Polyhedron 29 (2010) 2857–2861

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Synthesis of novel mercury heterocycles

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ARTICLE INFO

Article history:
Received 24 May 2010
Accepted 12 July 2010
Available online 13 August 2010

Dedicated to my Teacher Late Dr. (Smt.)
Geeta Manohar Kulkarni-
Naazneen Budanbaig

Keywords:
Mercuration
Metalation
Intramolecular cyclization
Neutral alumina

ABSTRACT

Ortho-mercurated 4-aryloxymethylcoumarins and 1-azacoumarins have been found to undergo smooth intramolecular metalation in refluxing xylene in the presence of activated neutral alumina and anhydrous potassium carbonate. This is the first report on the synthesis of heterocycles not possessing a metal heteroatom linkage.

1. Introduction

Organic compounds in which the aromatic hydrogens have been replaced by main group metal substituents represent a rare class of molecules [1]. Organomercurials have attracted much attention from the view point of their specific reactivity, attributed to the electropositive character of Hg.

Coumarins and 1-azacoumarins are a pair of isosteric heterocyclic systems, the derivatives of which have exhibited wide ranging biological properties [2]. Earlier work on chloro and acetoxy mercuration of coumarins has shown that mercuration was found to occur preferentially at the C-6 and C-8 positions [3]. Subsequently mercurated 3-4′-thiazolylcoumarins were reported for their fungicidal activity [4]. In recent years there has been a growing interest in the application of organomercurials in organic synthesis involving the synthesis of amino acids [5], austamide [6], oxyphenelations [7] and intramolecular annulation of carboxylic acids to triple bonds [8]. In all these reactions mercury is not retained in the final compound but they result in a C–C bond formation *via* halo/acetoxy demercuration.

4-Aryloxymethylcoumarins and 1-azacoumarins have been of both biological [9,10] and structural interest [11]. Reactivity of *o*-substituted 4-aryloxymethylcoumarins has been explored to synthesize biologically active 4-2′-benzo[b]furanylcoumarins [12], oxygenated triheterocycles [13] and fused polycyclic coumarins [14]. In light of the above observations and paucity of literature on heterocyclic systems containing mercury it was thought to be of immense interest to study the reactivity of 4-aryloxymethylcoumarins and 1-azacoumarins possessing *o*-halo/acetoxymercury substituents. The present investigation reports probably the first intramolecular mercuration at the C-3 position on coumarins and 1-azacoumarins leading to a new class of mercury heterocycles.

2. Experimental

2.1. Materials and methods

Reactions were performed in oven-dried glassware under nitrogen atmosphere containing a Teflon coated stir bar and dry septum. Butanone was dried over calcium chloride and dry distilled before use. Xylene was dried over Na pressed wire and dry distilled before use. Mercuric acetate was purchased from Fishers Scientific Ltd. TLC analyses were performed on commercial Kieselgel 60 F254 silica gel plates. IR spectra were recorded on a Bruker EQUINOX 55 FTIR. NMR spectra were obtained on Bruker spectrometer using DMSO as solvent, with proton and carbon resonances at 300, 400 and 75 MHz, respectively. Mass spectral data (ESI) were recorded on HCT Ultra ETD II Bruker Daltonics, Germany and FAB mass data were recorded on a JEOL SX 102/DA-6000 mass spectrometer.

2.1.1. Preparation of the 4-(2-chloromercury-phenoxymethyl)-6-chromene-2-ones (general procedure)

To a dry 100 mL flask equipped with a stir bar was added substituted 4-bromomethylcoumarins/1-azacoumarins (0.005 mol),

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0277-5387/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2010.07.010

o-chloro mercury phenol/*o*-acetoxy mercurated *p*-cresol (0.005 mol), anhydrous K_2CO_3 (1.72 g, 0.0125 mol) and dry butanone (50 mL). The solution was refluxed for 20–24 h. After this time the reaction was cooled to room temperature, the butanone was concentrated and the solution was poured onto crushed ice. The crude solid obtained was crystallized from warm acetic acid.

*2.1.1.1. 4-(2-Chloromercury-phenoxymethyl)-6-methyl-chromene-2-one (**3a**).* Yield: 2.20 g (86%). M.p. 238–240 °C. FT-IR (KBr, cm^{-1}) 1722. ^1H NMR (300 MHz, DMSO) δ: 7.45–7.09 (m, 7H), 6.67 (s, 1H, C_3–H of coum.), 5.27 (s, 2H, CH_2O), 2.39 (s, 3H, CH_3). ^{13}C NMR (75 MHz, DMSO) δ: 152.66, 151.64, 132.62, 131.89, 131.09, 130.69, 125.06, 123.22, 122.10, 121.62, 121.32, 117.32, 113.82, 112.26, 109.19, 67.03, 23.00. MS (ESI+) *m/z* = 502.3. *Anal.* Calc. for $C_{17}H_{13}ClHgO_3$: C, 40.73; H, 2.61. Found: C, 40.64; H, 2.53%.

*2.1.1.2. 4-(2-Chloromercury-phenoxymethyl)-7-methyl-chromene-2-one (**3b**).* Yield: 2.20 g (86%). M.p. 250–252 °C. FT-IR (KBr, cm^{-1}) 1728. ^1H NMR (300 MHz, DMSO) δ: 7.50–7.02 (m, 7H), 6.62 (s, 1H, C_3–H of coum.), 5.32 (s, 2H, CH_2O), 2.46 (s, 3H, CH_3). ^{13}C NMR (75 MHz, DMSO) δ: 152.45, 151.38, 132.82, 131.55, 130.89, 130.60, 125.08, 123.85, 122.98, 122.26, 121.64, 117.65, 113.82, 112.79, 110.00, 65.07, 22.53. MS (ESI+) *m/z* = 502.3. *Anal.* Calc. for $C_{17}H_{13}ClHgO_3$: C, 40.73; H, 2.61. Found: C, 40.72; H, 2.65%.

*2.1.1.3. 4-(2-Chloromercury-phenoxymethyl)-5,7-methyl-chromene-2-one (**3c**).* Yield: 2.00 g (78%). M.p. 260–262 °C. FT-IR (KBr, cm^{-1}) 1714. ^1H NMR (300 MHz, DMSO) δ: 7.51–7.02 (m, 6H), 6.56 (s, 1H, C_3–H of coum.), 5.55 (s, 2H, CH_2O), 2.70 (s, 3H, CH_3), 2.50 (s, 3H, CH_3). ^{13}C NMR (75 MHz, DMSO) δ: 152.76, 151.24, 132.52, 131.89, 131.09, 130.22, 125.86, 123.82, 122.60, 121.66, 121.22, 117.32, 113.88, 112.32, 109.86, 67.03, 23.52, 23.02. MS (ESI+) *m/z* = 516.3. *Anal.* Calc. for $C_{18}H_{15}ClHgO_3$: C, 41.95; H, 2.93. Found: C, 41.98; H, 2.99%.

*2.1.1.4. 4-(2-Chloromercury-phenoxymethyl)-7,8-methyl-chromene-2-one (**3d**).* Yield: 2.05 g (80%). M.p. 264–266 °C. FT-IR (KBr, cm^{-1}) 1704. ^1H NMR (300 MHz, DMSO) δ: 7.85–7.00 (m, 6H), 6.55 (s, 1H, C_3–H of coum.), 5.41(s, 2H, CH_2O), 2.37 (s, 3H, CH_3), 2.29 (s, 3H, CH_3). ^{13}C NMR (75 MHz, DMSO) δ: 152.76, 151.24, 131.99, 131.68, 131.14, 130.72, 130.36, 125.86, 123.88, 122.67, 121.66, 117.99, 113.57, 112.72, 109.72, 67.23, 23.02, 23.00. MS (ESI+) *m/z* = 516.3. *Anal.* Calc. for $C_{18}H_{15}ClHgO_3$: C, 41.95; H, 2.93. Found: C, 41.98; H, 2.92%.

*2.1.1.5. 4-(2-Chloromercury-phenoxymethyl)-6-methoxy-chromene-2-one (**3e**).* Yield: 2.12 g (82%). M.p. 216–218 °C. FT-IR (KBr, cm^{-1}) 1710. ^1H NMR (400 MHz, DMSO) δ: 7.48 (s, 1H, C5-H of coum.), 7.46–7.02 (m, 6H), 6.65 (s, 1H, C_3–H of coum.), 5.45 (s, 2H, CH_2O), 3.85 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, DMSO) δ: 153.22, 152.06, 138.22, 132.92, 132.62, 132.09, 125.02, 123.44, 122.82, 121.00, 120.90, 119.22, 115.68, 114.92, 110.00, 67.02, 48.02. MS (ESI+) *m/z* = 518.3. *Anal.* Calc. for $C_{17}H_{13}O_4HgCl$: C, 39.47; H, 2.53. Found: C, 39.49; H, 2.60%.

*2.1.1.6. 4-(2-Chloromercury-phenoxymethyl)-6-chloro-chromene-2-one (**3f**).* Yield: 1.97 g (79%). M.p. 260–264 °C. FT-IR (KBr, cm^{-1}) 1716. ^1H NMR (300 MHz, DMSO) δ: 7.99 (s, 1H, C5-H of coum.), 7.31–7.03 (m, 6H), 6.68 (s, 1H, C_3–H of coum.), 5.44 (s, 2H, CH_2O). ^{13}C NMR (75 MHz, DMSO) δ: 152.49, 151.31, 137.86, 132.54, 130.03, 129.44, 125.05, 122.75, 121.42, 119.27, 119.07, 117.61, 113.80, 112.89, 109.99, 65.76. MS (ESI+) *m/z* = 522.7. *Anal.* Calc. for $C_{16}H_{10}Cl_2HgO_3$: C, 36.83; H, 1.93. Found: C, 36.85; H, 1.99%.

*2.1.1.7. 4-(2-Chloromercury-phenoxymethyl)-5,6 benzo-chromene-2-one (**3g**).* Yield: 2.01 g (75%). M.p. 238–240 °C. FT-IR (KBr, cm^{-1}) 1722. ^1H NMR (300 MHz, DMSO) δ: 8.35–7.04 (m, 10H), 6.88 (s, 1H, C_3–H of coum.), 5.83 (s, 2H, CH_2O). ^{13}C NMR (75 MHz, DMSO) δ: 153.44, 152.16, 138.12, 132.62, 132.32, 132.09, 125.22, 125.16, 123.44, 123.26, 122.96, 122.82, 121.00, 120.90, 120.62, 119.22, 115.68, 114.92, 110.00, 67.08. MS (ESI+) *m/z* = 538.3. *Anal.* Calc. for $C_{20}H_{13}Cl{\cdot}HgO_3$: C, 44.70; H, 2.44. Found: C, 44.66; H, 2.43%.

*2.1.1.8. 4-(2-Chloromercury-phenoxymethyl)-7,8 benzo-chromene-2-one (**3h**).* Yield: 1.92 g (72%). M.p. 238–240 °C. FT-IR (KBr, cm^{-1}) 1722. ^1H NMR (300 MHz, DMSO) δ: 8.40–7.02 (m, 10H), 6.73 (s, 1H, C_3–H of coum.), 5.53 (s, 2H, CH_2O). ^{13}C NMR (75 MHz, DMSO) δ: 153.44, 152.12, 138.10, 132.64, 132.62, 132.39, 125.62, 123.34, 123.36, 122.96, 122.68, 121.22, 120.90, 120.58, 119.22, 115.88, 114.92, 114.12, 109.00, 67.10. MS (ESI+) *m/z* = 538.3. *Anal.* Calc. for $C_{20}H_{13}ClHgO_3$: C, 44.70; H, 2.44. Found: C, 44.62; H, 2.50%.

*2.1.1.9. 4-(2-Acetoxymercury, 4-methyl-phenoxymethyl)-6-methyl-chromene-2-one (**3i**).* Yield: 0.87 g (69%). M.p. 216–218 °C. FT-IR (KBr, cm^{-1}) 1749, 1723. ^1H NMR (300 MHz, DMSO) δ: 7.48–7.10 (m, 6H), 6.52 (s, 1H, C_3–H of coum.), 5.86 (s, 2H, CH_2O), 2.42 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 2.32 (s, 3H, CH_3). ^{13}C NMR (75 MHz, DMSO) δ: 169.22, 160.22, 160.02, 157.32, 157.12, 156.22, 155.88, 149.14, 147.04, 126.34, 124.58, 121.47, 118.09, 117.22, 112.10, 108.37, 67.22, 23.82, 23.12, 23.02. MS (ESI+) *m/z* = 539.9. *Anal.* Calc. for $C_{20}H_{18}HgO_5$: C, 44.57; H, 3.37. Found: C, 44.56; H, 3.39%.

*2.1.1.10. 4-(2-Acetoxymercury, 4-methyl-phenoxymethyl)-6-methoxy-chromene-2-one (**3j**).* Yield: 2.24 g (81%). M.p. 236–238 °C. FT-IR (KBr, cm^{-1}) 1748, 1729. ^1H NMR (300 MHz, DMSO) δ: 7.36–6.92 (m, 6H), 6.49 (s, 1H, C_3–H of coum.), 5.30 (s, 2H, CH_2O), 3.85 (s, 1H, OCH_3 of coum.), 2.43 (s, 1H, CH_3), 2.30 (s, 1H, CH_3). ^{13}C NMR (75 MHz, DMSO) δ: 170.04, 160.96, 160.22, 157.88, 157.33, 156.00, 155.92, 149.88, 147.62, 126.62, 124.72, 122.36, 118.12, 117.55, 112.00, 108.44, 67.28, 48.02, 23.44, 23.00. MS (FAB+) *m/z* = 555. *Anal.* Calc. for $C_{20}H_{18}HgO_6$: C, 43.29; H, 3.27. Found: C, 43.29; H, 3.25%.

*2.1.1.11. 4-(2-Chloromercury-phenoxymethyl)-azachromene-2-one (**8a**).* Yield: 1.94 g (80%). M.p. 230–232 °C. FT-IR (KBr, cm^{-1}) 1673. ^1H NMR (300 MHz, DMSO) δ: 11.74 (s, 1H, NH), 7.84–7.00 (m, 8H), 6.67 (s, 1H, C_3H of coum.), 5.43 (s, 2H, CH_2O). ^{13}C NMR (75 MHz, DMSO) δ: 169.48, 160.49, 160.22, 157.00, 155.86, 148.54, 147.03, 123.44, 119.05, 118.75, 115.42, 113.07, 112.61, 107.80, 106.89, 66.76. MS (ESI+) *m/z* = 487.3. *Anal.* Calc. for $C_{16}H_{12}ClHgNO_2$: C, 39.52; H, 2.49; N, 2.88. Found: C, 39.52; H, 2.50; N, 2.86%.

*2.1.1.12. 4-(2-Chloromercury-phenoxymethyl)-6-chloro-azachromene-2-one (**8b**).* Yield: 1.87 g (72%). M.p. 272–274 °C. FT-IR (KBr, cm^{-1}) 1682. ^1H NMR (300 MHz, DMSO) δ: 11.78 (s, 1H, NH), 7.89–7.06 (m, 7H), 6.68 (s, 1H, C_3–H of coum.), 5.72 (s, 2H, CH_2O). ^{13}C NMR (75 MHz, DMSO) δ: 170.12, 160.82, 160.00, 157.48, 150.62, 147.22, 134.24, 133.26, 129.26, 121.47, 118.88, 118.34, 117.62, 112.22, 108.12, 64.12. MS (ESI+) *m/z* = 521.7. *Anal.* Calc. for $C_{16}H_{11}Cl_2HgNO_2$: C, 36.90; H, 2.13; N, 2.69. Found: C, 36.92; H, 2.11; N, 2.62%.

2.1.2. Synthesis of substituted 13H-5, 12-dioxa-7-mercura-benzo[4,5]cyclohepta[1,2-a]naphthalene 6-ones (general procedure)

Preparation of activated Al_2O_3/K_2CO_3: A mixture of neutral Al_2O_3 (1 g, 0.001 mol) and anhydrous K_2CO_3 (2.76 g, 0.002 mol) is ground thoroughly in a glass mortar and heated on the Bunsen flame for 4 h followed by the direct usage into the reaction vessel without allowing the mixture to attain room temperature.

Table 1
Synthesis of substituted 13H-5,12-dioxa-7-mercura-benzo[4,5]cyclohepta[1,2-a]naphthalene 6-ones.

S. no.	Entry	Product R	R^1	Reaction time (h)	% Yield
1	**6a**	6-CH_3	H	24	80
2	**6b**	7-CH_3	H	20	73
3	**6c**	5,7-CH_3	H	24	77
4	**6d**	7,8-CH_3	H	23	79
5	**6e**	6-OCH_3	H	22	76
6	**6f**	6-Cl	H	27	62
7	**6g**	5,6-benzo	H	23	72
8	**6h**	7,8-benzo	H	23	71
9	**6i**	6-CH_3	–CH_3	21	71
10	**6j**	6-OCH_3	–CH_3	19	72
11	**9a**	H	H	18	76
12	**9b**	6-Cl	H	20	60

To a dry 100 mL round bottom flask equipped with a stir bar, was added substituted *o*-chloromercury phenoxy methylcoumarins/*o*-chloromercury phenoxy 1-azacoumarins (13 mmol), activated Al_2O_3:K_2CO_3 (1.41g) and dry xylene (25 mL). The solution was refluxed for 24–28 h under nitrogen atmosphere. After this time the solution was filtered hot and cooled to room temperature. The separated crude solid was filtered and washed with minimum amount of xylene. All the compounds were recrystallised from dry xylene (Table 1).

*2.1.2.1. 2-Methyl-13H-5,12-dioxa-7-mercura-benzo[4,5]cyclohepta-[1,2-a]naphthalene 6-one (**6a**).* Yield: 0.51 g (80%). FT-IR (KBr, cm^{-1}) 1685. ^{1}H NMR (300 MHz, DMSO) δ: 7.61 (s, 1H, C5-H), 6.71–7.41 (m, 6H), 4.08 (s, 2H, CH_2O), 2.48 (s, 3H, CH_3). ^{13}C NMR (75 MHz, DMSO) δ: 153.24, 152.62, 138.02, 132.22, 130.62, 130.02, 124.62, 123.10, 121.82, 119.62, 119.09, 117.22, 114.27, 113.06, 110.01, 57.07, 23.00. MS (ESI+) *m/z* = 465.8. *Anal.* Calc. for $C_{17}H_{12}HgO_3$: C, 43.92; H, 2.60. Found: C, 43.90; H, 2.60%.

*2.1.2.2. 3-Methyl-13H-5,12-dioxa-7-mercura-benzo[4,5]cyclohepta-[1,2-a]naphthalene 6-one (**6b**).* Yield 0.47 g (73%). FT-IR (KBr) 1686. ^{1}H NMR (300 MHz, DMSO) δ: 7.68 (s, 1H, C5-H), 6.65–7.38 (m, 6H), 4.08 (s, 2H, CH_2O), 2.42 (s, 3H, CH_3). ^{13}C NMR (75 MHz, DMSO) δ: 153.28, 152.66, 138.22, 132.68, 130.88, 130.62, 124.88, 123.62, 121.96, 119.62, 119.09, 117.32, 114.27, 113.26, 110.10, 57.10, 23.08. MS (ESI+) *m/z* = 465.8. *Anal.* Calc. for $C_{17}H_{12}HgO_3$: C, 43.92; H, 2.60. Found: C, 43.88; H, 2.65%.

*2.1.2.3. 1,3-Dimethyl-13H-5,12-dioxa-7-mercura-benzo[4,5]cyclohep-ta[1,2-a]naphthalene 6-one (**6c**).* Yield: 0.49 g (77%). FT-IR (KBr, cm^{-1}) 1690. ^{1}H NMR (300 MHz, DMSO) δ: 8.00–6.64 (m, 6H), 4.03 (s, 2H, CH_2O), 2.52 (s, 3H, CH_3), 2.32 (s, 3H, CH_3). ^{13}C NMR (75 MHz, DMSO) δ: 153.22, 152.44, 138.02, 132.40, 130.72, 130.23, 124.66, 123.09, 121.88, 119.84, 119.66, 117.32, 114.33, 113.12, 109.92, 57.22, 23.00, 22.95. MS (ESI+) *m/z* = 479.9. *Anal.* Calc. for $C_{18}H_{14}HgO_3$: C, 45.14; H, 2.95. Found: 45.10; H, 2.93%.

*2.1.2.4. 3,4-Dimethyl-13H-5,12-dioxa-7-mercura-benzo[4,5]cyclohep-ta[1,2-a]naphthalene 6-one (**6d**).* Yield: 0.50 g (79%). FT-IR (KBr, cm^{-1}) 1687. ^{1}H NMR (300 MHz, DMSO) δ: 8.20–6.72 (m, 6H), 4.09 (s, 2H, CH_2O), 2.48 (s, 3H, CH_3), 2.30 (s, 3H, CH_3). ^{13}C NMR (75 MHz, DMSO) δ: 153.27, 152.64, 138.22, 132.46, 130.62, 130.32, 124.72, 123.29, 121.78, 119.92, 119.57, 117.82, 114.82, 113.19, 109.97, 57.09, 23.00, 22.96. MS (ESI+) *m/z* = 479.9. *Anal.* Calc. for $C_{18}H_{14}HgO_3$: C, 45.14; H, 2.95. Found: 45.18; H, 2.93%.

*2.1.2.5. 2-Methoxy-13H-5,12-dioxa-7-mercura-benzo[4,5]cyclohepta-[1,2-a]naphthalene 6-one (**6e**).* Yield: 0.51 g (76%). FT-IR (KBr, cm^{-1}) 1663. ^{1}H NMR (300 MHz, DMSO) δ: 7.93 (s, 1H, C5-H), 7.69–6.96 (m, 6H), 4.08 (s, 2H, CH_2O), 3.89 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, DMSO) δ: 152.63, 151.76, 137.22, 130.23, 129.22, 124.09, 123.65, 122.32, 119.06, 119.02, 117.27, 113.44, 112.07, 112.05, 109.14, 57.02, 48.03. MS (FAB+) *m/z* = 481. *Anal.* Calc. for $C_{17}H_{12}HgO_4$: C, 42.46; H, 2.52. Found: C, 42.48; H, 2.50%.

*2.1.2.6. 2-Chloro-13H-5,12-dioxa-7-mercura-benzo[4,5]cyclohepta-[1,2-a]naphthalene 6-one (**6f**).* Yield: 0.41 g (62%). FT-IR (KBr, cm^{-1}) 1685. ^{1}H NMR (300 MHz, DMSO) δ: 7.93–7.02 (m, 7H), 4.09 (s, 2H, CH_2O). ^{13}C NMR (75 MHz, DMSO) δ: 152.66, 151.42, 148.21, 130.62, 130.09, 123.62, 123.12, 121.00, 119.99, 119.82, 117.06, 113.98, 113.00, 112.89, 109.82, 57.02. MS (ESI+) *m/z* = 486.2. *Anal.* Calc. for $C_{16}H_9ClHgO_3$: C, 39.60; H, 1.87. Found: C, 39.64; H, 1.81%.

*2.1.2.7. 1,2-Benzo-13H-5,12-dioxa-7-mercura-benzo[4,5]cyclohepta-[1,2-a]naphthalene 6-one (**6g**).* Yield: 0.50 g (72%). FT-IR (KBr, cm^{-1}) 1672. ^{1}H NMR (300 MHz, DMSO) δ: 8.20–7.22 (m, 10H), 4.12 (s, 2H, CH_2O). ^{13}C NMR (75 MHz, DMSO) δ: 153.48, 152.58, 138.20, 132.68, 130.68, 130.72, 124.66, 123.62, 121.82, 121.65, 120.98, 120.22, 119.72, 119.12, 117.42, 114.32, 113.82, 113.10, 110.10, 57.06. MS (ESI+) *m/z* = 501.9. *Anal.* Calc. for $C_{20}H_{12}HgO_3$: C, 47.96; H, 2.41. Found: C, 47.95; H, 2.46%.

*2.1.2.8. 3,4-Benzo-13H-5,12-dioxa-7-mercura-benzo[4,5]cyclohepta-[1,2-a]naphthalene 6-one (**6h**).* Yield: 0.51 g (71%). FT-IR (KBr, cm^{-1}) 1673. ^{1}H NMR (300 MHz, DMSO) δ: 8.40–7.10 (m, 10H), 4.10 (s, 2H, CH_2O). ^{13}C NMR (75 MHz, DMSO) δ: 153.42, 152.62, 138.08, 132.22, 130.24, 130.02, 124.82, 123.44, 121.82, 121.66, 120.58, 120.22, 119.22, 118.12, 117.19, 114.54, 113.66, 113.22, 110.66, 57.10. MS (ESI+) *m/z* = 501.9. *Anal.* Calc. for $C_{20}H_{12}HgO_3$: C, 47.96; H, 2.41. Found: C, 47.98; H, 2.42%.

*2.1.2.9. 2,9-Dimethyl-13sH-5,12-dioxa-7-mercura-benzo[4,5]cyclohe-pta[1,2-a]naphthalene-6-one (**6i**).* Yield: 0.44 g (71%). FT-IR (KBr, cm^{-1}) 1662. ^{1}H NMR (300 MHz, DMSO) δ: 8.28–7.28 (m, 6H), 4.08 (s, 2H, CH_2O), 2.30 (s, 3H, CH_3), 2.36 (s, 3H, CH_3). ^{13}C NMR (75 MHz, DMSO) δ: 152.72, 151.33, 138.17, 130.88, 130.09, 123.82, 123.12, 121.12, 119.92, 119.82, 117.06, 113.98, 113.00, 112.89, 109.82, 57.12, 23.22, 23.02. MS (ESI+) *m/z* = 479.9. *Anal.* Calc. for $C_{18}H_{14}HgO_3$: C, 45.14; H, 2.95. Found: C, 45.21; H, 2.94%.

*2.1.2.10.2-Methoxy-9-methyl-13H-5,12-dioxa-7-mercura-benzo[4,5]-cyclohepta[1,2-a]naphthalene-6-one (**6j**).* Yield: 0.44 g (72%). FT-IR (KBr, cm^{-1}) 1682. ^{1}H NMR (300 MHz, DMSO) δ: 8.40–7.35 (m, 6H), 4.08 (s, 2H, CH_2O), 3.85 (s, 1H, OCH_3 of coum.), 2.36 (s, 1H, CH_3). ^{13}C NMR (75 MHz, DMSO) δ: 153.72, 152.55, 138.17, 132.46, 130.77, 130.32, 124.65, 123.09, 121.78, 119.92, 119.57, 117.22, 114.66, 113.20, 109.88, 57.13, 48.00, 23.00. MS (ESI+) *m/z* = 495.9. *Anal.* Calc. for $C_{18}H_{14}HgO_4$: C, 43.68; H, 2.85. Found: C, 43.62; H, 2.87%.

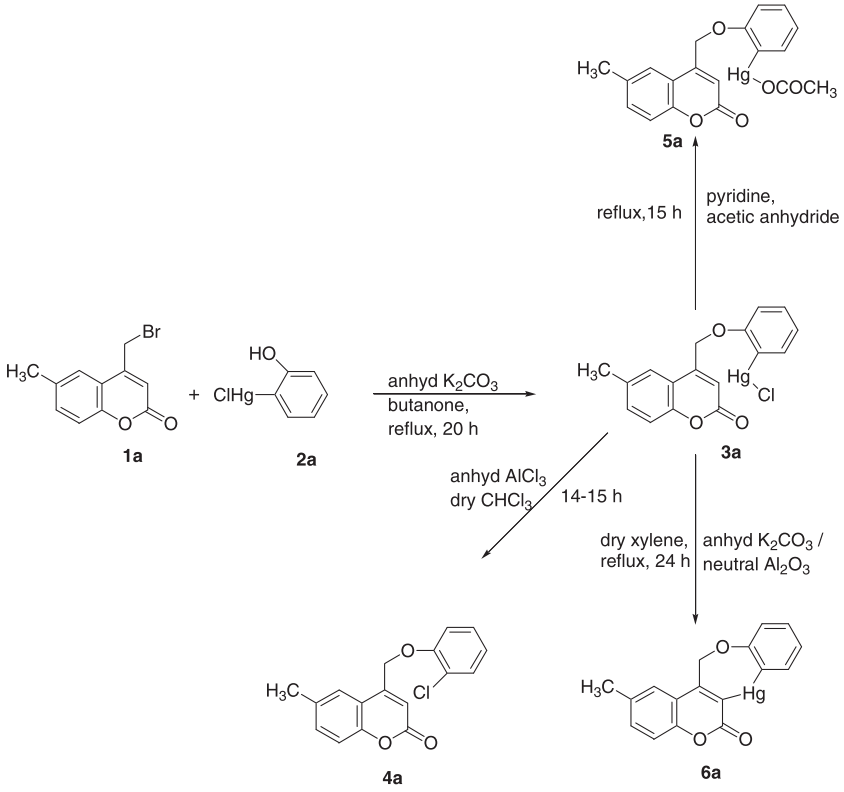
*2.1.2.11. 5H,13H-12-Oxa-5-aza-7-mercura-benzo[4,5]cyclohepta[1,2-a]naphthalene-6-one (**9a**).* Yield: 0.48 g (76%). FT-IR (KBr, cm^{-1}) 1650. ^{1}H NMR (300 MHz, DMSO) δ: 11.79 (s, 1H, NH), 7.88–7.06 (m, 8H), 4.08 (s, 2H, CH_2O). ^{13}C NMR (75 MHz, DMSO) δ: 152.32, 151.16, 137.26, 131.12, 130.42, 127.45, 126.82, 125.36, 119.23, 118.95, 117.45, 112.86, 112.26, 111.26, 110.26, 57.36. MS (ESI+) *m/z* = 450.8. *Anal.* Calc. for $C_{16}H_{11}HgNO_2$: C, 42.72; H, 2.46; N, 3.11. Found: C, 42.73; H, 2.42; N, 3.15%.

*2.1.2.12. 2-Chloro-5H,13H-12-Oxa-5-aza-7-mercura-benzo[4,5]cyclo-hepta[1,2-a]naphthalene-6-one (**9b**).* Yield: 0.39 g (60%). FT-IR (KBr, cm^{-1}) 1652. ^{1}H NMR (300 MHz, DMSO) δ: 11.82 (s, 1H, NH), 7.86–7.04 (m, 7H), 4.07 (s, 2H, CH_2O). ^{13}C NMR (75 MHz, DMSO) δ: 153.74, 152.22, 149.22, 130.86, 130.22, 125.22, 125.02, 122.86, 120.24, 119.32, 117.26, 116.62, 115.24, 111.14, 109.00, 57.24. MS

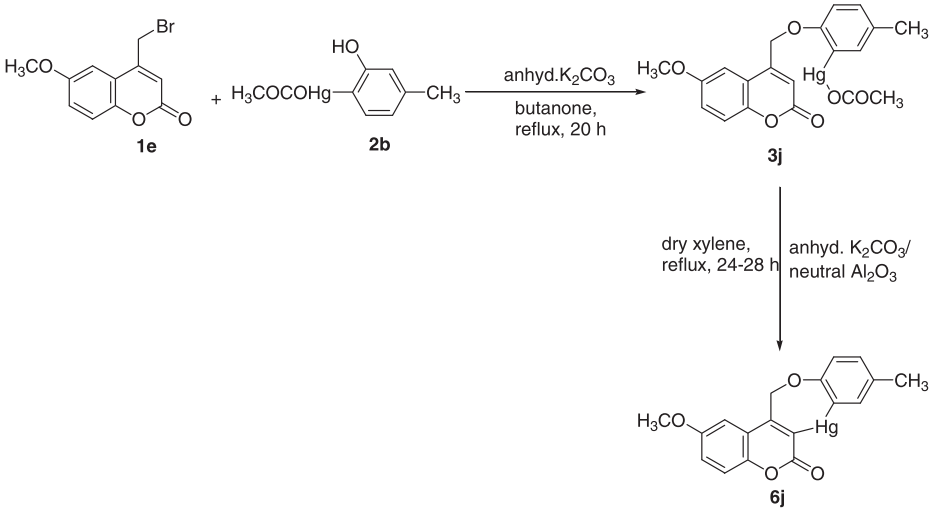
(ESI+) m/z = 485.3. *Anal.* Calc. for $C_{16}H_{10}ClHgNO_2$: C, 39.68; H, 2.08; N, 2.89. Found: C, 39.64; H, 2.10; N, 2.83%.

3. Results and discussion

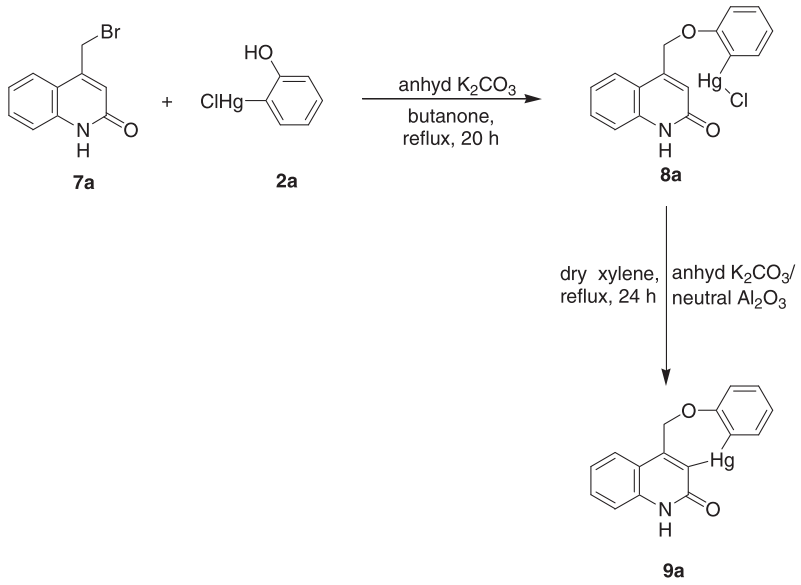
Initially the reaction of 6-methyl-4-bromomethylcoumarin [15] **1a** with *o*-chloro mercury phenol [16] **2a** in butanone was carried out at reflux temperature to obtain 2-*o*-chloromercurated 4-aryloxymethylcoumarin **3a** by the allylic nucleophilic displacement. The formation of intermediate **3a** was supported by the appearance of $-CH_2$ protons at 5.27 ppm, C_3–H at 6.67 ppm which is characteristic of 4-aryloxymethylcoumarins [17]. The ESI mass spectrum exhibited a peak at m/z 502. The carbon mercury bond formation, envisaged in terms of an intramolecular Friedel–Crafts reaction lead to chlorodemercuration resulting in the formation of 4-*o*-chlorophenoxymethylcoumarins **4a** which was identical with compound obtained by the reaction of **1a** with *o*-chlorophenol according to our earlier work [17]. Use of pyridine and acetic anhydride resulted in acetoxy mercurated compound **5a** (Scheme 1). Literature survey revealed that basic alumina has been employed to form carbon mercury bond at the alpha position in *p*-benzoquinones [18]. Due to the vulnerability of coumarins under basic conditions especially at higher temperatures we thought of



Scheme 1. Synthesis of 2-methyl-13H-5,12-dioxa-7-mercura-benzo[4,5]cyclohepta[1,2-a]naphthalene 6-one (**6a**).



Scheme 2. Synthesis of 2-methoxy-9-methyl-13H-5,12-dioxa-7-mercura-benzo[4,5]cyclohepta[1,2-a]naphthalene-6-one (**6j**).



Scheme 3. Synthesis of 5H,13H-12-oxa-5-aza-7-mercura-benzo[4,5]cyclohepta[1,2-a]naphthalene-6-one (**9a**).

using neutral alumina impregnated with anhydrous potassium carbonate in xylene and the reaction occurred only under reflux conditions. Under these conditions 2-*o*-chloromercurated 4-aryloxymethylcoumarin **3a** yielded the cyclized compound **6a** which exhibited significant changes in its spectral features. The lactone carbonyl exhibited lower stretching frequency at 1685 cm^{-1}. The ^{1}H NMR spectrum, apart from showing the absence of C_3–H, indicated an unusual up field shift of the CH_2 protons which appeared at 3.42 ppm and were clearly identified by protonation (DMSO + TFA) when they appeared at 4.08. ^{13}C NMR shift of the CH_2 carbons in the ether **3a** and **6a** were observed at 67.03 ppm and 57.07 ppm, respectively.

To determine the effect of groups on mercury on this two step sequence, *o*-acetoxy mercurated *p*-cresol **2b** was reacted with **1e** to obtain the intermediate ether **3j** which also underwent smooth intramolecular cyclization under the aforementioned experimental conditions (Scheme 2) which indicated the robustness of this reaction to different leaving groups on *o*-mercurated phenols.

Further, this reaction was also tried with the 4-bromomethyl-1-azacoumarin, **7a**. A comparison of the spectral properties of the intermediate ether **8a** and the cyclized compound **9a** (Scheme 3) indicated that the lactam carbonyl in the ether was observed at 1673 cm^{-1} whereas in the cyclized product it exhibited a band at 1650 cm^{-1}. The NMR and mass spectral data were in agreement with the structure and confirmed the above-mentioned data observed with coumarins. All the cyclized compounds were quite stable under atmospheric conditions.

Acknowledgments

N.B. Yaragatti is grateful to UGC (New Delhi) for the financial assistance in the form of Research Fellowship in Science for Meritorious Students. We thank University Scientific Instrumentation Center (USIC), Karnatak University Dharwad, Indian Institute of Science Bangalore for the spectral analysis.

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