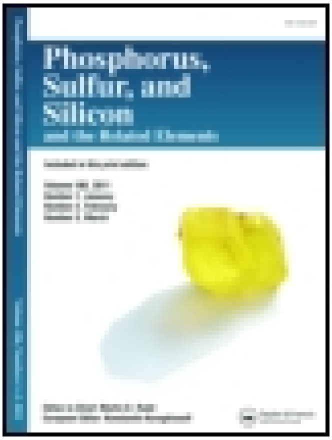

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COPPER-CATALYSED REARRANGEMENT OF 4-SUBSTITUTED-2,3-1H-BENZOXAZINE-1-THIONES

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COPPER-CATALYSED REARRANGEMENT OF 4-SUBSTITUTED-2,3–1H-BENZOXAZINE-1-THIONES

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4-Substituted-2,3–1H-benzoxazine-1-thiones were prepared by the treatment of the corresponding benzoxazine-1-ones with P_2S_5. The thermal rearrangement of 4-substituted-2,3–1H-benzoxazine-1-thiones, catalysed by metallic copper, yielded 4-substituted-2,3–1H-benzthiazine-1-ones.

Keywords: 2,3–1H-Benzoxazine-1-one; 2,3–1H-benzoxazine-1-thione; 2,3–1H-benzthiazine-1-one

Uncatalysed thion-thiol rearrangements of acyclic compounds have been extensively studied.[1–10] The temperature of these rearrangements ranges from 25°C to about 300°C depending on the structure of the thiones. The thion-thiol rearrangements of 1,2,4-oxadiazole-5-thiones were also studied as five membered heterocyclic ring systems.[11–15] Uncatalysed rearrangements of 1,2,4-oxadiazole-5-thiones were found to take place considerable less readily than copper-catalysed ones.

In this paper, we report the thion-thiol rearrangement of 4-substituted-2,3–1H-benzoxazine-1-thiones as six membered heterocyclic ring systems 4-Substituted-2,3–1H-benzoxazine-1-thiones(3) were prepared from thionation of the corresponding 2,3-benzoxazine-1-ones which were synthesized from the cyclication of o-benzoylbenzoic acids with hydroxylamine hydrochloride as described in the literature[16] (Scheme 1).

The thermal rearrangement of 4-substituted-2,3–1H-benzoxazine-1-thiones(3) were carried out with a catalytic amount of copper powder in xylene and yielded the corresponding 4-substituted-2,3–

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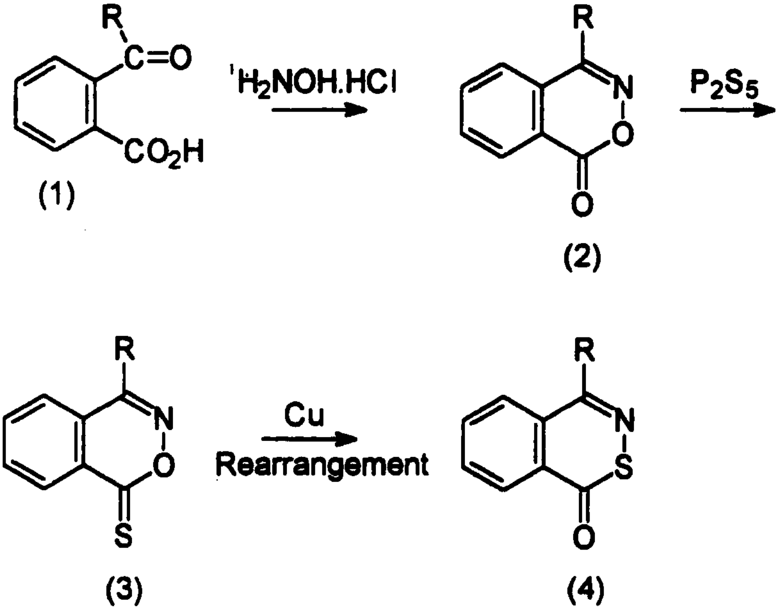
* Corresponding Author.



R

a; p-MeC_6H_4

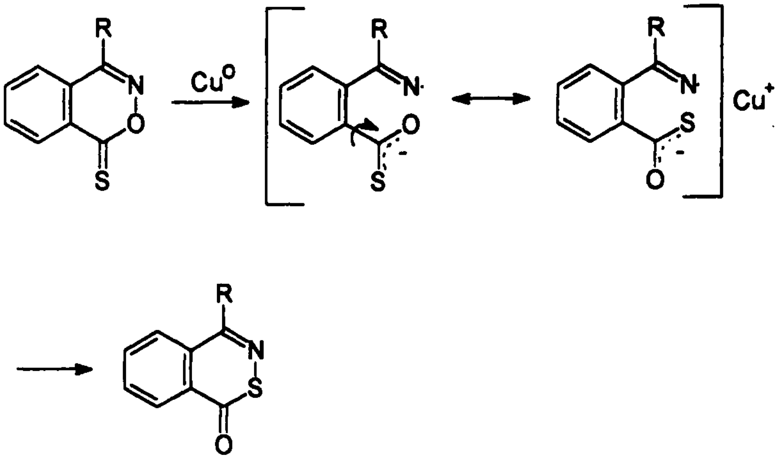
b; Ph

c; 3,4-$Me_2C_6H_3$

d; p-$Me_2CHC_6H_4$

SCHEME 1

1H-benzthiazine-1-ones(4). The reaction was normally completed in 8 h at 140°C. The analyses of compounds (3and 4) were carried out by following the disappearance of the C=O frequency(ir) at 1700–1800 cm^{-1} and the appearance of the C=S vibration in the region of 1200–1400 cm^{-1}. The mechanism of the copper-catalysed rearrangement of 4-substituted-2,3–1H-benzoxazine-1-thione very likely follows the mechanism of the copper-catalysed rearrangement of five membered heterocyclic ring system.[12,13] as shown below (scheme 2).



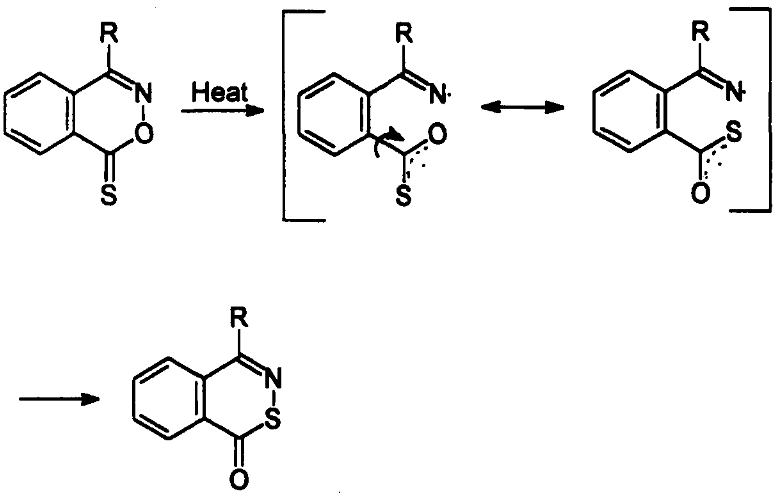
SCHEME 2

In order to test whether the rearrangement occurs without copper catalysis, compound(3a) was heated for 8h at 140°C in n-pentadecane, but it remained unchanged. However, when the same compound was submitted to the same treatment for 2h at 180°C, it was all converted into compoud(4a). Therefore, an alternative reasonable mechanism for the uncatalysed thermal rearrangement of 2,3-benzoxazine-1-thiones can be considered to proceed through a free radical intermediate as shown below (Scheme 3).

EXPERIMENTAL

IR spectra were taken on a Simadzu FTIR-821PC Fourier Transform IR spectrometer. ^{1}H NMR spectra were recorded on a Brucker AC 200-L (200 MHz) spectrometer. Mass spectra were run at 70 eV by direct inlet on a VCZAP SPEC instrument. Silica Gel (Fluka or Merck) were used for thin layer chromatography. Solvents were dried and purified by standard methods prior to use. Melting points were determined on a Büchi apparatus and are uncorrected.

o-Aroylbenzoic acids were prepared from the reaction of phthalic anhydride with substituted benzene as described in the literature[16].



SCHEME 3

4-(p-Tolyl)-2,3–1H-benzoxazine-1-one, 2a

General Procedure

A mixture of o-(4-methyl)benzoic acid (3.05g, 13mmole), hydroxylamine hydrochloride (2.01g, 29 mmole) and anhydrous sodium acetate (1.25g, 15mmole) in ethanol (40ml) was refluxed for 2h and cooled slowly to room temperature. The resultant white crystalline solid was filtered and washed repeatedly with water, then dried in air and recrystallized from ethanol to give compound (2a) (2.57g, 84%); mp 158–160°C (lit.[17]160°C).

4-(p-Tolyl)-2,3–1H-benzoxazine-1-thione, 3a

General Procedure

4-(p-Tolyl)-2,3–1H-benzoxazine-1-one (2a) (2.6g, 11mmole) and phosphorus pentasulphide (2.44g, 11mmole) were refluxed in xylene for 8h. The hot solution was filtered and xylene was evaporated under reduced pressure. The remaining solid was extracted with ether. The solvent was evaporated and the product was recrystallized from ethanol to give compound (3a) (1.63g, 63%); mp 112–114°C;

IR(KBr): 1514(C=N), 1278 cm^{-1}(C=S);

^{1}H NMR(DMSO-d_6): δ 2.45(s, 3H, CH_3), 7.26(m, 4 aromatic H), 7.80(m, 4 aromatic H);

MS (EI, 70eV): m/z 253(M^+).

4-Phenyl-2,3–1H-benzoxazine-1-thione, 3b

The compound was chromatographed on Silica Gel HF_{254} layer with ethylacetate: Light petroleum(40–60) (1:4) (Rf: 0.86) to give an oily compound (3b) (34 mg, 57%).

IR(KBr): 1589(C=N),[1] 1317 cm^{-1}(C=S);

^{1}H NMR(DMSO-d_6): δ 7.45(m, 5 aromatic H), 7.95(4 aromatic H); MS (EI, 70eV): m/z 239(M^+).

4-(3,4-Dimethylphenyl)-2,3–1H-benzoxazine-1-thione, 3c

The compound was chromatographed on Silica Gel HF_{254} layer with ethylacetate: light petroleum(40–60) (1:4) (Rf: 0.73) to give an oily compound (3c) (28 mg, 52%).

IR(KBr): 1608(C=N), 1446 cm^{-1}(C=S);

^{1}H NMR($CDCl_3$): δ 2.25(s, 3H, CH_3), 2.27(s, 3H, CH_3), 6.95(m, 2 aromatic H), 7.24(s, 1 aromatic H), 7.64(2 aromatic H), 7.87(2 aromatic H);

MS (EI, 70eV): m/z 267(M^+).

4-(p-Isopropylphenyl)-2,3–1H-benzoxazine-1-thione, 3d

The compound was chromatographed on Silica Gel HF_{254} layer with ethylacetate: light petroleum(40–60) (1:4) (Rf: 0.76) to give an oily compound (3d) (38 mg, 60%).

IR(KBr). 1510(C=N), 1315 cm^{-1}(C=S);

^{1}H NMR($CDCl_3$): δ 1.24(d, 6H, 2CH_3), 2.94(sep., 1H, CH), 7.15(m, 2 aromatic H), 7.31(m, 2 aromatic H), 7.70(m, 2 aromatic H), 7.88(m, 2 aromatic H),

MS (EI, 70eV): m/z 281 (M^+).

4-(p-Tolyl)-2,31H-benzothiazine-1-one, 4a

General Procedure

4-(p-Tolyl)-2,3–1H-benzoxazine-1-thione (3a)(0.56g, 2.2mmole) was refluxed in xylene for 8h in the presence of a catalytic quantity of copper powder. Xylene was evaporated under reduced pressure to give a crude solid. The solid product was extracted with ether and filtered. The solvent was evaporated and the remaining solid was recrystallized from ethanol to give compound (4a)(0.33g, 59%); mp 130–132°C; IR(KBr): 1512(C=N), 1745 cm^{-1}(C=O)

^1H NMR(DMSO-d_6): δ 2.50(s, 3H, CH_3), 7.32(m, aromatic 4H), 7.94(m, aromatic 4H).

MS (EI, 70eV): m/z 253(M^+).

4-Phenyl-2,3–1H-benzothiazine-1-one, 4b

The compound was chromatographed on Silica Gel HF_{254} layer with ethylacetate: light petroleum(40–60) (1:4) (Rf: 0.63) to give an oily compound (4b) (20 mg, 45%).

IR(KBr): 1515(C=N), 1716 cm^{-1}(C=O);

^1H NMR(DMSO-d_6): δ 7.38(m, aromatic 2H), 7.42(m, aromatic 3H), 7.94(m aromatic 5H);

MS (EI, 70eV): m/z 239(M^+).

4-(3,4-Dimethylphenyl)-2,3–1H-benzothiazine-1-one, 4c

The compound was chromatographed on Silica Gel HF_{254} layer with ethylacetate: light petroleum(40–60) (1:4) (Rf: 0.55) to give an oily compound (4c) (36 mg, 68%).

IR(KBr): 1504(C=N), 1720 $cm^{-1}{}_{(C=O)}$;

^1H NMR($CDCl_3$): δ 2.24(s, 6H, $2CH_3$), 7.10(m, aromatic 2H), 7.22(m, aromatic 1H) 7.73(m, aromatic 2H), 7.88(m, aromatic 2H); MS (EI, 70eV): m/z 267(M^+).

4-(p-Isopropylphenyl)-2,3–1H-benzothiazine-1-one, 4d

The compound was chromatographed on Silica Gel HF_{254} layer with ethylacetate: light petroleum(40–60) (1:4) (Rf: 0.59) to give an oily compound (4d) (32 mg, 53%).

IR(KBr): 1514(C=N), 1710 cm^{-1}(C=O);

^1H NMR($CDCl_3$); δ 1.21(d, 6H, $2CH_3$), 2.90(sep., 1H, CH), 7.19(m, aromatic 2H), 7.28(m, aromatic 2H), 7.72(m, aromatic 2H), 7.89(m, aromatic 2H);

MS (EI, 70eV): m/z 281(M^+).

Acknowledgements

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