimulating, antiarrhythmic, and central nervous system (CNS) depressants [6]. In particular, 1,4-benzothiazine-induced neurotoxic effects have been hypothesized to play a role in neurodegenerative diseases, such as Parkinson's and Alzheimer disease [7]. Their synthesis mainly involves treatment of 2-aminothiophenol with α -halocarbonyl compounds [8]. Bis-diaryl 1,4-benzothiazines have been

prepared either through oxidation of monomeric 1,4-benzothiazines [9], as condensation product of 2-aminothiophenol with isoxazolones [10] or from α,α -dihalocarbonyl compounds [11]. In this article, we report a new and expedient synthesis of mono- and bis-2H-diaryl 1,4-benzothiazines through silica-supported perchloric acid ($\text{HClO}_4\text{-SiO}_2$) catalyzed reaction cascade of double condensation and 1,4-Michael addition.

RESULTS AND DISCUSSION

When 1,2-diarylacetylene (**1**) is mixed with 2-aminothiophenol (**2**) at room temperature (25°C) with stirring in methanol and catalyzed by silica-supported perchloric acid, the reaction is very fast and completes within 20 min. Two major spots seen on thin layer chromatography (TLC) were isolated as crystalline yellow solids on purification by column chromatography in the ratio of 80:20. One compound showed all proton merged in aromatic region and mass value of 342 (M^++1), the second compound showed a sharp singlet at 4.1 δ ppm for two protons and five extra aromatic protons and a mass value of 448 (M^+). Reaction of 2-aminothiophenol with chalcones or alkynones [12] is reported to form the seven-membered 1,5-benzothiazepine derivatives; however, there is no report of reaction between 1,4-diarylacetylene and 2-

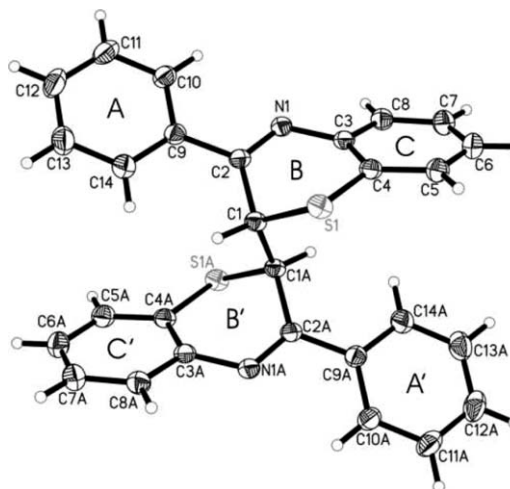
Scheme 1. Synthetic pathways for the synthesis of mono- and bis-diaryl-2*H*-1,4 benzothiazines.

aminothiophenol, although 1,4-diarylacetylenes are reported to form six-membered quinoxaline derivatives with 1,2-diaminobenzenes [13].

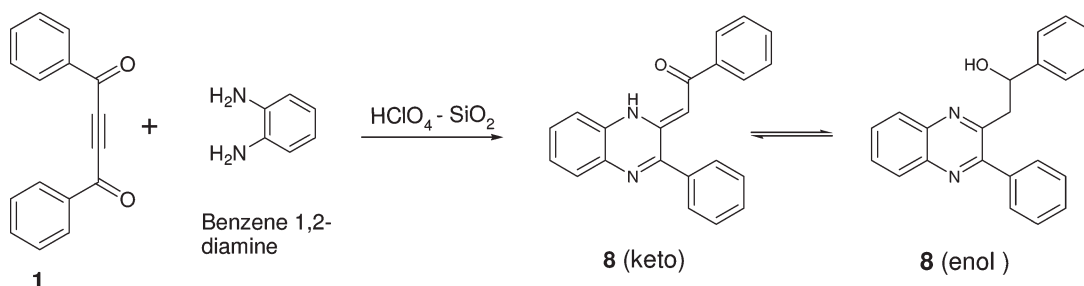
With the above observations, there existed the possibility of formation of either six- or seven-membered ring compounds as the reaction may follow any of the two pathways as shown in Scheme 1. (i) Conjugate addition of the sulfhydryl group resulting in the formation of thia Michael adduct (**3**) which on subsequent intramolecular aldol condensation and dehydration may form 1,5-benzothiazepine derivative (**4**) or (ii) initial aldol condensation product (**5**) followed by intramolecular conjugate addition by the sulfhydryl group and rearrangement to form the 1,4-benzothiazine derivative (**6**). Since the molecular ion peak of second compound showed higher mass value of approx. 448, indicated further conjugate addition of another molecule of 2-aminothiophenol. We tried the same reaction with two equivalents of 2-aminothiophenol, and in just 15 min of stirring an orange-yellow solid (**7**) precipitated out in quantitative yield. It showed a sharp singlet at 4.1 δ ppm for two protons and same number of aromatic protons and also molecular ion peak of mass value 448 (M^+) in the mass spectrum.

This confirmed double condensation reaction but still the formation of six- or seven-membered ring skeleton of the

compound being either **4** or **6** could not be ascertained. To confirm the molecular structure between benzothiazepine or benzothiazine skeleton, we tried to develop crystals of **4**, **6**, and **7**. Fortunately, single crystal X-ray diffraction studies confirmed the structure of compound **7** as 2,2'-bis-2*H*-3,3'-diaryl-1,4-benzothiazine shown in the Oak Ridge thermal ellipsoid plot (ORTEP) diagram (Fig. 1).

**Figure 1.** ORTEP diagram of **7** showing its molecular structure.

Scheme 2. Synthesis of 1-aryl-2-[(3-arylquinoxalin-2(1H)-ylidene) ethanone 8.



This conclusively proved the first compound **6** as the six-membered benzothiazine derivative, (Z)-1-phenyl-2-(3-phenyl-2H-benzo[b][1,4]thiazin-2-ylidene)ethanone in which the exocyclic ene proton merged with the aromatic protons. In ^{13}C -NMR spectrum, it shows a clear peak at 118 δ ppm. It undergoes double condensation to give the bis-compound **7** in the presence of excess thiophenol due to the exocyclic enone system and shows a two-proton singlet at 4.1 δ ppm in the proton nuclear magnetic resonance (NMR). This structure confirmation was supported by the formation of six-membered 1-aryl-2-[(3-arylquinoxalin-2(1H)-ylidene) ethanone (**8**) on reaction of **1** with benzene-1, 2-diamine (Scheme 2). Its X-ray crystal structure is shown in the ORTEP diagram (Fig. 2).

With the confirmation of structures of compounds **6**, **7**, and **8**, the effect of catalyst and its loading was next studied by carrying out the above reactions using different solid acid catalysts. The results are noted in Table 1. When both the reactants are used in equimolar amounts with the catalyst loading of 1 mol %, compound **6** predominates (>70%) although minor amount of bis compound **7** is also formed. However, if thiophenol is present in excess (2 equiv.), bis compound **7** is obtained in almost quantitative yields with the same catalyst loading of 1 mol %. The reaction was also studied using other protic acids immobilized on silica like, H_2SO_4 –

SiO_2 , HBF_4 – SiO_2 , and trifluoroacetic acid (TFA)– SiO_2 , the catalytic efficiency followed the order HClO_4 – $\text{SiO}_2 > \text{H}_2\text{SO}_4$ – $\text{SiO}_2 > \text{TFA}$ – $\text{SiO}_2 > \text{HBF}_4$ – SiO_2 . With other catalysts like TFA, para toluene sulfonic acid (PTSA), $\text{BF}_3 \cdot \text{Et}_2\text{O}$, acetic acid, and SiO_2 , mixture of **6** and **7** was obtained. The formation of bis derivative was found to be independent of catalyst loading, the best yields of **7** were obtained with silica-supported perchloric acid (HClO_4 – SiO_2) and in less time. An increase in the catalyst loading did not have any significant effect on the yields of either **6** or **7**. The catalyst can be recovered by simple filtration and can be reused after proper washing and drying without any significant loss of activity.

To extend the scope of reaction, we next focussed our attention on the reaction of 1,4-diaroylethylene with **2** under the same reaction conditions (Scheme 3 and Table 2).

TLC of the reaction mixture showed only one major spot which was isolated as yellow oil in 88% yield by column chromatography. Its structure was determined from the one-dimensional ^1H - and ^{13}C -NMR and by using 2D correlation spectroscopy (COSY), heteronuclear single quantum coherence (HSQC), and heteronuclear multiple bond coherence (HMBC) sequences. The ^1H -NMR spectrum exhibited two doublet of doublets at δ 2.86 and δ 3.42 ppm and another doublet of doublet at δ 4.89 ppm. In our opinion, the downfield doublet of doublet at δ 4.89 corresponds to the Ha proton being adjacent to the carbonyl group and sulfur atom, whereas the doublet of doublets at δ 2.86 and δ 3.42 ppm correspond for

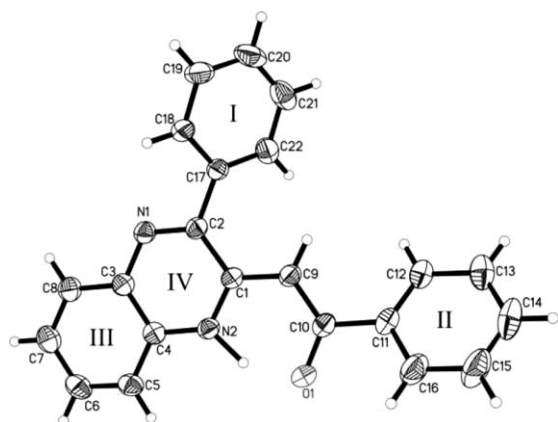
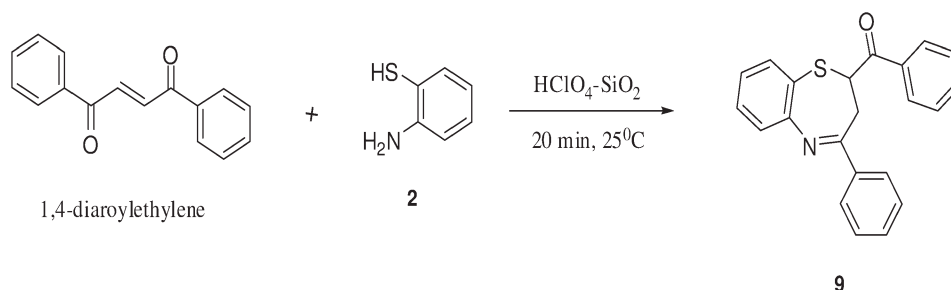
Figure 2. ORTEP diagram showing molecular structure of **8**.

Table 1

Direct condensation of **1** and **2** (2 mmol) to form compound **7** using different solid acid catalysts in methanol at room temperature (25°C).

Entry	Catalyst	Time (min)	Yield (%)
1	HClO_4 – SiO_2	20	85
2	H_2SO_4 – SiO_2	30	60
3	HBF_4 – SiO_2	40	48
4	$\text{BF}_3 \cdot \text{Et}_2\text{O}$	25	58
5	PTSA	35	55
6	TFA – SiO_2	30	52
7	TFA	20	62
8	CH_3COOH	30	68

Scheme 3. Synthesis of (E)-phenyl(4-phenyl-2,3-dihydrobenzo[b][1,4]thiazepin-2-yl)methanone.

the two geminal protons Hb and Hc (methylene protons, Fig. 3). This was also confirmed from 135 distortionless enhancement by polarization transfer (DEPT) and HSQC experiments. In the COSY experiment, cross-peaks were observed between the methylene proton indicating that the Hb and Hc protons are geminal, also confirmed by the help of HSQC experiment. The structure was fully established from the HMBC sequences. In the HMBC spectrum, the proton of doublet of doublet at δ_{Ha} 4.89 ppm showed cross peak at δ_{C} 157.9 ppm (C=N) and a quaternary aromatic carbon bonded with sulfur at δ_{C} 120.3 ppm. The proton signal at δ_{Hb} 3.42 ppm and δ_{Hc} 2.86 ppm showed cross-peaks to a carbonyl carbon at δ_{C} 196.1 ppm (C=O). Cross-peaks of proton at δ_{Ha} 4.89 ppm showed stronger cross-coupling with carbon at δ_{C} 157.9 ppm (C=N) than the carbonyl carbon and protons Hb and Hc showed stronger cross-coupling with carbonyl carbon at δ_{C} 196.1 ppm (C=O) than carbon at δ_{C} 157.9 ppm (C=N). This HMBC correlation confirmed the presence of a seven-membered cyclic ring establishing the structure of the compound **8** as phenyl (4-phenyl-2,3-dihydro-benzo[b][1,4]thiazepin-2-yl)methanone, shown in Figure 3.

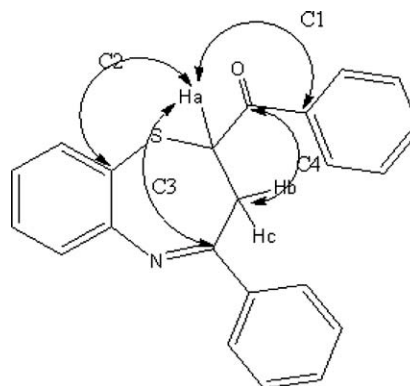
In summary, to the best of our knowledge this is the first report of an expedient and eco-friendly synthesis of mono- and bis-diaryl-2H-1,4 benzothiazines through the coupling of 1,2-diaroylethylene and 2-aminothiophenol using heterogenous catalyst system which is recyclable, easy to use, and environmentally benign. Further, it was observed that diaroylacetylenes and ethylenes react dif-

ferently with 2-aminothiophenol under the same reaction conditions forming different heterocyclic compounds. The stability of six-membered ring and its dimerisation to a more stable bis-derivative may be the driving force for the preferred formation of 1,4-benzothiazine derivatives with 1,2-diaroylethylenes.

EXPERIMENTAL

Melting points were taken in open capillaries on an electrically heated melting point apparatus Comlab and are uncorrected. Infra red (IR) spectra were recorded on Perkin-Elmer RX-1 spectrophotometer using KBr pellets. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were recorded on Bruker DPX-200 (200 MHz for ^1H and at 50 MHz for ^{13}C) or DRX-300 (300 MHz for ^1H and at 75 MHz for ^{13}C) spectrometers using CDCl_3 as solvent. Tetramethylsilane served as an internal standard in $^1\text{H-NMR}$ and CDCl_3 in ^{13}C spectra. Silica gel (60–120 mesh) was used for column chromatography while silica gel (230–400 mesh) was used for flash chromatography. TLC was run on precoated silica gel 60F 254 and RP-18 F 254 (Merck) plates. Detection of spots was done either by iodine vapors or spraying with 1% ceric sulfate in 1M H_2SO_4 followed by heating at 100°C . All the compounds were characterized by spectroscopic data and elemental analysis carried was out on Vario EL-III, German analyzer.

(E)-1-Phenyl-2H-benzo[b][1,4]thiazin-2-ylidene)ethanone (6). Diaroylacetylene (**1**, 236 mg, 1 mmol) was dissolved in methanol (2 mL) and stirred for 2 min. Silica-supported perchloric acid ($\text{HClO}_4\text{-SiO}_2$, 1.62 mg, 1 mol %) was then added to the solution, followed by 2-aminothiophenol (**2**,

**Figure 3.** Significant HMBC (H → C) correlation of compound **9**.**Table 2**

Direct condensation of 1,4-diaroylethylene and **2** (2 mmol) to form compound **9** using different solid acid catalysts in methanol at room temperature (25°C).

Entry	Catalyst	Time (min)	Yield (%)
1	$\text{HClO}_4\text{-SiO}_2$	20	88.4
2	$\text{HBF}_4\text{-SiO}_2$	30	54
3	$\text{H}_2\text{SO}_4\text{-SiO}_2$	35	58
4	TFA-SiO_2	25	60
5	TFA	25	61
6	$\text{BF}_3\cdot\text{EtO}$	25	52.98
7	AcOH/piperidine	30	62.39

0.106 mL, 1 mmol). The reaction mixture was stirred for 20 min at room temperature (25°C). Thereafter, the progress of the reaction was checked on TLC which showed complete consumption of **1** and formation of two major spots. The solution was filtered to remove the solid catalyst and washed with methanol (2 mL). Excess of methanol was removed under reduced pressure. The crude residue was washed with water to remove acidic impurities and extracted with ethylacetate. After drying over anhydrous sodium sulfate and removal of excess ethylacetate, the mixture was purified by flash column chromatography (90:10, EtOAc/hexane). Two compounds were isolated, one as pale yellow solid **6** (73.45%), m.p. 147–151°C; m/z 342 [M+1]; IR: 3021, 2360(C=N), 1216, 760 cm^{-1} ; ^1H -NMR (300 MHz, CDCl_3): δ 7.35–7.46 (m, 5H), 7.46–7.52 (m, 2H), 7.52–7.58 (m, 3H), 7.68–7.76 (m, 3H), 7.77–7.83 (m, 2H) ppm; ^{13}C -NMR (300 MHz, CDCl_3): δ 118.1, 123.4, 125.6, 127.8, 128.70, 129.2, 129.8, 131.1, 132.5, 138.1, 138.9, 139.2, 142.4, 157.8, 188.6 ppm; Anal. Calcd. for $\text{C}_{22}\text{H}_{15}\text{NOS}$: C, 77.39; H, 4.43; N, 4.10. Found: C, 78.00; H, 5.10; N, 3.95. high resolution mass spectroscopy (HRMS) (ESI) calcd for $[\text{C}_{22}\text{H}_{15}\text{NOS} + \text{H}]^+$ 342.0952, found 342.0963 and a second orange-yellow solid **7** (12%), m.p. 234–35°C, m/z 448(M⁺); ^1H -NMR (300 MHz, CDCl_3): δ 4.1 (s, 2H, S—CH), 6.94–6.91 (m, 2H), 7.17–7.12 (m, 2H), 7.45–7.30 (m, 9H), 7.70–7.64 (m, 5H) ppm; ^{13}C -NMR (300 MHz, CDCl_3): δ 31.1, 120.1, 126.8, 127.0, 127.6, 127.8, 128.2, 128.3, 130.5, 137.9, 142.9, 156.0 ppm; Anal. Calcd. for $\text{C}_{28}\text{H}_{20}\text{N}_2\text{S}_2$: C, 74.97; H, 4.49; N, 6.24. Found: C, 75.04; H, 4.16; N, 5.95.

2,2'-Bis-2H-3,3-diaryl-1,4-benzothiazine (7). This was synthesized by reacting **1** (1 equiv.) with two equivalents of **2** following the procedure described above. The reaction was complete within 15 min with the precipitation of the bis compound **7** in almost quantitative yield. The compound was dissolved in excess of ethanol and filtered to remove the catalyst. The catalyst was washed with ethanol (four to five times) and dried for reuse. Crystallization from ethanol gave pure compound **7** (85%). The spectral data was exactly the same as described above. The structure of compound **7** was absolutely confirmed by single crystal X-ray diffraction analysis.

The compound **7** crystallizes in $P2(1)/c$ space group and two molecules of compound are in asymmetric unit. The molecule consists of two similar halves joined to form dimer through single covalent bond between C1 and C1A (1.54 Å). Each monomer unit is having three rings A, B, C and A', B', C'. Ring A, C, A', and C' are almost planar. The ring B and B' adopts distorted envelope conformations with C and C1A forming the flaps, respectively. (The deviation of atom C1 is $-0.859(1)$ Å from the least square mean plane through atom C2, N1, C3, C4, and S1 for ring B. The deviation of atom C1A is $0.859(1)$ Å from the least square mean plane through atom C2A, N1A, C3A, C4A, and S1A for ring B'). The crystal data of **7**, $\text{C}_{28}\text{H}_{20}\text{N}_2\text{S}_2$, $M = 448.58$, monoclinic, $P2(1)/c$, $a = 7.094(4)$ Å, $b = 11.927(6)$ Å, $c = 12.693(6)$ Å, $\alpha = 90^\circ$, $\beta = 91.294(1)^\circ$, $\gamma = 90^\circ$, $V = 1073.76$ Å³, $Z = 2$, $D_c = 1.387$ g cm^{-3} , $\mu(\text{Mo-K}\alpha) = 0.27$ mm⁻¹, $F(0\ 0\ 0) = 468.0$, rectangular block, yellowish, size = $0.275 \times 0.15 \times 0.3$ mm³, 12,240 reflections measured ($R_{\text{int}} = 0.0146$), 4893 unique, $wR_2 = 0.106$ for all data, conventional $R = 0.0365$ for 4372 $F_o > 4\sigma(F_o)$ and 0.04 for all 4893 data, goodness of fit $S = 1.059$ for all data and 289 parameters and zero restraints. Unit cell determination and intensity data collection was performed on a

Bruker SMART APEX CCD diffractometer at 293(2) K. Structure solutions by direct methods and refinements by full-matrix least-squares methods on F^2 . Programs: SMART (Bruker, 2001), SAINT (Bruker, 2001) and SHELXTL-NT [Bruker AXS, Madison, WI, 1997]. CCDC (deposit No. 803514) contains the supplementary crystallographic data. These data can be obtained free of charge from www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internet) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

1-Phenyl-2-(3-phenylquinoxalin-2(1H)-ylidene) ethanone (8). This was synthesized by the process as described for **6**. The crude solid was purified by flash column chromatography using EtOAc/hexane (90:10) to give the pure compound **8** as yellow solid (86%), m.p. 76–77°C, m/z 325 (M+1); IR: 3020 (NH), 1591 (C=O), 1534, 1216, 761 cm^{-1} ; ^1H -NMR (300 MHz, CDCl_3): δ 6.41 (s, CH), 7.44–7.41 (m, 4H), 7.76–7.58 (m, 5H), 7.90–7.79 (m, 4H), 7.93 (d, $J = 7.98$, 1H), 15.85 (s, NH) ppm; ^{13}C -NMR (300 MHz, CDCl_3): δ 91.2, 119.6, 125.9, 126.5, 128.2, 128.4, 128.6, 128.7, 128.8, 129.3, 130.7, 130.8, 132.1, 137.2, 137.3, 138.1, 147.6, 156.8, 181.3 ppm; Anal. Calcd. for $\text{C}_{22}\text{H}_{16}\text{N}_2\text{O}$: C, 81.46; H, 4.97; N, 8.64. Found: C, 80.19; H, 4.71; N, 8.42. HRMS (EI) calcd for $\text{C}_{22}\text{H}_{16}\text{N}_2\text{O}$ [M]⁺ 324.1263, found 324.1268.

The structure of the compound **8** was characterized by single crystal X-ray diffraction studies. The molecule consists of four rings (I, II, III, IV), which all are almost planar (the mean deviation of fitted atoms is 0.005, 0.002, and 0.012 Å, respectively from the least square plane formed by atoms C17 to C22 for ring I, C11 to C16 for ring II, and C6, C5, C4, N2, C1, C2, N1, C3, C8, and C7 for ring III and IV. At atom C10 of the molecule, a carbonyl group is substituted. X-ray study further reveals that the keto–enol tautomerisation [14,15] occur in the molecule due to intramolecular proton sharing between nitrogen of ring IV and oxygen atom of carbonyl group (N1—H1...O1) and this affects in elongation of single bond distance (N1—H1 = 1.164 Å) and double bond of carbonyl group (C10—O1 = 1.29 Å). The crystal data of **8**, $\text{C}_{22}\text{H}_{16}\text{N}_2\text{O}$, $M = 324.37$, triclinic, $P1$, $a = 9.260(1)$ Å, $b = 9.930(2)$ Å, $c = 10.820(2)$ Å, $\alpha = 79.37(3)^\circ$, $\beta = 65.46(3)^\circ$, $\gamma = 68.97(3)^\circ$, $V = 844.0(3)$ Å³, $Z = 2$, $D_c = 1.276$ g cm^{-3} , $\mu(\text{Mo-K}\alpha) = 0.08$ mm⁻¹, $F(0\ 0\ 0) = 340.0$, rectangular block, yellowish, size = $0.2 \times 0.3 \times 0.35$ mm³, 9790 reflections measured ($R_{\text{int}} = 0.021$), 3881 unique, $wR_2 = 0.1394$ for all data, conventional $R = 0.0473$ for 2891 $F_o > 4\sigma(F_o)$ and 0.0634 for all 3881 data, Goodness of fit $S = 1.039$ for all data and 230 parameters and zero restraints. Unit cell determination and intensity data collection was performed on a Bruker SMART APEX CCD diffractometer at 293(2) K. Structure solutions by direct methods and refinements by full-matrix least-squares methods on F^2 . Programs: SMART (Bruker, 2001), SAINT (Bruker, 2001), and SHELXTL-NT [Bruker AXS, Madison, WI, 1997]. CCDC (deposit No.803515) contains the supplementary crystallographic data. These data can be obtained free of charge from www.ccdc.cam.ac.uk/conts/retrieving.html.

(E)-Phenyl(4-phenyl-2,3-dihydrobenzo[b][1,4]thiazepin-2-yl)methanone (9). The reaction was performed in the similar manner as described for compound **6** using diaroylethylene and compound **2** in equimolar quantities. The crude residue obtained on workup was purified by flash column chromatography using EtOAc/hexane (90:10) giving one major product **9**

isolated as yellow oil, (88.39%), m/z 344 $[\text{M}+1]$; IR: 3021, 2360($\text{C}=\text{N}$), 1731($\text{C}=\text{O}$), 1219, 761 cm^{-1} ; ^1H -NMR (300 MHz, CDCl_3): δ 2.86 (dd, $J = 2.9$ Hz, 17.7 Hz, 1H), 3.42 (dd, $J = 10.1$, 17.7 Hz, 1H), 4.89 (dd, $J = 2.9$ Hz, 10.1 Hz, 1H), 6.98–7.11 (m, 1H, ArH), 7.12–7.23 (m, 2H, ArH), 7.23–7.33 (m, 2H, ArH), 7.33–7.55 (m, 5H, ArH), 7.62–7.76 (m, 2H, ArH), 7.94–8.11 (m, 2H, ArH), ^{13}C -NMR (300 MHz, CDCl_3): δ 29.8, 38.3, 120.3, 126.6, 127.2, 127.2, 127.6, 127.8, 127.9, 128.1, 128.2, 128.3, 128.3, 128.6, 128.8, 131.1, 133.6, 136.6, 142.5, 157.9, 197.1 ppm; Anal. Calcd. for $\text{C}_{22}\text{H}_{17}\text{NOS}$: C, 76.94; H, 4.99; N, 4.08. Found: C, 77.54.19; H, 5.36; N, 4.16. HRMS (ESI) exact mass calcd for $[\text{C}_{22}\text{H}_{17}\text{NOS} + \text{H}]^+$ 344.1109, found 344.1118.

Acknowledgments. The authors, Mohd. Imran Ansari, Ravi Shankar and Mohd. Kamil Hussain are thankful to CSIR for JRF & SRF fellowships. Financial assistance from Ministry of Health & Family Welfare is highly acknowledged and all are also grateful to SAIF for spectroscopic analysis of the compounds. PRM thank CSIR, New Delhi, for the Grant-in-aid of Emeritus Scientistship Scheme [No.:21(0766)/09/EMR-II], CDRI Commun. no. 7999.

REFERENCES AND NOTES

- [1] (a) Rao, L. *Resonance* 2007, 65; (b) Sherington, D. C.; Kybett, A. P. *Supported Catalysts and their Application*; Royal Society of Chemistry: Great Britain, 2001, Vol. 12.
- [2] (a) Chakraborti, A. K.; Gulhane, R. *Chem Commun* 2003, 1896; (b) Chakraborti, A. K.; Gulhane, R. *Tetrahedron Lett* 2003, 44, 1521; (c) Chakraborti, A. K.; Gulhane, R. *Indian Pat.*, 266/DEL/2003(10–3-2003).
- [3] Gopal, K. L.; Sharma, G.; Kumar, R.; Chakraborti, A. K. *Tetrahedron* 2007, 63, 1200; (b) Sharma, G.; Kumar, R.; Chakraborti, A. K. *Tetrahedron Lett* 2008, 49, 4272; (c) Kumar, D.; Kumar, R.; Chakraborti, A. K. *Synthesis* 2008, 1249; (d) Chakraborti, A. K.; Singh, B.; Chankeshwara, S. V.; Patel, A. P. *J Org Chem* 2009, 74, 5967.
- [4] (a) Colinas, P. A.; Bravo, R. D. *Carbohydr Res* 2007, 342, 2297; (b) Shaterian, H. R.; Yarahmadi, H.; Ghashang, M. *Tetrahedron* 2008, 64, 1263; (c) Heydari, A.; MaMani, L. *Appl Organomet Chem* 2008, 22, 12; (d) Wu, L.; Yang, C.; Zhang, C.; Yang, L. *Lett Org Chem* 2009, 6, 234.
- [5] (a) Mandal, P. K.; Misra, A. K. *Lett Org Chem* 2006, 3, 848; (b) Agrawal, A.; Rani, S.; Vankar, Y. D. *J Org Chem* 2004, 69, 6137.
- [6] Fringuelli, R.; Milanese, L.; Schiaffella, F. *Mini Rev Med Chem* 2005, 5, 1061.
- [7] Shen, X. M.; Dryhurst, G. *J Med Chem* 1996, 39, 2018.
- [8] Wilhelm, M.; Schmidt, P. *J Heterocycl Chem* 1969, 6, 635.
- [9] Donato, S.; Ciro, S.; Prota, G. *J Heterocycl Chem* 1970, 7, 1143.
- [10] Rao, M. H.; Reddy, M. P. R.; Veeranaiaiah, V. *Synth Commun* 1991, 21, 1715.
- [11] Prakash, O.; Sharma, N.; Pannu, K. *Synth Commun* 2007, 37, 1995.
- [12] Nakhmanovich, A. S.; Glotova, T. E.; Skvortsova, G. G.; Komarova, T. N.; Skorobogatova, V. I.; Mansurov, Yu. A. *Seria Khimicheskaya* 1982, 6, 1371.
- [13] Yavari, I.; Mirzaei, A.; Moradi, L. *Helv Chim Acta* 2006, 89, 2825.
- [14] Bertolasi, V.; Gilli, P.; Gilli, G. *Curr Org Chem* 2009, 13, 250.
- [15] Somma, M. S.; Medforth, C. J.; Nelson, N. Y.; Olmstead, M. M.; Khoury, R. G.; Smith, K. M. *Chem Commun* 1999, 13, 1221.