

Diacetoxiodobenzene mediated oxidative dethiation of *N*-substituted 5-arylmethylidene rhodanines: an efficient synthesis of *N*-substituted 5-arylmethylidene thiazolidine-2,4-diones

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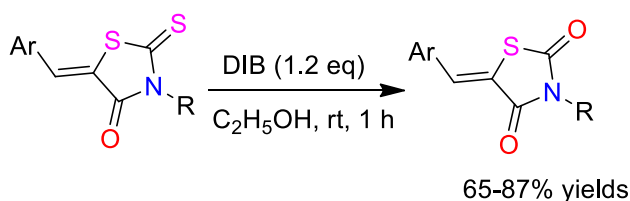
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Abstract

A simple and efficient synthesis of *N*-substituted-5-arylmethylidene thiazolidine-2,4-diones has been developed via oxidative dethiation of *N*-substituted-5-arylmethylidene rhodanines using diacetoxiodobenzene (DIB) in ethanol at room temperature. This protocol is simple, mild, column free, obviates the need of acids and bases, and offers a broad substrate scope.



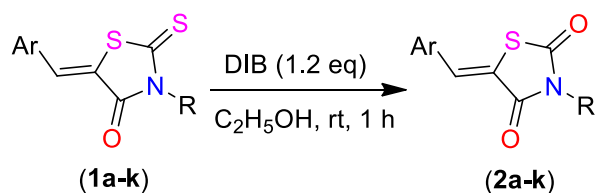
Keywords: Rhodanines, thiazolidine-2,4-diones, diacetoxiodobenzene, oxidation, dethiation

Introduction

Thiazolidine-2,4-diones are important five membered N,S-heterocycles, which serve as the core components of numerous compounds that have been claimed to possess a wide range of interesting biological activities such as anti-inflammatory,¹ antidiabetic,² antimicrobial,³ antimalarial,⁴ and anticancer.⁵ They are building blocks of many commercially available drugs such as troglitazone, pioglitazone, and rosiglitazone.⁶ These derivatives are clinically used for treatment of type II diabetes mellitus. Further, thiazolidine-2,4-diones derivatives have been reported as inhibitors of targets such as glycogen synthase kinase-3 (GSK-3),⁷ aldose reductase,⁸ Pim protein kinases⁹ and 15-hydroxyprostaglandin dehydrogenase.¹⁰ Because of the prominent biological activities of thiazolidine-2,4-dione derivatives, development of clean synthetic methods is of great significance.

Various methods have been developed to convert thioxo to oxo in 2-thioxo-4-thiazolidinones. The use of reagents such as hydrogen peroxide,¹¹ aqueous chloroacetic acid,¹² bromine in acetic acid,¹³ and dimethyl sulfate¹⁴ has been reported for this transformation. Moreover, *N*-substituted 5-arylmethylidene thiazolidine-2,4-diones are also prepared by alkylation of 5-arylmethylidene rhodanine with alkyl halide in presence of base.^{15,16} However, the conversion of thioxo group in *N*-substituted-5-arylmethylidene rhodanines into their corresponding oxo analogue has never been realized using hypervalent iodine compounds.

Hypervalent iodine compounds occupy an important place for the construction of carbon-carbon and carbon-heteroatom bond forming reactions.^{17,18} In particular, diacetoxyiodobenzene (DIB) is useful for the oxidative transformation of various functional groups.¹⁹⁻²¹ Recently, it has been used for oxidative desulfurization reactions.^{22,23} We therefore surmised that thioxo groups in *N*-substituted-5-arylmethylidene rhodanine may be transformed into their corresponding oxo analogue in presence of diacetoxyiodobenzene (DIB). Herein, we report an efficient synthesis of *N*-substituted 5-arylmethylidene thiazolidine-2,4-diones via oxidative dethiation of *N*-substituted-5-arylmethylidene rhodanines using diacetoxyiodobenzene (DIB) in ethanol at room temperature (Scheme 1).



Scheme 1. Conversion of thioxo to oxo in *N*-substituted 5-arylmethylidene rhodanines

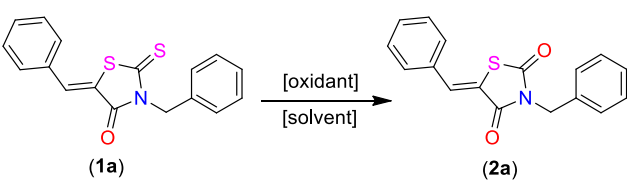
Results and Discussion

The desired *N*-substituted-5-arylmethylidene rhodanine (**1a-k**) were synthesized in good yields by condensation reaction of *N*-substituted rhodanines with aromatic aldehydes in the presence of piperidine using ethanol as solvent.²⁴ Initially, a trial reaction was carried out by treating (*Z*)-3-benzyl-5-benzylidene-2-thioxothiazolidin-4-one (**1a**) (0.5 mmol) with diacetoxyiodobenzene (DIB) (0.5 mmol) in acetonitrile at room temperature. A new product was detected after 1 h stirring at room temperature and then the solvent was evaporated under reduced pressure. The product was isolated (55%) by recrystallization from ethanol and

spectroscopic analysis (^1H NMR, ^{13}C NMR, IR, HRMS) reveals its structure to be (*Z*)-3-benzyl-5-benzylidenethiazolidine-2,4-dione (**2a**).

To optimize the reaction conditions, various solvents such as EtOH, CHCl_3 , THF, 1,4-dioxane, DMF, and toluene were screened. The yield of target product (**2a**) was increased to 60% using ethanol as solvent (Table 1, entry 2). Then, various oxidants such as hydrogen peroxide, tert-butyl hydroperoxide (TBHP), iodine (I_2), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), and bis(trifluoroacetoxy)iodobenzene (PIFA) were screened. The use of hydrogen peroxide, tert-butyl hydroperoxide (TBHP), iodine (I_2), and DDQ fail to give the product; however, bis(trifluoroacetoxy)iodobenzene (PIFA) afforded the product (53%) in lower yield. Next, the effect of oxidant loading was examined. Increasing DIB to (0.6 mmol) led to a higher yield (75%) of the product (Table 1, entry 13); further increasing it to (0.75 mmol) did not improve the yield.

Table 1. Optimization of reaction conditions^{a,b}



Entry	Oxidant	Solvent	Yield (%) ^b
1	DIB	CH_3CN	55
2	DIB	$\text{C}_2\text{H}_5\text{OH}$	60
3	DIB	CHCl_3	50
4	DIB	THF	51
5	DIB	1,4-dioxane	45
6	DIB	DMF	47
7	DIB	Toluene	43
8	H_2O_2	$\text{C}_2\text{H}_5\text{OH}$	0
9	TBHP (in dec)	$\text{C}_2\text{H}_5\text{OH}$	0
10	I_2	$\text{C}_2\text{H}_5\text{OH}$	0
11	DDQ	$\text{C}_2\text{H}_5\text{OH}$	0
12	$\text{Ph}(\text{OCOCF}_3)_2$	$\text{C}_2\text{H}_5\text{OH}$	53
13	DIB ^c	$\text{C}_2\text{H}_5\text{OH}$	75

^a Reaction conditions: (**1a**) (0.5 mmol), oxidant (0.5 mmol), and solvent (2 mL) at room temperature for 1 h.

^b Isolated yield.

^c 0.6 mmol of DIB was used.

Having established the appropriate reaction conditions, a variety of *N*-substituted-5- arylmethylidene rhodanines can be easily transformed into their corresponding *N*-substituted-5- arylmethylidene thiazolidine-2,4-diones using diacetoxyiodobenzene (DIB) (0.6 mmol) in ethanol at room temperature (Table 2). Next, we examined the effects of substituent (R^1) on aryl ring (Ar) of *N*-substituted-5-arylmethylidene rhodanines. When the substitution (R^1) on aryl ring (Ar) is fixed as electronically neutral (H) and other substituents (R^2) on the *N*-atom of the rhodanine ring such as benzyl, methyl and allyl gave the desired product (**2a**) (75%), (**2b**) (80%) and (**2c**) (78%) respectively. The substrates bearing electron withdrawing substituents (R^1) such as 4-Cl

(1f) and electron donating substituents (R^1) such as 4-Me (1d) and 4-OMe (1e) on aryl ring (Ar) while the other substituent (R^2) fixed as benzyl, yielded their respective product in good to high yield. Similarly, when methyl was fixed on (R^2) and the aryl ring having electron withdrawing substituents such as 2-F (1i), and 2-Br (1j) and electron donating groups such as 4-CH₃ (1g), and 4-OCH₃ (1h) gave their corresponding product in good to excellent yield. As can be seen from Table 1, compared to substrates bearing electron-donating groups, electron-withdrawing substrates gave better yields. This synthetic protocol can also be applied to rhodanine bearing heterocycle (1k) affording an antimicrobial compound (2k) in good yield.²⁵

Table 2. Substrate scope for oxidative dethionation of *N*-substituted rhodanines^a

Entry	Ar	R ²	Product	Yield (%) ^b
1	C ₆ H ₅	C ₆ H ₅ CH ₂	2a	75
2	C ₆ H ₅	CH ₃	2b	80
3	C ₆ H ₅	CH ₂ =CH-CH ₂	2c	78
4	4-CH ₃ C ₆ H ₄	C ₆ H ₅ CH ₂	2d	70
5	4-CH ₃ OC ₆ H ₄	C ₆ H ₅ CH ₂	2e	67
6	4-ClC ₆ H ₄	C ₆ H ₅ CH ₂	2f	83
7	4-CH ₃ C ₆ H ₄	CH ₃	2g	75
8	4-CH ₃ OC ₆ H ₄	CH ₃	2h	71
9	2-FC ₆ H ₄	CH ₃	2i	87
10	2-BrC ₆ H ₄	CH ₃	2j	85
11	2-Furyl	CH ₃	2k	65

^a Reaction conditions: (1a-k) (0.5 mmol), oxidant (0.6 mmol), and solvent (2 mL) at room temperature for 1 h.

^b Isolated yield.

Conclusions

In summary, we have demonstrated a simple and efficient protocol for easy and facile access to *N*-substituted-5-arylmethylidene thiazolidine-2,4-diones derivatives by oxidative dethionation of *N*-substituted-5-arylmethylidene rhodanines using diacetoxyiodobenzene (DIB). The reaction proceeded under mild condition and the desired product can be obtained by recrystallization from ethanol in good to high yields.

Experimental Section

General. All the compounds were commercial grade and were used without further purification. Solvents were removed in a rotary evaporator under reduced pressure. Reactions were monitored by TLC on silica gel 60 GF₂₅₄ (0.25 mm). Silica gel (60–120 mesh size) was used for the column chromatography. ¹H NMR spectra were recorded on 400/600 MHz in CDCl₃ and ¹³C NMR spectra were recorded on 100/150 MHz in CDCl₃ using TMS as internal standard. High-resolution mass spectral analysis (HRMS) data were recorded using ESI mode (Q-TOF type Mass Analyzer).

General procedure for synthesis of *N*-substituted-5-arylmethylidene thiazolidine-2,4-diones (2a-k). To a solution of (*Z*)-3-benzyl-5-benzylidene-2-thioxothiazolidin-4-one (1a) (0.5 mmol) in ethanol (2 ml), diacetoxyiodo benzene (DIB) (0.6 mmol) was added. The reaction mixture was stirred for 1 h at room temperature. After completion of the reaction (monitored by TLC), the solvent was evaporated under reduced pressure. The solid obtained was collected, and washed with water. It was dried and recrystallized from ethanol to give (*Z*)-3-benzyl-5-benzylidenethiazolidine-2,4-dione (2a).

(*Z*)-3-Benzyl-5-benzylidenethiazolidine-2,4-dione (2a). Yellow solid; mp 134-135 °C (Lit.¹⁶ mp 133-134 °C); *R_f* = 0.60 (EtOAc/Hexane 2:8); yield 111 mg, 75%; ¹H NMR (400 MHz, CDCl₃): δ 4.90 (s, 2H), 7.30-7.35 (m, 3H), 7.43-7.50 (m, 7H), 7.90 (s, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 45.4, 121.6, 128.5, 129.0, 129.1, 129.4, 130.4, 130.7, 133.4, 134.2, 135.3, 166.3, 168.0; MS (ESI): *m/z* 296.0751[M+H]⁺.

(*Z*)-3-Methyl-5-benzylidenethiazolidine-2,4-dione (2b). Yellow solid; mp 128-129 °C (Lit.¹⁶ mp 125-128 °C); *R_f* = 0.70 (EtOAc/Hexane 2:8); yield 88 mg, 80%; ¹H NMR (400 MHz, CDCl₃): δ 3.25 (s, 3H), 7.43-7.52 (m, 5H), 7.91 (s, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 28.0, 121.7, 129.3, 130.3, 130.7, 133.2, 133.9, 166.7, 168.0; MS (ESI): *m/z* 220.0430 [M+H]⁺.

(*Z*)-3-allyl-5-benzylidenethiazolidine-2,4-dione (2c). Yellow solid; mp 88-89 °C (Lit.¹⁶ mp 88-90 °C); *R_f* = 0.70 (EtOAc/Hexane 2:8); yield 96 mg, 78%; ¹H NMR (400 MHz, CDCl₃): δ 4.35 (d, *J* = 5.4 Hz, 2H), 5.24–5.31 (m, 2H), 5.82–5.89 (m, 1H), 7.45–7.52 (m, 5H), 7.91 (s, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 44.0, 119.1, 121.5, 128.5, 129.4, 138.4, 130.7, 133.3, 134.2, 166.2, 168.0; MS (ESI): *m/z* 245.0515 [M+H]⁺.

(*Z*)-3-Benzyl-5-(4-methylbenzylidene)thiazolidine-2,4-dione (2d). Yellow solid; mp 141-142 °C (Lit.¹⁵ mp 140-142 °C); *R_f* = 0.60 (EtOAc/Hexane 2:8); yield 108 mg, 70%; ¹H NMR (400 MHz, CDCl₃): δ 2.40 (s, 3H), 4.90 (s, 2H), 7.26-7.33 (m, 5H), 7.38 (d, *J* = 7.2 Hz, 2H), 7.43-7.48 (m, 2H), 7.88 (s, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 21.8, 45.4, 120.4, 128.4, 128.9, 129.0, 130.1, 130.3, 130.5, 134.4, 135.4, 141.5, 166.5, 168.1; MS (ESI): *m/z* 310.0898 [M+H]⁺.

(*Z*)-3-Benzyl-5-(4-methoxybenzylidene)thiazolidine-2,4-dione (2e). Yellow solid; mp 147-148 °C; *R_f* = 0.60 (EtOAc/Hexane 2:8); yield 109 mg, 67%; ¹H NMR (600 MHz, CDCl₃): δ 3.86 (s, 3H), 4.90 (s, 2H), 6.97 (d, *J* = 9.0 Hz, 2H), 7.29-7.34 (m, 3H), 7.43 (t, *J* 9.0 Hz, 3H), 7.86 (s, 1H); ¹³C NMR (150 MHz, CDCl₃): δ 45.4, 55.6, 115.0, 118.6, 126.0, 128.4, 128.8, 128.9, 129.0, 132.4, 134.1, 135.5, 166.6, 168.1; MS (ESI): *m/z* 326.0850 [M+H]⁺.

(*Z*)-3-Benzyl-5-(4-chlorobenzylidene)thiazolidine-2,4-dione (2f). Yellow solid; mp 153-154 °C; *R_f* = 0.50 (EtOAc/Hexane 2:8); yield 136 mg, 83%; ¹H NMR (400 MHz, CDCl₃): δ 4.90 (s, 2H), 7.32 (d, *J* = 7.8 Hz, 3H), 7.41-7.48 (m, 6H), 7.84 (s, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 45.6, 122.2, 128.5, 129.0, 129.1, 129.8, 131.4, 131.9, 132.8, 135.2, 136.9, 166.1, 167.6; MS (ESI): *m/z* 330.0355 [M+H]⁺.

(*Z*)-3-Methyl-5-(4-methylbenzylidene)thiazolidine-2,4-dione (2g). Yellow solid; mp 146-147 °C (Lit.¹⁶ mp 146-148 °C); *R_f* = 0.70 (EtOAc/Hexane 2:8); yield 88 mg, 75%; ¹H NMR (600 MHz, CDCl₃): δ 2.00 (s, 3H), 3.22 (s, 3H),

7.26 (d, $J = 7.8$ Hz, 2H), 7.38 (d, $J = 8.4$ Hz, 2H), 7.85 (s, 1H); ^{13}C NMR (150 MHz, CDCl_3): δ 21.8, 28.0, 122.0, 130.3, 130.5, 130.9, 133.5, 141.8, 166.7, 168.0; MS (ESI): m/z 233.0512 $[\text{M}+\text{H}]^+$.

(Z)-3-Methyl-5-(4-methoxybenzylidene)thiazolidine-2,4-dione (2h). Yellow solid; mp 145-146 °C (Lit.¹⁶ mp 145-147 °C); $R_f = 0.70$ (EtOAc/Hexane 2:8); yield 89 mg, 71%; ^1H NMR (600 MHz, CDCl_3): δ 3.26 (s, 3H), 3.81 (s, 3H), 6.98 (d, $J = 7.8$ Hz, 2H), 7.28 (d, $J = 7.8$ Hz, 2H), 7.83 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 23.9, 52.0, 114.5, 114.9, 125.9, 130.0, 132.2, 132.4, 166.8, 168.3; MS (ESI): m/z 249.0463 $[\text{M}+\text{H}]^+$.

(Z)-5-(2-Fluorobenzylidene)-3-methylthiazolidine-2,4-dione (2i). Light yellow solid; mp 125-126 °C; $R_f = 0.50$ (EtOAc/Hexane 2:8); yield 103 mg, 87%; ^1H NMR (600 MHz, CDCl_3): δ 3.27 (s, 3H), 7.16 (t, $J = 9$ Hz, 1H), 7.27 (s, 1H), 7.42 (q, $J = 7.2$ Hz, 1H), 7.50 (t, $J = 7.2$ Hz, 1H), 8.14 (s, 1H); ^{13}C NMR (150 MHz, CDCl_3): δ 28.2, 116.3 (d, $J = 21.6$ Hz), 121.8 (d, $J = 11.7$ Hz), 123.8, 124.9 (d, $J = 3.7$ Hz), 128.0 (d, $J = 6.6$ Hz), 129.1, 132.5 (d, $J = 8.7$ Hz), 162.5, 166.3, 168.0; MS (ESI): m/z 238.0337 $[\text{M}+\text{H}]^+$.

(Z)-5-(2-Bromobenzylidene)-3-methylthiazolidine-2,4-dione (2j). Yellow solid; mp 127-128 °C; $R_f = 0.50$ (EtOAc/Hexane 2:8); yield 126 mg, 85%; ^1H NMR (600 MHz, CDCl_3): δ 3.27 (s, 3H), 7.28 (d, $J = 7.8$ Hz, 1H), 7.41 (t, $J = 7.2$ Hz, 1H), 7.50 (d, $J = 7.8$ Hz, 1H), 8.19 (s, 1H); ^{13}C NMR (150 MHz, CDCl_3): δ 28.1, 125.0, 126.4, 128.0, 129.2, 131.7, 132.9, 133.8, 133.9, 166.0, 168.0; MS (ESI): m/z 299.9536 $[\text{M}+\text{H}]^+$.

(Z)-5-(Furan-2-ylmethylene)-3-methylthiazolidine-2,4-dione (2k). Yellow solid; mp 143-144 °C (Lit.²⁵ mp 144-145 °C); $R_f = 0.60$ (EtOAc/Hexane 2:8); yield 68 mg, 65%; ^1H NMR (600 MHz, CDCl_3): δ 3.23 (s, 3H), 6.58 (dd, $J = 1.8$ Hz), 6.79 (d, $J = 3.0$ Hz, 1H), 7.66 (d, $J = 11.4$ Hz); ^{13}C NMR (150 MHz, CDCl_3): δ 28.0, 113.3, 118.0, 119.4, 119.8, 146.6, 149.9, 166.5, 169.1; MS (ESI): m/z 210.0224 $[\text{M}+\text{H}]^+$.

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