Research Article

A Facile Method for the Synthesis of Oxoketene-*N,S*- and -*N,N*-acetals from Reactions of Amino Compounds

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2-Aroyl-3,3-bis(alkylsulfanyl)acrylaldehydes reacted with various primary amines, namely, *o*-phenylenediamine, ethylenediamine, and anilines to produce functionalized oxoketene-*N,S*-acetals and *N,N*-acetals in good yields. Imidazolo derivatives synthesized with *o*-phenylenediamine and ethylenediamine containing a formyl group could act as valuable starting materials for a variety of substituted heterocyclic compounds.

1. Introduction

Oxoketene-*N,S*- and -*N,N*-acetals are highly versatile synthons for heterocyclic synthesis [1–3]. They are quite stable and can be stored indefinitely without any decomposition. They exhibit the nucleophilic displacement reactions by various binucleophiles followed by intramolecular cyclisation leading to the formation of cyclic compounds, and such reactions are characteristics of enamines [1–3]. Junjappa and coworkers prepared a series of functionalized heterocycles by treating them with binucleophiles like hydrazines, hydroxylamines, guanidines, cyanoacetamides, and so forth, [4–6]. They have also prepared functionalized quinolines from α -oxoketene-*N,S*-acetals employing Vilsmeier-Haack reaction [7]. A similar strategy was reported for the synthesis of quinoxalines from nitroketene-*N,S*-acetals, important benzoheterocycles displaying a broad spectrum of biological activities [8]. Our research group has also made attempts to explore the synthetic utility of oxoketene-*N,S*-acetals derived from thioamides [9]. We have shown that their reactions with α -halo ketones or ethyl bromoacetates afford amino thiophenes [10].

The α -oxoketene-*N,S*-acetals are generally prepared by the direct amination reactions of oxoketene-*S,S*-acetals by appropriate amines which resulted in a mixture of

oxoketene-*N,S*-acetals and -*N,N*-acetals in most of the cases. They have also been synthesized directly from active methylene ketones by treating them with phenyl isothiocyanate followed by alkylation. We envisioned that the 2-aryol-3,3-bis(alkylsulfanyl)acrylaldehydes **2** which we had reported recently could be transformed into aroyl formyl ketene-*N,S*-acetals or aroyl formyl ketene-*N,N*-acetals by direct amination reaction. The literature survey shows that such formyl ketene-*N,S*-acetals and formyl ketene-*N,N*-acetals have not been reported so far, and such compounds will be established in near future as valuable pivot for a variety of amino substituted heterocyclic compounds. Therefore, it appeared worthwhile to utilize 2-aryol-3,3-bis(alkylsulfanyl)acrylaldehydes for the synthesis of those synthons.

In this paper, we report the reactions of 2-aryol-3,3-bis(alkylsulfanyl) acrylaldehydes with various primary amines, namely, *o*-phenylenediamine, ethylenediamine, and anilines, producing aroyl ketene-*N,S*- or -*N,N*-acetals.

2. Results and Discussions

Earlier we had reported the synthesis of 2-aryol-3,3-bis(alkylsulfanyl) acrylaldehydes **2** from oxoketene dithioacetals **1** (Scheme 1) [11].

SCHEME 1

Our experience on the reactivity of 2-aryl-3,3-bis(alkylsulfanyl)acrylaldehydes shows that the alkylsulfanyl groups on these molecules can easily be substituted by other nucleophiles [12]. So we refluxed 2-benzoyl-3,3-bis(alkylsulfanyl)acrylaldehydes **2a** with *o*-phenylenediamine (1 equivalent) in acetonitrile for 3 hrs. The reaction afforded 2-(1,3-dihydro-2H-1,3-benzimidazol-2-yliden)-3-oxo-3-phenylpropanal **3a** in 50% yield as the major product. We could not able to isolate the rest of the products in pure form from the column. The reaction was extended to other substituted acrylaldehydes as well (Scheme 2), and the yield was between 50% and 75%. ¹H NMR spectrum of the 2-(1,3-dihydro-2H-1,3-benzimidazol-2-yliden)-3-oxo-3-phenylpropanal (**2a**) itself is enough for the confirmation of the proposed structure. The Proton NMR spectrum has no SMe peak, confirming the substitution of both of the methylsulfanyl groups. Similarly the presence of two NH protons was visible at δ 12.78 and 12.88, and so also the nine aromatic protons were between δ 7.37–7.60. Such *N,N*-acetals have been effectively utilized for the synthesis of pyrrole fused 1,3-diazaheterocycles [13]. An additional formyl moiety further enhances their synthetic utility.

There are numbers of reports on the synthesis of imidazole derivatives from ketene dithioacetals and ethylenediamine [1–3]. So for the synthesis of 3-aryl-3-oxo-2-tetrahydro-2-H-imidazol-2-ylidenpropanal **4** from 2-aryl-3,3-bis(alkylsulfanyl)acrylaldehydes **2**, we refluxed the 2-(4-bromobenzoyl)-3,3-bis(alkylsulfanyl)acrylaldehyde in acetonitrile with ethylenediamine (1 equivalent) for 2 h. The reaction afforded 3-(4-bromophenyl)-3-oxo-2-tetrahydro-2-H-imidazol-2-ylidenpropanal in 75% yield. The reaction was extended to other substituted acrylaldehydes also (Scheme 3). The structure was confirmed by ¹H NMR spectrum of 3-(4-bromophenyl)-3-oxo-2-tetrahydro-2-H-imidazol-2-ylidenpropanal (**4a**). No SMe peak was seen and four methylene protons were visible in the ¹H NMR spectrum of **4a**. Paulsen et al. had utilized the synthetic potential of imidazoles for the synthesis of different heterocycles [14]. The formyl groups on the new molecules enhance their synthetic utility, and in this aspect the newly synthesized 2-H-imidazol-2-ylidenpropanals are expected to be highly useful synthons.

Singh et al. had reported the synthesis of a number of functionalized ketene-*N,S*-acetals by treating ketene dithioacetals with lithiated primary amines like anilines [15]. We expected the reaction of 2-aryl-3,3-bis(alkylsulfanyl)acrylaldehydes **2** with aniline would be a facile

method for synthesizing formylketene-*N,S*-acetals or formylketene-*N,N*-acetals. So we treated 2-(4-bromobenzoyl)-3,3-bis(methylsulfanyl)acrylaldehyde with one equivalent aniline. Contrary to our expectations in this case, both formyl group as well as ketene dithioacetal moiety involved in the reaction to afford 3-anilino-1-(4-bromophenyl)-3-(methylsulfanyl)-2-[(phenylimino)methyl]-2-propene-1-one **5** in low yields. Later the reaction was optimized by treating the substituted acrylaldehydes with two equivalents aniline in acetonitrile at reflux temperature for 5 h in order to get corresponding 3-anilino-1-aryl-3-(methylsulfanyl)-2-[(phenylimino)methyl]-2-propene-1-ones (Scheme 4).

In ¹H NMR spectrum of **5**, a doublet at δ 8.11–8.07 with a coupling constant $J = 12.9$ Hz, corresponding to a vinylic proton was present, and the doublet revealed the presence of a neighbouring proton. The NH proton was also appeared as a doublet at δ 11.92–11.49 ($J = 12.9$ Hz) showing a non hydrogen bonded NH group with a neighboring proton. Due to the presence of doublet for NH proton and vinylic proton in the ¹H NMR spectrum of **5**, we expected the structure of the compound as **5B**. In the IR spectrum, there was no characteristic NH peaks indicating that there was a chance for rapid exchange of the NH protons between the two structures **5A** and **5B**.

The literature survey shows that such α -oxoketene-*N,S* acetals can be transformed to functionalized quinolines by Vilsmeier-Haack reaction [7]. So we expected **5** would be easily cyclized under Vilsmeier condition. Therefore, 2-benzoyl-3,3-bis(methylsulfanyl)acrylaldehyde **2a** dissolved in DMF was heated with aniline for 10 hrs at 100°C after 5 h Vilsmeier-Haack reagent was added to the reaction mixture, and it was further stirred for 5 hrs. The reaction on workup gave a mixture of products which we could not isolate in pure forms. Then we expected 3-anilino-1-aryl-3-(methylsulfanyl)-2-[(phenylimino)methyl]-2-propene-1-ones **5** may be cyclized in the presence of glacial acetic acid to get substituted quinolines. Therefore, the acrylaldehydes were treated with two equivalents of aniline in acetonitrile in the presence of glacial acetic acid. The reaction afforded 1-aryl-3,3-dianilino-2-propen-1-ones in moderate yields. As these compounds have been effectively prepared from α -oxoketene dithioacetals in good yields [1–3], we have not made further attempts to establish their synthetic utility.

In conclusion, we have developed facile methods for the synthesis of various structurally diverse α -formylketene-*N,S*-acetals and α -formylketene-*N,N*-acetals which can serve as starting materials for functionalized heterocyclic compounds.

3. Experimental

Melting points were determined on Buchi 530 melting point apparatus and were uncorrected. The IR spectra were on KBr pellets on a Shimadzu IR-470 spectrometer, and the frequencies are reported in cm⁻¹. The ¹H NMR & ¹³C NMR spectra were recorded on a Bruker WM (300 & 75.47 MHz) spectrometer using TMS as internal standard and CDCl₃ or acetone as solvents. The CHN analyses were done on an

SCHEME 2

SCHEME 3

Elementar VarioEL III Serial Number 11042022 instrument. The FAB mass spectra were recorded on a JOEL SX 102/DA-6000 Mass Spectrometer/Data System using Argon as the FAB gas. The EIMS spectra were recorded on a MICROMASS QUATTRO 11 triple quadrupole mass spectrometer

All reagents were commercially available and were purified before use. The previously reported aroylketene dithioacetals and formylketene dithioacetals were prepared by the known procedure [1–3, 11]. Anhydrous sodium sulphate was used as drying agent. All purified compounds gave a single spot upon TLC analyses on silicagel 7GF using an ethyl acetate/hexane mixture as eluent. Iodine vapors or KMnO₄ solution in water was used as developing agent for TLC.

3.1. General Procedure for the Synthesis of 3-aryl-2-(1,3-dihydro-2H-1,3-benzimidazol-2-yliden)-3-oxopropanal (3). Appropriate 2-aryl-3-bis(alkylsulfanyl)acrylaldehyde (1 mmol) was dissolved in acetonitrile (10 mL) and refluxed with *o*-phenylenediamine (0.25 g, 1 mmol) for 5 h. The reaction mixture was cooled, and it was added to 5N HCl (25 mL) solution slowly. The precipitate was filtered and recrystallized from methanol.

2-(1,3-dihydro-2H-1,3-benzimidazol-2-yliden)-3-oxo-3-Phenylpropanal (3a). Pale yellow solid; yield % 50 (0.13 g); mp 275°C; IR (KBr): 3220, 1623, 1612, 1573, 1542 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 7.37–7.60 (m, 9H, ArH), 9.53 (s, 1 H, CHO), 12.78 and 12.88 (b, 2H, NH); Anal: C₁₆H₁₂N₂O₂ (264.28) Calcd.; C, 72.72; H, 4.58; N, 10.60 Found; C, 73.02; H, 4.45; N, 10.53.

2-(1,3-dihydro-2H-1,3-benzimidazol-2-yliden)-3-(4-methylphenyl)-3-oxopropanal (3b). Pale yellow solid; yield % 75 (0.20 g); mp > 260°C; IR (KBr): 3210, 1620, 1610, 1566, 1542 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 2.42 (s, 3 H, CH₃), 6.95–6.98 (m, 4H, ArH), 7.37–7.58 (m, 4H, ArH), 9.55 (s, 1H, CHO), 12.68 and 13.06 (b, 2H, NH); Anal: C₁₇H₁₄N₂O₂ (278.31) Calcd.; C, 73.37; H, 5.07; N, 10.07 Found; C, 73.12; H, 4.96; N, 10.23.

2-(1,3-dihydro-2H-1,3-benzimidazol-2-yliden)-3-(4-methoxyphenyl)-3-oxopropanal (3c). Pale yellow solid; yield % 74 (0.21 g); mp > 260°C; IR (KBr): 3213, 1630, 1608, 1573, 1542 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 3.9 (s, 3H, OCH₃), 6.95–6.98 (m, 4 H, ArH), 7.36–7.71 (m, 4H, ArH), 9.58 (s, 1H, CHO), 12.7 and 12.9 (b, 2H, NH); Anal: C₁₇H₁₄N₂O₃ (294.30) Calcd.; C, 69.38; H, 4.79; N, 9.52 Found; C, 68.98; H, 4.84; N, 10.03.

2-(1,3-dihydro-2H-1,3-benzimidazol-2-yliden)-3-(4-chlorophenyl)-3-oxopropanal (3d). Pale yellow solid; yield % 74 (0.21 g); mp > 260°C; IR (KBr): 3225, 1634, 1610, 1563, 1552 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 7.12–7.23 (m, 4H, ArH), 7.38–7.78 (m, 4H, ArH), 9.53 (s, 1H, CHO), 12.72 and 12.89 (b, 2H, NH); Anal: C₁₆H₁₁ClN₂O₂ (298.72) Calcd.; C, 64.33; H, 3.71; N, 9.38 Found; C, 64.58; H, 3.84; N, 9.22.

3.2. General Procedure for the Synthesis of 3-(Aryl)-3-Oxo-2-Tetrahydro-2-H-Imidazol-2-ylidenpropanal (4). Appropriate 2-aryl-3-bis(alkylsulfanyl)acrylaldehyde (1 mmol), dissolved in acetonitrile (10 mL) was refluxed with ethylene diamine (0.12 g, 2 mmol) for 5 h. The reaction mixture was cooled, and it was added to 5N HCl (25 mL) solution

SCHEME 4

slowly. The precipitate was filtered and recrystallized from methanol.

3-(4-bromophenyl)-3-oxo-2-tetrahydro-2-H-imidazol-2-ylidenpropanal (4a). Pale yellow solid; yield % 75 (0.24 g); mp 190°C; IR (KBr): 3301, 1623, 1589 cm^{-1} . δ 3.83 (s, 4H, $-\text{CH}_2\text{CH}_2-$), 7.35–7.32 (d, $J = 9$ Hz, 2H, ArH), 7.55–7.52 (d, $J = 9$ Hz, 2H, ArH), 9.23 (b, 1H, NH), 9.29 (s, 1H, CHO) and 9.38 (b, 1H, NH); Anal: $\text{C}_{12}\text{H}_{11}\text{BrN}_2\text{O}_2$ (295.13) Calcd.; C, 48.84; H, 3.76; N, 9.49 Found; C, 49.12; H, 3.87; N, 9.28.

3-(4-methoxyphenyl)-3-oxo-2-tetrahydro-2-H-imidazol-2-ylidenpropanal (4b). Pale yellow solid; Yield % 87 (0.24 g); mp 194°C; IR (KBr): 3297, 1637, 1580 cm^{-1} . δ 3.80 (s, 4H, $-\text{CH}_2\text{CH}_2-$), 3.842 (s, 3H, OMe), 6.919–6.89 (m, 2H, ArH), 7.483–7.454 (m, 2H, ArH), 9.39 (b, 3H, NH and CHO); Anal: $\text{C}_{13}\text{H}_{14}\text{N}_2\text{O}_3$ (246.26) Calcd.; C, 63.40; H, 5.73; N, 11.38 Found; C, 63.16; H, 5.96; N, 11.23.

3-(4-methylphenyl)-3-oxo-2-tetrahydro-2-H-imidazol-2-ylidenpropanal (4c). Pale yellow solid; yield % 75 (0.19 g); mp 188°C; IR (KBr): 3310, 1631, 1575 cm^{-1} . δ 2.384 (s, 3H, Me), 3.801 (s, 4H, $-\text{CH}_2\text{CH}_2-$), 7.208–7.189 (d, $J = 5.7$ Hz, 2H, ArH), 7.389–7.370 (d, $J = 5.7$ Hz, 2H, ArH), 9.35 (b, 3H, two NH and CHO); Anal: $\text{C}_{13}\text{H}_{14}\text{N}_2\text{O}_2$ (230.26) Calcd.; C, 67.81; H, 6.13; N, 12.17 Found; C, 67.56; H, 5.98; N, 12.22.

3-(4-chlorophenyl)-3-oxo-2-tetrahydro-2-H-imidazol-2-ylidenpropanal (4d). Pale yellow solid; yield % 75 (0.21 g); mp 180–182°C; IR (KBr) 3311, 1625, 1605 cm^{-1} . δ 3.89 (s, 4H, $-\text{CH}_2\text{CH}_2-$), 7.34–7.7.31 (d, $J = 9$ Hz, 2H, ArH), 7.58–7.55 (d, $J = 9$ Hz, 2H, ArH), 9.34 (b, 1H, NH), 9.38 (s, 1H, CHO) and 9.40 (b, 1H, NH); Anal: $\text{C}_{12}\text{H}_{11}\text{ClN}_2\text{O}_2$ (250.68) Calcd.; C, 57.49; H, 4.42; N, 11.17 Found; C, 57.65; H, 4.23; N, 10.98.

3.3. General Procedure for the Synthesis of 3-Anilino-1-(aryl)-3-(methylsulfanyl)-2-[(phenylimino)methyl]-2-propen-1-

one (5). Appropriate 2-aryl-3,3-bis(alkylsulfanyl) acrylaldehyde (1 mmol), dissolved in acetonitrile (10 mL) was refluxed with aniline (0.186 g, 2 mmol) for 10 h. The reaction mixture was cooled, and it was added to 5N HCl (25 mL) solution slowly. The precipitate was filtered and recrystallized from methanol.

3-Anilino-1-(4-bromophenyl)-3-(methylsulfanyl)-2-[(phenylimino)methyl]-2-propen-1-one (5a). Yellow solid; mp 132°C, yield % 37 (0.18 g); IR (KBr): 1623, 1589, 1292 cm^{-1} . ^1H NMR (300 MHz CDCl_3): $\delta = 2.6$ (s, 3H, SMe), 6.272–6.246 (d, $J = 7.8$ Hz, 2H ArH), 6.6–7.8 (12H, ArH), 8.118–8.075 ($J = 12.9$ Hz, Vinylic), 11.9 (d, 1H, NH), ^{13}C NMR (75.47 CDCl_3) δ 14.4 (SMe), 108.1 (C=C near the carbonyl group), 117–139.3 (17 ArH carbons), 147.7 (N=C), 149.4 (one ArH carbon connected to N=C), 165.1 (C=C connected to SMe), 191.4 (CO). FABMS m/z (%) 453., 451.

3-Anilino-1-(4-methoxyphenyl)-3-(methylsulfanyl)-2-[(phenylimino)methyl]-2-propen-1-one (5b). Yellow solid; mp 120°C, Yield % 44 (0.19 g); IR (KBr): 2923, 1627, 1581, 1245 cm^{-1} . ^1H NMR (300 MHz CDCl_3): $\delta = 2.51$ (s, 3H, SMe), 3.84 (s, 3H, OMe), 6.275–6.250 (d, $J = 7.5$ Hz, 2H ArH), δ 6.73–7.4 (12H, ArH), 8.05–8.01 ($J = 12$ Hz, Vinylic), 12.0198–11.9860 (d, 1H, $J = 10.5$ Hz, NH).

3-Anilino-3-methylsulfanyl-1-phenyl-2-[(phenylimino)methyl]-2-propen-1-one (5c). Yellow solid; mp 138°C; yield % 41 (0.16g); IR (KBr): 1627, 1581, 1234. cm^{-1} . ^1H NMR 300 MHz CDCl_3): $\delta = 2.6$ (s, 3H, SMe), 6.221–6.203 (d, $J = 7.8$ Hz, 2H ArH), δ 6.85–7.8 6 (12H, ArH), 8.0997–8.0680 ($J = 9.75$ Hz, Vinylic), 11.97 (d, 1H, NH).

1-(4-chlorophenyl)-2-[(4-methylphenylimino)methyl]-3-(methylsulfanyl)-3-(4-toluidino)-2-propen-1-one (5d). Yellow solid; mp 123°C, yield % 40 (0.17 g); IR (KBr): 2923, 1623, 1589, 1288 cm^{-1} ^1H NMR 300 MHz CDCl_3):

δ = 2.22 and 2.35 (2 toluidine CH_3), 2.49 (s, 3H, SMe), 6.183–6.161 (d, J = 6.6 Hz, 2H ArH), δ 6.79–7.2 (10 H, ArH), 8.048–8.006 (J = 12.6 Hz, 1H Vinylic), 11.95–11.91 (d, J = 12 Hz, 1H, NH).

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