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Novel Sulfur-to-Nitrogen Migration of Ethenylmethyl Moiety in Benz[d]oxazole System via Internal Radical Capture

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Abstract: 2-Ethenylmethylthiobenz[d]oxazoles **9**–**11**, on heating at high temperature in bromobenzene, underwent migration of ethenylmethyl moieties without rearrangement from sulfur to nitrogen in an internal radical capture pathway, instead of [3,3]-sigmatropic change, to furnish 3-ethenylmethylbenz[d]oxazole-2(3*H*)-thiones **13**–**15**.

Keywords: Sulfur to nitrogen migration, ethenylmethyl, internal radical capture, benz[d]oazole, AIBN

INTRODUCTION

The structural analogy of benz[d]oxazole with indole, a heterocyclic system with diverse biological activity, has evoked recent interest in suitably constructed benz[d]oxazole compounds.[1] In connection with ongoing studies on Claisen-type sulfur-to-nitrogen rearrangement in a heterocyclic matrix,[2] we report here the results of studies on the thermal reaction of 2-ethenylmethylthiobenz[d]oxazoles.

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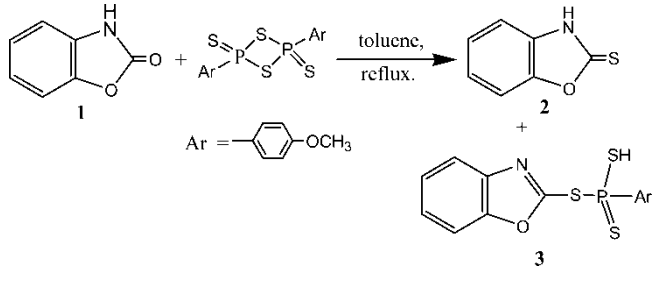
RESULTS AND DISCUSSION

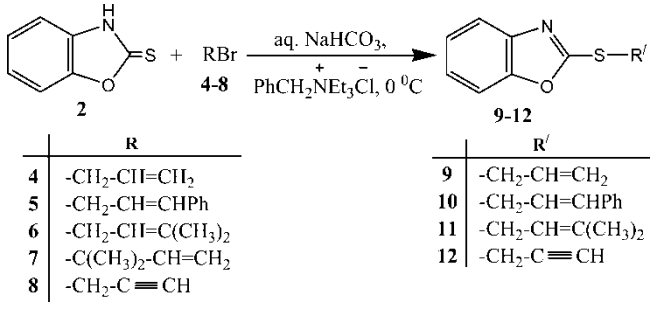
Benz[d]oxazol-2(3*H*)-one (**1**) was heated under reflux in dry toluene with Lawesson's reagent[3] for 5 h to furnish benz[d]oxazole-2(3*H*)-thione (**2**) and benz[d]oxazol-2-yl trithio-4-methoxyphenylphosphonate (**3**) (Scheme 1). However, exclusive formation[4] of **2** by reaction of **1** with Lawesson's reagent has been reported. Compound **3** might have resulted from the reaction of **2** with Lawesson's reagent (Scheme 1). Alkylation of **2** with (ethenyl/ethynyl)methyl bromides **4**–**8** in the presence of benzyltriethylammonium chloride (BTEAC) and aqueous sodium bicarbonate solution at 0°C (Scheme 2) led to, as expected, S-alkylated products 2-(ethenyl/ethynyl)-methylthiobenz[d]oxazoles **9**–**12.** However, N-alkylated product **13** was concomitantly formed as a minor product (16%) in the case of alkylation of **2** with allyl bromide.

Upon heating compounds **9**–**11** in dry bromobenzene at a sufficiently high temperature in an autoclave (Table 1), products **13**–**15** were obtained in low yields accompanied by some charring. The presence of unrearranged ethenylmethyl moieties in the products **13**–**15** was revealed from N-CH_2 proton signals in the region of δ4.8–5.0 and the corresponding carbon signals at δ44.3–48.1 in ^{13}C NMR spectra. This migration might occur via an ionic or radical route. To ascertain the feature, reaction of 2-(3-methylbut-2-enyl)thiobenz[d]oxazole (**11**) was conducted in refluxing bromobenzene containing a catalytic amount (20 mol%) of azo*bis*isobutyronitrile (AIBN). This led to completion of the rearrangement in 25 h at 150°C, producing **15** in 95% yield, whereas the same substrate was completely resistant to rearrangement at 150°C for 30 h in the absence of AIBN (Table 1). Although AIBN usually promotes radical reactions by abstracting hydrogen by its decomposition product, it is also known to promote homolysis of a carbon-to-heteroatom bond.[5] In our case, the promotional role of AIBN in the cleavage of C-S bond is explained in Scheme 3. This mechanism depicts detachment of the allyl radical from the substrate. This feature of the rearrangement viz. intra- or intermolecular nature has not been ascertained by crossover experiment, and, therefore, the suggested mechanism



1 2 3

Scheme 1.



	R
4	$-CH_2-CH=CH_2$
5	$-CH_2-CH=CHPh$
6	$-CH_2-CH=C(CH_3)_2$
7	$-C(CH_3)_2-CH=CH_2$
8	$-CH_2-C\equiv CH$

	R′
9	$-CH_2-CH=CH_2$
10	$-CH_2-CH=CHPh$
11	$-CH_2-CH=C(CH_3)_2$
12	$-CH_2-C\equiv CH$

Scheme 2.

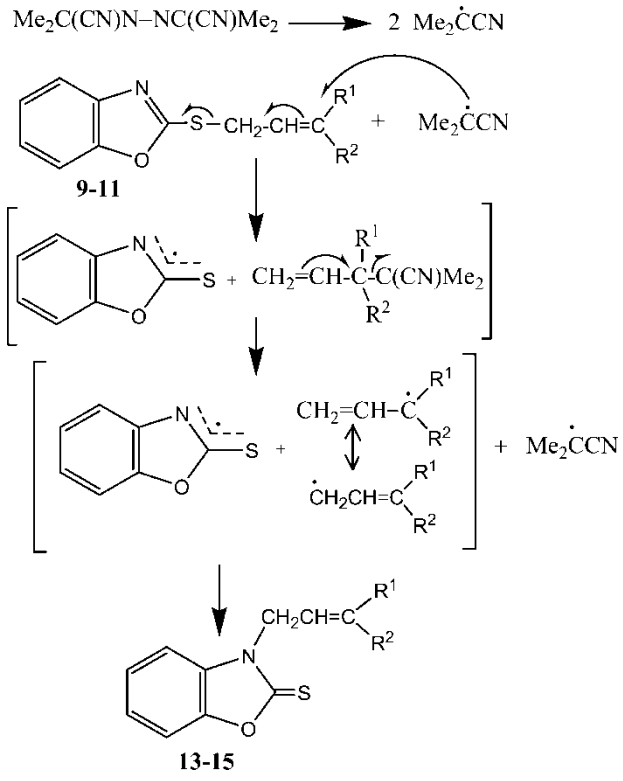
is only tentative. Formation of **13**–**15** via a tight radical pair cannot be ruled out. To the best of our knowledge, this constitutes the first report of migration of a skeletally unrearranged ethenylmethyl group from sulfur to nitrogen in preference to thio-Claisen rearrangement. However, there is an early report of a similar example of sulfur-to-carbon migration[6] without rearrangement of the ethenylmethyl skeleton accompanied by subsequent ring closure.

Reaction of 2-propargylthiobenz[d]oxazole (**12**) in bromobenzene under reflux for 5 h furnished two products, **16** and **17.** The UV (ethanol) spectrum of **16** [λ_{max} (logε) at 286.5 (4.0), 246.5 (3.9) nm and λ_{min} (logε) at 290.5 (4.0), 266.0 (3.8), 237.0 (3.9) nm] compares well with that of **9** with N=C-S-CH_2 moiety [λ_{max} (logε, ethanol) 285 (4.02), 248 (4.0); λ_{min} (logε, ethanol) at 282 (3.96), 264.6 (3.0), 226 (3.75) nm]. Significantly, the UV spectral features of **13** with S=C-N-CH_2 moiety [λ_{max} (logε, ethanol) at 300 (4.37) and 258.0 (3.90) nm and λ_{min} (logε, ethanol) at 270.5 (3.40), 238.5 (3.38) nm] is quite different. Compound **16** displayed a diagnostic methylene carbon signal at δ 29.1 in addition to eight aromatic methine and two olefinic methane carbon signals at δ 128.8, 125.1, 124.7, 124.3, 124.1, 122.4, 118.6, 110.6, 110.2, and 109.9 in its ^{13}C NMR spectrum. The appearance of a

Table 1. Thermal reaction of 3-ethenylmethylthiobenz[d]oxazoles **9**–**11** (Scheme 3)

			Reaction conditions				
Substrate	R_1	R_2	Temp (°C)	Time (h) Cat.	Product	Mp (°C)	Yield (%)
9	H	H	170	6 nil	**13**	80–82	27
10	H	Ph	210–220[a]	22 nil	**14**	128–130	15
11	CH_3	CH_3	210–220[a]	9 nil	**15**	86–88	26.6
11	CH_3	CH_3	150	25 AIBN[b]	**15**	86–88	95

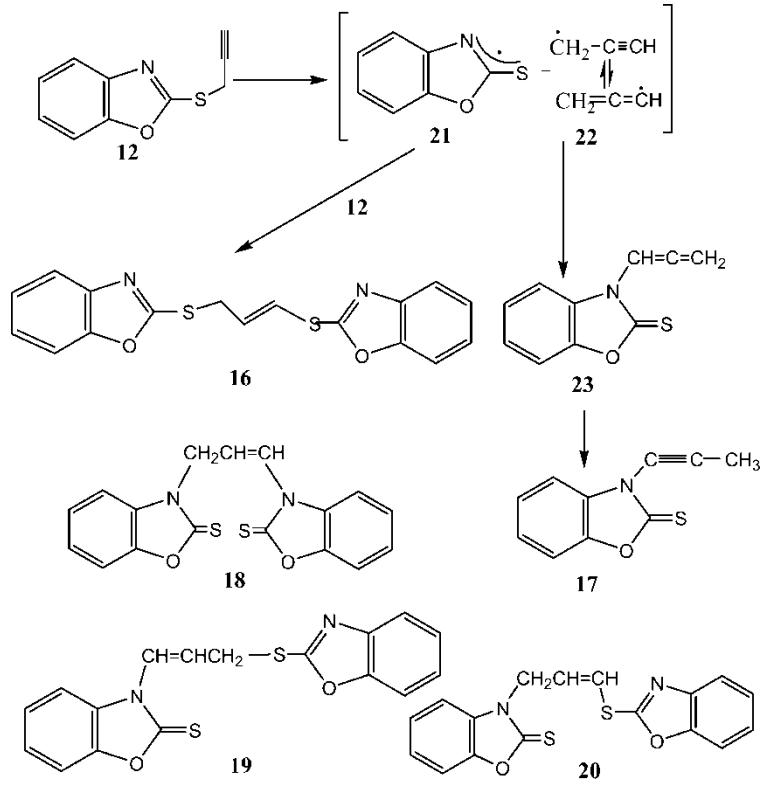
[a]Reaction was carried out in sealed tube.
[b]AIBN was used in 20 mol%.



Scheme 3.

methylene signal at δ 29.1 is consistent with its attachment to sulfur rather than nitrogen because it is expected to appear in the vicinity of δ 44 in that case. The product was assigned the structure **16** on the basis of these spectral features and other possible structures **18**, **19**, and **20** (Scheme 4) were ruled out.

The other product was assigned the structure 3-(1-propynyl)benz[d]oxazole-2(3*H*)-thione (**17**) on the basis of its ^{1}H NMR and ^{13}C NMR characteristics. It displayed a stretching absorption at 2210 cm^{-1} (C≡C) in its IR spectrum. The UV spectral features of **17** showing λ_{max} (logε) 323.5 (3.98), 284.5 (3.8), 222.0 (4.0) nm and λ_{min} (logε) at 294.0 (3.7), 262.0 (3.6) nm are in agreement with the attachment of -C≡C- with the N-3 of the benzoxazole ring. A plausible mechanism of formation of **16** and **17** by thermal change of 2-propargylthiobenz[d]oxazole (**12**) is shown in Scheme 4. The 2-thiobenz[d]oxazolyl radical **21** undergoes addition along its S-center to the CH-terminal of the acetylenic moiety of a second molecule of **12**, resulting in **16**. On the other hand, formation of **17** can be rationalized by internal combination of the allenyl radical formed by isomerization of the



Scheme 4.

preformed propargyl radical **22**, with the N-3 center of **21** producing 3-allenyl-benz[d]oxazole-2(3*H*)-thione (**23**). This is followed by prototropic change in the allenyl unit.

EXPERIMENTAL

The melting points are uncorrected. IR spectra were recorded as KBr pellets on a Perkin-Elmer-782 spectrophotometer, and UV spectra of ethanolic solution of the compounds were recorded on a Hitachi U-2000 spectrophotometer. The ^{1}H NMR spectra in $CDCl_3$ were run on a Bruker AM-300L instrument operating at 300 MHz with TMS as internal standard, and the ^{13}C NMR spectra were run in $CDCl_3$ on the same instrument operating at 75 MHz. The degree of proton attachment of the carbons was verified using the Distortionless Enhancement by Polarization Transfer (DEPT) sequence. Silica gel (60–120 mesh) was used for chromatographic purification. The solvents used were dried and distilled before use. Light petrol refers to one with a boiling range 60–80°C.

Synthesis of Benz[d]oxazole-2(3*H*)-thione (2) and Benz[d]oxazol-2-yl Trithio-4-methoxyphenylphosphonate (3)

A mixture of benz[d]oxazol-2(3*H*)-one (**1**) (3.0 g, 0.022 mol) and Lawesson's reagent (6.0 g, 0.0148 mol) in dry toluene (80 mL) was heated under reflux for 10 h until all starting material was consumed (TLC monitoring). The solvent was removed from the reaction mixture under reduced pressure, and the residue was subjected to separation by column chromatography on silica gel using a petrol–chloroform mixture as eluent. Benz[d]oxazol-2-yl trithio-4-methoxyphenylphosphonate (**3**) was isolated using a petrol–chloroform (1 : 1) mixture as eluent. This was followed by isolation of benz[d]oxazole-2(3*H*)-thione (**2**) on elution with a petrol–chloroform (1 : 3) mixture.

Data

Benz[d]oxazole-2(3*H*)-thione (2): White fluffy crystalline solid (yield 2.77 g, 68%), mp 188–190°C (chloroform–petrol); IR: ν (cm^{-1}) 3600–3400, 1650, 1532, 1500, 1475, 1440; UV: λ_{max} (logε) 299.5 (4.30), 263.0 (3.99), 216.0 (4.08)nm; ^{1}H NMR: δ7.13–7.20 (m, 3H, **H**-5, **H**-6 and **H**-7), 7.41 (dd, J 7.8 Hz and 1.5 Hz, 1H, **H**-4), 13.82 (s, 1H, N-**H**);^{13}C NMR: δ_C 180.3 (s, **C**-2), 148.3 (s, **C**-7a), 131.4 (s, **C**-3a), 125.3 (d, **C**-5), 123.8 (d, **C**-6), 110.6 and 110.1 (each d, **C**-4 and **C**-7). Found: C, 55.41; H, 3.25; N, 9.06. C_7H_5NOS requires C, 55.63; H, 3.31; N, 9.27%.

Benz[d]oxazol-2-yl trithio-4-methoxyphenylphosphonate (3): White crystalline solid (yield 1.27 g, 18%), mp 158–160°C (chloroform–petrol); IR: ν (cm^{-1}) 2560, 1600, 1570, 1509, 1465, 1440; UV: λ_{max} (logε) 242.5 (4.20) nm; ^{31}P NMR (200.47 MHz, $CDCl_3$): δ 94.6 (m); ^{1}H NMR δ 3.86 (s, 3H, -O**C**$\mathbf{H}_3$), 7.88 (m, 4H, **H**-4, **H**-5, **H**-6, and **H**-7 of benzoxazole), 8.09 (dd, $^4J_{P,H}$ 16.0 Hz and $^3J_{H,H}$ 8.8 Hz, 2H, *meta* Hs to phosphorus), 8.22 (dd, $^3J_{P,H}$ 22.5 Hz, $^3J_{H,H}$ 8.8 Hz, 2H, *ortho* Hs to phosphorus); ^{13}C NMR: δ_C 134.0, 134.4, and 134.8 (each d, **C**-4, **C**-5, and C-6 of benzoxazole), 134.0 (d, $^2J_{P,C}$ 23.9 Hz, *ortho* **C** to P), 114.3 (d, **C**-7), 114.1 (d, $^3J_{P,C}$ 7.7 Hz, *meta* **C** to P), 56.5 (q, **C**H_3); MS: m/z 353($M^{+\cdot}$), 255, 145. Found: C, 47.75; H, 3.21; N, 3.75. $C_{14}H_{12}NPO_2S_3$ requires C, 47.60; H, 3.40; N, 3.97%.

General Procedure for the Synthesis of 2-(Ethenyl/ethynyl) methylthiobenz[d]oxazoles 9–12

A solution of sodium bicarbonate (2.58 g, 0.03 mol) in water (40 mL) was added to a stirred solution of benz[d]oxazole-2(3*H*)-thione (**2**) (1.5 g, 0.009 mol) in dichloromethane (100 mL), cooled in an ice bath, at 0°C, and then benzyltriethylammonium chloride (2.27 g, 0.01 mol) in water (20 mL)

was also added. A solution of the (ethenyl/ethynyl)methyl bromide **4**–**8** (0.015 mol) in dichloromethane (10 mL) was added dropwise to the reaction mixture during 40 min, and stirring continued for 5 h for completion of the reaction. The organic layer was then removed, and the aqueous layer was extracted with dichloromethane (3 × 40 mL). The combined dichloromethane extract was washed with cold water (2 × 5 mL) and dried over anhydrous sodium sulfate. The solvent was removed from the dried extract, and the residue was subjected to chromatographic separation on silica gel using a petrol–chloroform mixture as eluent. In case of allyl bromide as the alkylating agent, a second product, 3-allylbenz[d]oxazole-2(3*H*)-thione (**13**), was also isolated (yield: 16%).

Data

2-Allylthiobenz[d]oxazole (9): Colorless liquid (yield 50%); IR: ν (cm^{-1}) 3100, 1650, 1610, 1510, 1480 1465; UV: λ_{max} (logε) 285.0 (4.02), 278.0 (4.03), 248 (4.00), 212.0 (3.94) nm; ^{1}H NMR: δ 3.93 (d, *J* 7.5 Hz, 2H, S-C**H**$_2$), 5.37 and 5.19 (m, *J* 18 Hz and 9 Hz, each 1H, =C**H**$_2$), 5.96–6.10 (m, 1H, CH$_2$=C**H**), 7.22 and 7.23 (each t, *J* 7.5 Hz, each 1H, **H**-5 and **H**-6), 7.41 (d, *J* 7.5 Hz, 1H, **H**-7), 7.59 (d, *J* 7.5 Hz, 1H, **H**-4); ^{13}C NMR: δ_C 164.1 (s, **C**-2), 151.9 (s, **C**-7a), 142.0 (s, **C**-3a), 132.2 (d, **C**H=CH$_2$), 124.1 and 123.9 (each d, **C**-5 and **C**-6), 118.9 (t, CH=**C**H$_2$), 118.4 (d, **C**-4), 109.7 (d, **C**-7), 34.8 (t, S-**C**H$_2$). Found: C, 62.82; H, 4.50; N, 7.45. $C_{10}H_9NOS$ requires C, 62.83; H, 4.71; N, 7.33%.

3-Allylbenz[d]oxazole-2(3*H*)-thione (13): This was isolated as the second product during the reaction of **2** with allyl bromide under the phase-transfer-catalyzed condition. Colorless crystalline solid (yield 16%); mp 80–82°C (chloroform–petrol); IR: ν (cm^{-1}) 1650, 1620, 1490, 1460; UV: λ_{max} (logε) 300.0 (4.37), 258.0 (3.90), 213.5 (4.04)nm; ^{1}H NMR: δ 4.85 (distorted d, *J* 5.7 Hz, 2H, N-C**H**$_2$), 5.28–5.35 (m, 2H, =C**H**$_2$), 5.87–5.99 (m, 1H, CH$_2$=C**H**-), 7.09–7.12 (m, 1H, **H**-7), 7.22–7.28 (m, 2H, **H**-4 and **H**-5), 7.33–7.36 (m, 1H, **H**-6); ^{13}C NMR: δ_C 180.6 (s, **C**-2), 147.3 (s, **C**-7a), 131.8 (s, **C**-3a), 129.4 (d, **C**H=CH$_2$), 124.8 and 124.2 (each d, **C**-5 and **C**-6), 119.4 (t, CH=**C**H$_2$), 110.3 (d, **C**-4), 109.7 (d, **C**-7), 48.2 (t, N-**C**H$_2$). Found: C, 62.68; H, 4.60; N, 7.12. $C_{10}H_9NOS$ requires C, 62.83; H, 4.71; N, 7.33%.

2-Cinnamylthiobenz[d]oxazole (10): Colorless solid (yield 2.22 g, 83.7%); mp 53–55°C (petrol–chloroform at −10°C); IR: ν (cm^{-1}) 3030, 1785, 1610, 1590; UV, λ_{max} (logε) 286.0 (3.99), 278.5 (4.02), 251.5 (4.10)nm;^{1}H NMR: δ 4.15 (d, *J* 8.1 Hz, 2H, S-C**H**$_2$), 6.42 (m, 1H, =C**H**-CH$_2$), 6.73 (d, *J* 15.6 Hz, 1H, =C**H**Ph), 7.34 (m, 8H, **H**-4, **H**-5 and **H**-7 of benzoxazole ring and C$_6$**H**$_5$, 7.66 (m, 1H, **H**-6); ^{13}C NMR: δ_C 164.3, (s, **C**-2), 151.9 (s, **C**-7a), 142.0 (s, **C**-3a), 136.3 (s, q-**C** of C$_6$H$_5$), 134.4 (d, CH=**C**HPh), 128.5

(d, two *meta* **C**s of C_6H_5), 126.9 (d, *para* **C** of C_6H_5), 126.5 (d, two *ortho* **C**s of C_6H_5), 124.8, 124.2 and 123.3 (each d, **C**-5, **C**-6 and **C**H═CH_2), 118.5 (d, **C**-4), 109.8 (d, **C**-7), 34.8 (t, S-**C**H_2); MS: m/z 268 ($MH^{+\cdot}$, 100%), 246 (14.5%), 238 (19%), 204 (45%), 169 (85%), 167 (67%), 126 (73%), 121 (98%). Found: C, 71.65; H, 4.81; N, 5.45. $C_{16}H_{13}NOS$ requires C, 71.91; H, 4.87; N, 5.24%.

2-(3-Methylbut-2-enylthio)benz[d]oxazole (11): Colorless liquid (yield 0.87 g, 89%); IR: ν (cm^{-1}) 2980, 1670, 1600, 1505; **UV:** λ_{max} (logε) 286.0 (3.99), 278.5 (4.02), 251.5 (4.10)nm; ^{1}H NMR: δ 1.75 (d, J 3.5 Hz, 6H, two -C**H**$_3$), 3.98 (d, J 7.8 Hz, 2H, S-C**H**$_2$), 5.42 (t, 1H, C**H**═CMe_2), 7.27 (m, 2H, **H**-5 and **H**-6), 7.41 (m, 1H, **H**-7), 7.6 (dd, 1H, **H**-4); ^{13}C NMR: δ_C 165.0 (s, **C**-2), 151.7 (s, **C**-7a), 142.0 (s, **C**-3a), 138.7 (s, CH═**C**Me_2), 124.5 (d, **C**-5), 123.7 (d, **C**-6), 118.3 (d, **C**-4), 117.4 (d, ═**C**HCH_2), 109.7 (d, **C**-7), 30.3 (t, **C**H_2), 25.6 and 17.8 (two q, two **C**H_3). Found: C, 65.59; H, 5.87; N, 6.11. $C_{12}H_{13}NOS$ requires C, 65.75; H, 5.94; N, 6.39%.

2-Propargylthiobenz[d]oxazole (12): Colorless flakes (yield 1.39 g, 74.5%); mp 42–43°C (petrol–chloroform at −10°C); IR: ν (cm^{-1}) 3260, 1510, 1460; UV: λ_{max} (logε) 284.5 (4.05), 277.5 (4.05), 242.5 (4.04) nm;^{1}H NMR: δ 2.26 (t, J 2.6 Hz, 1H, C≡C**H**), 4.02 (d, J 2.6 Hz, 2H, C**H**$_2$), 7.24 and 7.22 (each t, J 7.5 Hz, 2H, **H**-5 and **H**-6), 7.40 (d, J 7.5 Hz, 1H, **H**-7), 7.54 (d, J 7.5 Hz, 1H, **H**-4);^{13}C NMR: δ_C 163.0, (s, **C**-2), 152.2 (s, **C**-7a), 142.0 (s, **C**-3a), 124.4 (d, **C**-5), 124.1 (d, **C**-6), 118.8 (d, **C**-4), 109.9 (d, **C**-7), 78.0 (s, **C**≡C-H), 72.3 (d, ≡**C**H), 20.8 (t, S-**C**H_2). Found: C, 63.45; H, 3.50; N, 7.20. $C_{10}H_7NOS$ requires C, 63.49; H, 3.70; N, 7.41%.

General Procedure for the Thermal Rearrangement of 2-Ethenylmethylthiobenz[d]oxazoles in the Absence of AIBN

2-Ethenyl-methylthiobenz[d]oxazole **9**–**11** was heated in dry bromobenzene (10 mL/1 mmol of the substrate) in an oil bath; bath temperatures are indicated in Table 1. The progress of the reaction of **9** was monitored intermittently by TLC. After heating for the requisite period, the solvent was evaporated under reduced pressure from the reaction mixture and the residue was subjected to column chromatography on silica gel with the chloroform–petrol mixture as the eluent to get the title compound **13**–**15**.

Data

Compound 13: The compound, 3-allylbenz[d]oxazole-2(3*H*)-thione (yield 27%), was found to be identical with the product obtained during synthesis of **9**.

3-Cinnamylbenz[d]oxazole-2(3*H*)-thione (14): Colorless solid purified by preparative TLC using petrol containing 30% chloroform solvent as

eluent (yield 15%); mp 128–130°C; IR: ν (cm^{-1}) 1770, 1490, 1450; UV: λ_{max} (logε) 301.0 (3.60), 253.0 (3.57) nm; ^{1}H NMR: δ 5.01 (dd, J 6.3 Hz and 1.5 Hz, 2H, N-C**H**$_2$), 6.27 (td, J 15.8 Hz and 6.3 Hz, 1H, C**H**=CHPh), 6.70 (d, J 15.8 Hz, 1H, =C**H**Ph), 7.16 (m, 1H, 7-**H**), 7.30 (m, 8H, five aromatic Hs of cinnamyl group and **H**-4, **H**-5 and **H**-6 of benzoxazole); ^{13}C NMR: δ_C 180.3 (s, **C**-2), 147.2 (s, **C**-7a), 135.6 (s, q-**C** of Ph), 134.9 (d, Ph**C**H=), 131.7 (s, **C**-3a), 128.7 (d, two *meta* **C** of Ph), 128.4 (d, *para* **C** of Ph), 126.6 (d, two *ortho* **C**s of Ph), 125.0 and 124.3 (each d, **C**-5 and **C**-6), 120.5 (d, =**C**HCH$_2$), 110.4 (d, **C**-4), 109.8 (d, **C**-7), 20.8 (t, N**C**H$_2$). Found: C, 71.56; H, 4.62; N, 5.30. $C_{10}H_9NOS$ requires C, 71.91; H, 4.87; N 5.24%.

3-(3-Methylbut-2-enyl)benz[d]oxazole-2(3*H*)-thione (15): Colorless scale-like crystalline solid (yield 26.6%); mp 86–88°C (chloroform–petrol); IR: ν (cm^{-1}) 2970, 1470, 1430, 1400; UV: λ_{max} (logε) 304.5 (4.29), 258.0 (3.77) nm; ^{1}H NMR: δ 1.65 and 1.80 [pair of s, each 3H, =C(C**H$_3$**)$_2$], 4.83 (d, J 7.0 Hz, 2H, NC**H$_2$**), 5.28 (t, J ~7.0 Hz, 1H, C**H**=CMe$_2$), 7.06 (distorted d, 1H, **H**-7), 7.23–7.34 (m, 3H, **H**-4, **H**-5, and **H**-6); ^{13}C NMR: δ_C 180.3 (s, **C**-2), 147.3 (s, **C**-7a), 142.0 (s, **C**-3a), 132.0 (s, =**C**Me$_2$), 124.7 and 124.0 (each d, **C**-5 and **C**-6), 116.4 (d, =**C**HCH$_2$), 110.2 (d, **C**-4), 109.6 (d, **C**-7), 44.3 (t, N**C**H$_2$), 25.5 and 18.4 (each q, two **C**H$_3$). Found: C, 65.51; H, 5.84; N, 6.51. $C_{12}H_{13}NOS$requires C, 65.75; H, 5.94; N, 6.39%.

Rearrangement of 2-(3-methylbut-2-enyl)thiobenz[d]oxazole (11) in the Presence of AIBN to 3-(3-methylbut-2-enyl)benz[d]oxazole-2(3*H*)-thione (15): 2-(3-Methylbut-2-enyl)thiobenz[d]oxazole (**11**) (100 mg, 0.46 mmol) was taken in dry bromobenzene (4 mL) and warmed. At the incipient boiling condition, AIBN (10 mg, 0.07 mmol) was added. The mixture was heated under reflux for 25 h (TLC monitoring). The solvent was removed from the reaction mixture, and the residue on chromatography over silica gel with a chloroform–petrol mixture as eluent afforded 3-(3-methylbut-2-enyl)benz[d]oxazole-2(3*H*)-thione (**15**) as a colorless flake-like crystalline solid (95 mg, 95%). It was recrystallized from a chloroform–petrol mixture. The product was identical with **15** in all respects (IR, UV, ^{1}H NMR, ^{13}C NMR, co-TLC, and mixed mp).

Rearrangement of 2-propargylthiobenz[d]oxazole (12) to 1,3-bis(benz [d]oxazol-2-ylthio)-1-propene (16) and 3-(1-propynyl)benz[d]oxazole-2(3*H*)-thione (17): **2**-Propargylthiobenz[d]oxazole (**12**) (250 mg, 1.32 mmol) in dry bromobenzene (10 mL) was heated under reflux for 12 h. The solvent was removed from the reaction mixture under reduced pressure, and the residue was chromatographed on silica gel to isolate 1,3-bis(benz[d]oxazol-2-ylthio)-1-propene (**16**) upon elution with chloroform–petrol (1 : 1) followed by 3-(1-propynyl)benz[d]oxazole-2(3*H*)-thione (**17**) with chloroform containing 2% methanol as the eluent.

1,3-Bis(benz[d]oxazol-2-ylthio)-1-propene (16): Light yellow crystalline solid (yield 20 mg, 9%); mp 99–100°C (chloroform–petrol); IR: ν (cm^{-1}) 2980, 1520, 1500, 1470; UV: λ_{max} (logε) 300.0 (4.10), 286.5 (4.00), 246.5 (3.91) nm; ^{1}H NMR: δ 3.87 (d, *J* 8.0 Hz, 2H, -SC**H$_2$**), 6.21 (q, *J* 8.0 Hz, 1H, =C**H**CH$_2$), 6.46 (d, *J* 8.0 Hz, 1H, SC**H**=), 6.93–6.98 (m, 2H, **H**-7 of both rings), 7.12–7.14 (m, 6H, **H**-4, **H**-5, and **H**-6 of both rings); ^{13}C NMR: δ_C 163.2 (s, **C**-2 of both rings), 152.1 (s, **C**-7a of both rings), 141.8 (s, **C**-3a of both rings), 128.8 (d, CH$_2$-**C**H=), 124.1, 124.3, 124.7, and 125.1 (each d, **C**-5 and **C**-6 of both rings), 122.5 (d, =**C**HS), 110.6 and 118.6 (each d, **C**-4 of both rings), 109.9 and 110.2 (each d, **C**-7 of both rings), 29.1 (t, S**C**H$_2$). Found: C, 59.65; H, 3.41; N, 8.09. $C_{17}H_{12}N_2O_2S_2$ requires C, 60.00; H, 3.53; N, 8.24%.

3-(1-Propynyl)benz[d]oxazole-2(3*H*)-thione (17): Light yellow crystalline solid (yield 25 mg, 10%); mp 81–82°C (chloroform–petrol); IR: ν (cm^{-1}) 2210, 1620, 1520, 1470; **UV:** λ_{max} (logε) 323.5 (3.98), 284.50 (3.80), 222.0 (4.00)nm; ^{1}H NMR: δ 2.20 (s, 3H, C**H$_3$**), 6.80–7.34 (m, 4H, **H**-4, **H**-5, **H**-6, and **H**-7);^{13}C NMR: δ_C 185.7 (s, **C**-2), 150.8 (s, **C**-7a), 130.9 (d, **C**-5), 128.6 (s, **C**-3a), 126.0 (d, **C**-6), 121.9 and 121.5 (both d, **C**-7 and **C**-4), 77.8 (s, N-**C**≡), 12.6 (q, **C**H$_3$). Found: C, 63.65; H, 3.57; N, 7.26. $C_{10}H_7NOS$ requires C, 63.49; H, 3.70; N, 7.41%.

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