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Cationic and Mesoionic 1,3-Thiazolo-[3,2-c]quinazoline Derivatives

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ABSTRACT: *4-Allylthio-2-arylquinazolines* **4a–c** *undergo cyclization by action of bromine to furnish 5-aryl-3-bromomethyl-2,3-dihydrothiazolo[3,2-c]quinazolin-4-ium bromides* **5a–c**. *Compounds* **5a–c** *undergo ring opening by action of water under acid catalysis to afford the corresponding dibromide derivatives* **6a–c**. *Bromination of 3-allyl-2-aryl-4(3H)quinazolinethiones* **7a–c** *leads to 5-aryl-2-bromomethyl-2,3-dihydrothiazolo[3,2-c]quinazolin-4-ium bromides* **8a–c**. *However, anhydro-3-hydroxy-5-aryl-1,3-thiazolo[3,2-c]quinazolin-4-ium hydroxide* **10a–c** *were prepared by the cyclodehydration of the corresponding thioglycolic acids* **9a–c** *with* Ac_2O. © 2003 Wiley Periodicals, Inc. Heteroatom Chem 14:576–580, 2003; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10148

INTRODUCTION

We previously reported [1] the synthesis of bridgehead nitrogen heterocycles of neutral character which contain the quinazoline moiety, e.g., 3-oxo-2*H*-imidazo[1,2-c]- and 4-oxo-2*H*,3*H*-pyrimido-[1,2-c]quinazolines. In this context we wish to communicate here the synthesis of some new cationic or mesoionic annelated derivatives of the thiazolo[3,2-c]quinazoline ring system based on quinazoline-4(3*H*)-thione. In continuation of our studies on thione ⇌ thiol tautomeric equilibria in heterocyclic diazines namely, quinazoline-4(3*H*)-thione [1] and pyrimidine-2(1*H*)-thione [2], we have now investigated the behavior of the quinazoline-4(3*H*)-thione derivatives **3a–c** towards unsaturated alkylating reagents in different reaction conditions. Unsaturated S- and N-alkyl derivatives were aimed for the synthesis of the title compounds.

Three representative members of quinazoline-4(3*H*)-thiones [3] **3** (R = benzyl, 2-chlorophenyl, 2-naphthyl) were selected for the present investigation and these were conveniently prepared by heating of the corresponding 4*H*-3,1-benzothiazine-4-thiones [4] **2**, readily available from direct thiation of 3,1-benzoxazin-4-one derivatives [5] **1**, with formamide at 150°C. We now report the synthesis of otherwise not available cationic derivatives of the thiazolo[3,2-c]quinazoline ring system. It has been briefly mentioned [6,7], that thiazolo[3,2-c]quinazolinum cations are intermediates in the preparation of 2-(*o*-aminophenyl)thiazoles from 2-(4-quinazolinylthio)acetophenones and perchloric acid or phosphoryl chloride.

The rational approach to thiazolo[3,2-c]quinazolinium cations is based on the cyclization of S- and N-allyl derivatives **4a–c** and **7a–c** of quinazoline-4(3*H*)-thiones **3a–c**. In this type of compounds the allylic side-chain can provide a secondary carbonium ion appropriately placed for attack of N-3 or exocyclic S to form the thiazole ring.

As alkylation in heterocyclic thioureas with an exocyclic thio function proceeds at the sulfur atom, 4-allylthioquinazolines **4a–c** are obtained in excellent yields from 2-benzyl-, 2-(2-chlorophenyl)-, or 2-(2-naphthyl)-4(3*H*)-quinazolinethiones (**3a–c**) and allyl bromide in the presence of triethylamine. Compounds **4a–c** undergo ring closure by action of bromine in glacial acetic acid at room temperature to furnish the corresponding 3-bromomethyl-2,

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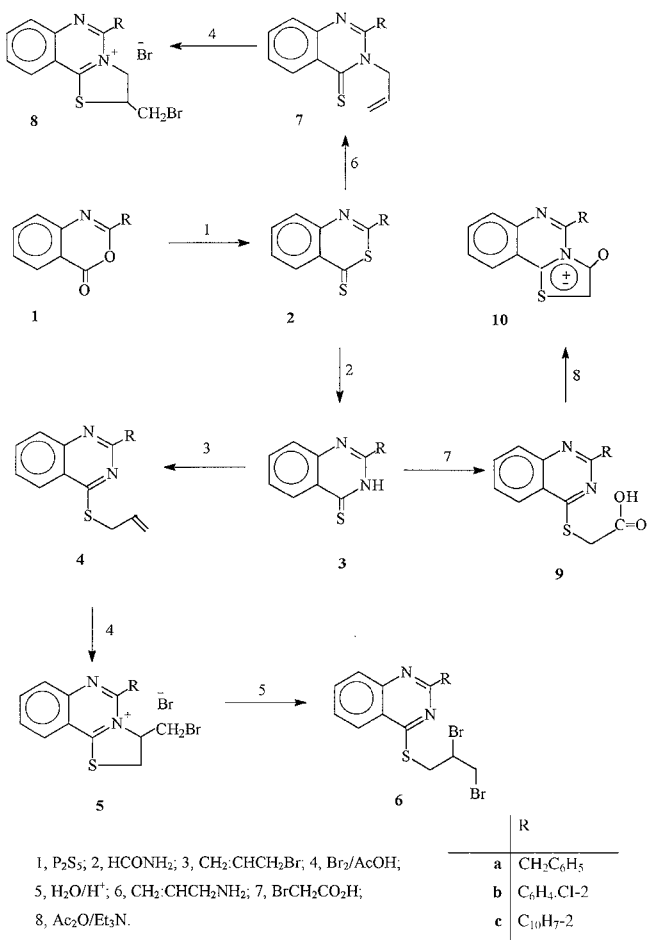
3-dihydrothiazolo-[3,2-c]quinazolin-4-ium bromide **5a–c** in good yield.

Compounds **5a–c** undergo ring opening of the thiazole moiety by action of water under acid catalysis to furnish the corresponding (2,3-dibromopropyl)thioquinazolines **6a–c** in moderate yields. Attempts to prepare the N-allyl derivatives **7a–c** by direct allylation of quinazoline-4(3*H*)-thiones **3a–c** is impeded by the preferential reactivity of the sulfur atom. In consequence of that, the regioisomers of **4a–c**, 3-allyl-4(3*H*)-quinazolinethiones **7a–c** have been prepared in good yields by the reaction of the 4*H*-3,1-benzothiazine-4-thiones **2a–c** with allylamine. In agreement with the reported results [8], bromination of **7a–c** in acetic acid solution at room temperature gave 2-bromomethyl-2,3-dihydrothiazolo[3,2-c]-quinazolin-4-ium bromides **8a–c** in good yields.

A variety of monocyclic mesoionic compounds are known [9], but derivatives containing fused mesoionic rings are less common, especially those with the second ring heteroaromatic [10]. The author has now attempted to synthesize some of fused-ring mesoionic systems based on 4(3*H*)-quinzolinethiones. The condensation of 4(3*H*)-quinazolinethiones **3a–c** with bromoacetic acid under basic condition readily gave the corresponding carboxymethylthio derivatives **9a–c**, in fair yields, and these were smoothly converted into the corresponding mesoionic 1,3-thiazolo[3,2-c]-4-quinazolinium-3-ones **10a–c** by treatment with acetic anhydride in the presence or absence of Et_3N.

The structural assignments of all the compounds (Scheme 1) were based on elemental analyses and characteristic IR and ^{1}H NMR spectral data.



SCHEME 1

EXPERIMENTAL

Melting points were taken in open capillary tubes and were uncorrected. IR spectra in KBr were recorded on a shimadzu 470 spectrophotometer and ^{1}H NMR spectra were recorded on a JOEL Fx 90 Q9 spectrometer using TMS as an internal reference. Mass spectra were recorded on an HP Model MS 5988 spectrometer.

*2-Benzyl-, 2-Chlorophenyl-, or 2-Naphthyl-4H-3, 1-benzothiazine-4-thione (**2a–c**)*

These were prepared from **1a–c** (0.07 mol) and phosphorus pentasulphide (0.14 mol) according to literature [4]. Recrystallization from benzene furnished **2a–c**.

2a: Yield 5.6 g (30%), mp 147–149°C (lit. [4] 148°C); IR (cm^{-1}): 2910 (alkyl-H), 1620 (C=N), 1325 (C=S). Found: C, 66.92; H, 4.38; N, 5.42%. Calcd for $C_{15}H_{11}NS_2$: C, 66.88; H, 4.12; N, 5.20%.

2b: Yield 8.7 g (43%), mp 144–146°C (lit. [4] 145°C); IR (cm^{-1}): 1615 (C=N), 1310 (C=S). Found: C, 58.30; H, 2.82; N, 4.91%. Calcd for $C_{14}H_8ClNS_2$: C, 58.02; H, 2.78; N, 4.83%.

2c: Yield 10.6 g (50%), mp 155–157°C (lit. [4] 157°C); IR (cm^{-1}): 1610 (C=N), 1295 (C=S). Found: C, 70.84; H, 3.82; N, 4.62%. Calcd for $C_{18}H_{11}NS_2$: C, 70.79; H, 3.63; N, 4.59%.

*2-Benzyl-, 2-Chlorophenyl-, or 2-Naphthyl-4(3H)-quinazolinethione (**3a–c**)*

A mixture of **2a–c** (0.024 mol) and formamide (1.2 ml, 0.03 mol) was heated in an oil bath at 150°C for 4 h. The resulting solid product was cooled and crystallized from ethanol to furnish **3a–c**.

3a: Yield 3.6 g (59%), mp 220–222°C (lit. [3] 221°C); IR (cm^{-1}): 3300–3240 (NH), 2960 (alkyl-H), 2560 (SH), 1625 (C=C), 1260 (C=S); ^{1}H NMR

($CDCl_3$): δ = 3.36 (s, 2H, CH_2Ph), 7.11–8.74 (m, 9H, Ar H and quinazoline ring), 9.52 (s, 1H, NHC=S, ratio 55.8), 11.14 (s, 1H, SH, ratio 44.2). Found: C, 71.48; H, 4.82; N, 11.22%. Calcd for $C_{15}H_{12}N_2S$: C, 71.40; H, 4.79; N, 11.10%.

3b: Yield 3.7 g (57%), mp 204–206°C (lit. [3] 206°C); IR (cm^{-1}): 3340–3210 (NH), 2550 (SH), 1615 (C=C), 1255 (C=S). Found: C, 61.71; H, 3.39; N, 10.20%. Calcd for $C_{14}H_9ClN_2S$: C, 61.65; H, 3.33; N, 10.27%.

3c: Yield 3.8 g (55%), mp 219–220°C (lit. [3] 219.5°C); IR (cm^{-1}): 3280–3170 (NH), 2570 (SH), 1618 (C=C), 1250 (C=S). Found: C, 74.87; H, 4.22; N, 9.94%. Calcd for $C_{18}H_{12}N_2S$: C, 74.97; H, 4.19; N, 9.71%.

*4-Allylthio-2-benzyl-, 2-(2-Chlorophenyl)-, or 2-(2-Naphthyl)quinazoline (**4a–c**)*

To a solution of the appropriate thione **3a–c** (8 mmol) in benzene (50 ml), triethylamine (1.2 ml, 8.6 mmol) and allyl bromide (0.7 ml, 8.3 mmol) were added; after 4 h of heating under reflux, triethylammonium bromide was deposited. After cooling, the salt was separated by filtration and the filterate concentrated to dryness to afford a crude product which recrystallized from ethanol to give **4a–c**.

4a: Yield 2.1 g (90%), mp 71–73°C, yellow needles; IR (cm^{-1}): 2920, 1539, 1480, 1447, 1340, 1313, 990, 927, 860, 770, 765; ^1H NMR ($CDCl_3$): δ = 3.32 (s, 2H, CH_2Ph), 4.10 (d, 2H, J = 7.1 Hz, SCH_2), 5.18–5.74 (m, 2H, $CH=CH_2$), 5.90–6.55 (m, 1H, $CH=CH_2$), 7.28–8.60 (m, 9H, Ar H); MS (70 eV): m/z (%) = 293 ($M^+ + 1$) (18), 292 (M^+) (38), 291 (100). Found: C, 73.81; H, 5.34; N, 9.62%. Calcd for $C_{18}H_{16}N_2S$: C, 73.94; H, 5.52; N, 9.58%.

4b: Yield 2.2 g (88%), mp 64–66°C, yellow needles; IR (cm^{-1}): 1590, 1584, 1475, 1360, 1340, 1200, 1080, 1019, 960, 817, 760, 710; ^1H NMR ($CDCl_3$): δ = 4.22 (d, 2H, J = 7.1 Hz, SCH_2), 5.10–5.66 (m, 2H, $CH=CH_2$), 5.80–6.44 (m, 1H, $CH=CH_2$), 7.42–8.34 (m, 8H, Ar H); MS (70 eV): m/z (%) = 314 ($M^+ + 2$) (17), 313 (40), 312 (M^+) (36), 311 (100). Found: C, 65.20; H, 4.24; N, 8.88%. Calcd for $C_{17}H_{13}ClN_2S$: C, 65.27; H, 4.19; N, 8.96%.

4c: Yield 2.3 g (87%), mp 85–87°C, yellow needles; IR (cm^{-1}): 1620, 1558, 1530, 1480, 1382, 1300, 1250, 1107, 990, 907, 830, 790, 755; ^1H NMR ($CDCl_3$): δ = 4.20 (d, 2H, J = 7.1 Hz, SCH_2), 5.12–5.62 (m, 2H, $CH=CH_2$), 5.92–6.66 (m, 1H, $CH=CH_2$), 7.44–8.42 (m, 11H, Ar H); MS (70 eV): m/z (%) = 329 ($M^+ + 1$) (11), 328 (M^+) (36), 327 (100). Found: C, 76.74; H, 4.68; N, 8.64%. Calcd for $C_{21}H_{16}N_2S$: C, 76.80; H, 4.91; N, 8.53%.

*3-Bromomethyl-5-benzyl-, 5-(2-Chlorophenyl)-, or 5-(2-Naphthyl)-2,3-dihydrothiazolo[3,2-c]-quinazolin-4-ium bromide (**5a–c**)*

A solution of bromine (1 g, 6.3 mmol) in acetic acid (20 ml) was added dropwise to a well-stirred solution of the appropriate quinazoline **4a–c** (6 mmol) in the same solvent (20 ml) at room temperature. When the addition was completed, the yellow precipitate which gradually separated during the reaction, was filtered off, washed several times with diethyl ether and crystallized from ethanol to furnish **5a–c**.

5a: Yield 1.7 g (64%), mp 192–194°C, colorless needles; IR (cm^{-1}): 2940, 1610, 1590, 1576, 1559, 1489, 1425, 1400, 1342, 1290, 1170, 1050, 960, 886, 850, 718, 660; ^1H NMR ($CDCl_3 + CF_3CO_2H$): δ = 3.25–3.65 (m, with interference, 4H, CH_2Br and CH_2Ph), 4.04–4.84 (m, 2H, SCH_2), 6.25–6.85 (m, 1H, $CHCH_2Br$), 7.40–8.50 (m, 9H, Ar H); MS (70 eV): m/z (%) = 373 ($M^+ + 2$) (6), 371 (M^+) (8), 219 (100). Found: C, 47.94; H, 3.67; N, 6.28%. Calcd for $C_{18}H_{16}Br_2N_2S$: C, 47.81; H, 3.57; N, 6.19%.

5b: Yield 1.7 g (62%), mp 176–178°C, yellow needles; IR (cm^{-1}): 2935, 1610, 1590, 1560, 1500, 1440, 1400, 1309, 1290, 1140, 1082, 1012, 950, 880, 760, 685; ^1H NMR ($CDCl_3 + CF_3CO_2H$): δ = 3.35–3.68 (m, 2H, CH_2Br), 3.95–5.04 (m, 2H, SCH_2), 6.40–6.90 (m, 1H, $CHCH_2Br$), 7.28–8.45 (m, 8H, Ar H); MS (70 eV): m/z (%) = 393 ($M^+ + 2$) (4), 391 (M^+) (5), 239 (100). Found: C, 43.42; H, 2.88; N, 5.66%. Calcd for $C_{17}H_{13}Br_2ClN_2S$: C, 43.20; H, 2.77; N, 5.93%.

5c: Yield 1.7 g (60%), mp 223–225°C, yellow needles; IR (cm^{-1}): 2960, 1625, 1560, 1546, 1480, 1410, 1370, 1340, 1248, 1170, 1040, 990, 830, 790, 730, 625; ^1H NMR ($CDCl_3 + CF_3CO_2H$): δ = 3.32–3.70 (m, 2H, CH_2Br), 3.90–4.89 (m, 2H, SCH_2), 6.30–6.78 (m, 1H, $CHCH_2Br$), 7.22–8.32 (m, 11H, Ar H); MS (70 eV): m/z (%) = 409 ($M^+ + 2$) (8), 407 (M^+) (5), 255 (100). Found: C, 51.94; H, 3.60; N, 5.88%. Calcd for $C_{21}H_{16}Br_2N_2S$: C, 51.66; H, 3.30; N, 5.74%.

*2-Benzyl-, 2-(2-Chlorophenyl)-, or 2-(2-Naphthyl)-4-[(2,3-dibromopropyl)thio]quinazoline (**6a–c**)*

A solution of the appropriate bromide **5a–c** (2.5 mmol) in acetic acid/water (60 ml, 2:1, v/v) was stirred at room temperature for 6 h. The solution was poured into ice and the resultant precipitated solid was filtered, washed with water, and recrystallized from acetone to give **6a–c**.

6a: Yield 0.47 g (42%), mp 114–116°C, colorless needles; IR (cm^{-1}): 2950, 1618, 1558, 1544, 1480, 1442, 1344, 1318, 1255, 1190, 1030, 994, 860, 840, 772, 658; ^1H NMR ($CDCl_3$): δ = 3.34 (s, 2H,

CH_2Ph), 3.75–4.45 (m, 4H, $CH_2CHBrCH_2Br$), 4.58–5.12 (m, 1H, CHBr), 7.35–8.65 (m, 9H, Ar H); MS (70 eV): *m/z* (%) = 452 ($M^+ + 2$) (7), 450 (M^+) (4), 219 (100). Found: C, 47.94; H, 3.78; N, 6.49%. Calcd for $C_{18}H_{16}Br_2N_2S$: C, 47.81; H, 3.57; N, 6.19%.

6b: Yield 0.47 g (40%), mp 128–130°C, colorless needles; IR (cm^{-1}): 2935, 1618, 1585, 1565, 1542, 1530, 1450, 1401, 1342, 1318, 1250, 1170, 1082, 1030, 871, 792, 735, 700; ^1H NMR ($CDCl_3$): δ = 3.82–4.28 (m, 4H, $CH_2CHBrCH_2Br$), 4.45–4.95 (m, 1H, CHBr), 7.27–8.54 (m, 8H, Ar H); MS (70 eV): *m/z* (%) = 474 ($M^+ + 4$) (4), 472 ($M^+ + 2$) (8), 470 (M^+) (5), 239 (100). Found: C, 43.42; H, 2.93; N, 5.79%. Calcd for $C_{17}H_{13}Br_2ClN_2S$: C, 43.20; H, 2.77; N, 5.93%.

6c: Yield 0.53 g (44%), mp 134–136°C, colorless needles; IR (cm^{-1}): 2970, 1625, 1560, 1540, 1501, 1456, 1349, 1262, 1160, 1020, 840, 780, 718, 685; ^1H NMR ($CDCl_3$): δ = 3.66–4.37 (m, 4H, $CH_2CHBrCH_2Br$), 4.45–4.82 (m, 1H, CHBr), 7.39–8.66 (m, 11H, Ar H); MS (70 eV): *m/z* (%) = 488 ($M^+ + 2$) (10), 486 (M^+) (7), 255 (100). Found: C, 51.88; H, 3.60; N, 5.89%. Calcd for $C_{21}H_{16}Br_2N_2S$: C, 51.66; H, 3.30; N, 5.74%.

*3-Allyl-2-benzyl-, 2-(2-Chlorophenyl)-, or 2-(2-Naphthyl)-4(3H)-quinazolinethione (**7a–c**)*

To a suspension of the appropriate 1,3-benzothiazine-4(*H*)-thione **2a–c** (8 mmol) in ethanol (50 ml), allylamine (0.7 ml, 9.4 mmol) was added. The reaction mixture was refluxed for 2 h. After cooling at 0°C, the yellow precipitated solid was collected by filtration and the crude product recrystallized from ethanol to give **7a–c**.

7a: Yield 1.8 g (77%), mp 110–112°C, yellow needles; IR (cm^{-1}): 2965, 1575, 1520, 1470, 1350, 1330, 1210, 940, 910, 850, 760, 650; ^1H NMR ($CDCl_3$): δ = 3.38 (s, 2H, CH_2Ph), 4.70–5.60 (m, 4H, $CH_2{-}CH{=}CH_2$), 5.90–6.50 (m, 1H, $CH{=}CH_2$), 7.18–8.22 (m, 9H, Ar H); MS (70 eV): *m/z* (%) = 292 (M^+) (25), 219 (100). Found: C, 73.80; H, 5.58; N, 9.46%. Calcd for $C_{18}H_{16}N_2S$: C, 73.94; H, 5.52; N, 9.58%.

7b: Yield 2 g (80%), mp 115–117°C, yellow needles; IR (cm^{-1}): 1620, 1560, 1540, 1480, 1420, 1338, 1080, 1000, 990, 880, 790, 730, 690; ^1H NMR ($CDCl_3$): δ = 4.72–5.58 (m, 4H, $CH_2{-}CH{=}CH_2$), 5.75–6.45 (m, 1H, $CH{=}CH_2$), 7.25–8.18 (m, 8H, Ar H); MS (70 eV): *m/z* (%) = 314 ($M^+ + 2$) (14), 313 (22), 312 (M^+) (40), 297 (100). Found: C, 65.27; H, 4.25; N, 8.84%. Calcd for $C_{17}H_{13}ClN_2S$: C, 65.27; H, 4.19; N, 8.96%.

7c: Yield 2 g (77%), mp 127–129°C, yellow needles; IR (cm^{-1}): 1618, 1570, 1557, 1470, 1365, 1342, 1210, 1118, 1030, 950, 912, 810, 762, 724, 620; ^1H NMR ($CDCl_3$): δ = 4.75–5.52 (m, 4H, $CH_2{-}CH{=}CH_2$), 5.70–6.50 (m, 1H, $CH{=}CH_2$), 7.30–8.10 (m, 11H, Ar H); MS (70 eV): *m/z* (%) = 329 ($M^+ + 1$) (12), 328 (M^+) (41), 327 (100). Found: C, 76.77; H, 4.67; N, 8.66%. Calcd for $C_{21}H_{16}N_2S$: C, 76.80; H, 4.91; N, 8.53%.

*2-Bromomethyl-5-benzyl-, 5-(2-Chlorophenyl)-, or 5-(2-Naphthyl)-2,3-dihydrothiazolo[3,2-c]-quinazolin-4-ium bromide (**8a–c**)*

A solution of bromine (0.9 g, 5.6 mmol) in acetic acid (15 ml) was added dropwise to a well-stirred solution of the appropriate thione **7a–c** (5 mmol) in the same solvent (25 ml) at room temperature. The reaction mixture was stirred at room temperature for 3 h and the yellow solid which gradually separated during the reaction was collected by filtration, washed with water, and recrystallized from methanol to give **8a–c**.

8a: Yield 1.5 g (67%), mp 238–240°C, colorless needles; IR (cm^{-1}): 2954, 1618, 1590, 1560, 1480, 1350, 1300, 1245, 1029, 966, 825, 788, 727, 628; ^1H NMR ($CDCl_3 + CF_3CO_2H$): δ = 3.36 (s, 2H, CH_2Ph), 3.68–4.18 (m, 2H, CH_2Br), 4.95–5.70 (m, 3H, $=N^+{-}CH_2{-}CH$), 7.38–8.54 (m, 9H, Ar H); MS (70 eV): *m/z* (%) = 373 ($M^+ + 2$) (6), 371 (M^+) (7), 219 (100). Found: C, 47.90; H, 3.68; N, 6.25%. Calcd for $C_{18}H_{16}Br_2N_2S$: C, 47.81; H, 3.57; N, 6.19%.

8b: Yield 1.48 g (63%), mp 281–283°C, colorless needles; IR (cm^{-1}): 2940, 1625, 1590, 1560, 1480, 1405, 1345, 1305, 1094, 1025, 826, 770, 728, 709; ^1H NMR ($CDCl_3 + CF_3CO_2H$): δ = 3.78–4.26 (m, 2H, CH_2Br), 5.14–5.77 (m, 3H, $=N^+{-}CH_2{-}CH$), 7.40–8.56 (m, 8H, Ar H); MS (70 eV): *m/z* (%) = 393 ($M^+ + 2$) (8), 391 (M^+) (4), 239 (100). Found: C, 43.47; H, 2.84; N, 5.69%. Calcd for $C_{17}H_{13}Br_2ClN_2S$: C, 43.20; H, 2.77; N, 5.93%.

8c: Yield 1.58 g (65%), mp 225–227°C, colorless needles; IR (cm^{-1}): 2928, 1615, 1557, 1522, 1478, 1404, 1346, 1255, 1178, 1020, 960, 842, 775, 740, 620; ^1H NMR ($CDCl_3 + CF_3CO_2H$): δ = 3.75–4.15 (m, 2H, CH_2Br), 4.90–5.80 (m, 3H, $=N^+{-}CH_2{-}CH$), 7.43–8.70 (m, 11H, Ar H); MS (70 eV): *m/z* (%) = 409 ($M^+ + 2$) (6), 407 (M^+) (7), 255 (100). Found: C, 51.90; H, 3.62; N, 5.84%. Calcd for $C_{21}H_{16}Br_2N_2S$: C, 51.66; H, 3.30; N, 5.74%.

*4-Carboxymethylthio-2-benzyl-, 2-(2-Chlorophenyl)-, or 2-(2-Naphthyl)quinazoline (**9a–c**)*

Thiones **3a–c** (4.5 mmol) and bromoacetic acid (0.63 g, 4.5 mmol) in anhydrous benzene (50 ml) were treated with Et_3N (0.64 ml, 4.6 mmol) and stirred overnight at room temperature. The solution was filtered to remove all $Et_3N{\cdot}HBr$, and the benzene was evaporated in vacuo. The products **9a–c** were finally

obtained as small yellow needles by recrystallization from ethanol.

9a: Yield 1 g (72%), mp 176–178°C; IR (cm^{-1}) (br) 3500–3400, 1710, 1620, 1542, 1464, 1420, 1320, 1090, 980, 920, 845, 770, 690; ^{1}H NMR (Me_2SO-d_6): δ = 3.41 (s, 2H, CH_2Ph), 4.46 (s, 2H, SCH_2CO), 7.40–8.55 (m, 9H, Ar H); MS (70 eV): *m/z* (%) = 310 (M^+) (18), 266 (22), 219 (100). Found: C, 65.55; H, 4.29; N, 9.22%. Calcd for $C_{17}H_{14}N_2O_2S$: C, 65.79; H, 4.55; N, 9.03%.

9b: Yield 1 g (70%), mp 161–163°C; IR (cm^{-1}) (br) 3540–3425, 1715, 1618, 1590, 1572, 1470, 1365, 1320, 1210, 1180, 1002, 980, 828, 750, 680; ^{1}H NMR (Me_2SO-d_6): δ = 4.37 (s, 2H, SCH_2CO), 7.35–8.62 (m, 8H, Ar H); MS (70 eV): *m/z* (%) = 330 (M^+) (22), 286 (42), 239 (100). Found: C, 58.33; H, 3.53; N, 8.62%. Calcd for $C_{16}H_{11}ClN_2O_2S$: C, 58.10; H, 3.35; N, 8.47%.

9c: Yield 1 g (68%), mp 182–184°C; IR (cm^{-1}) (br) 3560–3414, 1705, 1628, 1590, 1530, 1490, 1381, 1310, 1270, 1100, 982, 910, 840, 780, 750, 690; ^{1}H NMR (Me_2SO-d_6): δ = 4.40 (s, 2H, CH_2), 7.28–8.48 (m, 11H, Ar H); MS (70 eV): *m/z* (%) = 346 (M^+) (25), 302 (19), 255 (100). Found: C, 69.44; H, 4.32; N, 8.22%. Calcd for $C_{20}H_{14}N_2O_2S$: C, 69.35; H, 4.10; N, 8.10%.

*Anhydro-3-hydroxy-5-benzyl-, 5-(2-Chlorophenyl)-, or 5-(2-Naphthyl)-1,3-thiazolo[3,2-c]quinazolin-4-ium Hydroxide (**10a–c**)*

The thioglycolic acids **9a–c** (2 mmol) were added to a mixture of Ac_2O (3 ml) and Et_3N (3 ml). After the mixture was stirred for 15 min, anhydrous ether was added (20 ml). The dark-red solids of **10a–c** recrystallized from chloroform/cyclohexane, giving dark-red needles.

10a: Yield 0.38 g (65%), mp 286–288°C; IR (cm^{-1}): 1648s (polarized CO), 1620, 1602, 1562, 1545, 1489, 1420, 1347, 1338, 1310, 1245, 1170, 1040, 990, 835, 791, 730, 622; ^{1}H NMR (Me_2SO-d_6): δ = 3.51 (s, 2H, CH_2Ph), 7.30–8.66 (m, 10H, Ar H); MS (70 eV): *m/z* (%) = 292 (M^+) (22), 219 (100). Found: C, 69.62; H, 4.22; N, 9.61%. Calcd for $C_{17}H_{12}N_2OS$: C, 69.84; H, 4.14; N, 9.58%.

10b: Yield 0.39 g (63%), mp 269–271°C; IR (cm^{-1}): 1654s (polarized CO), 1625, 1598, 1582, 1557, 1471, 1360, 1340, 1206, 1088, 1016, 961, 822, 769, 720; ^{1}H NMR (Me_2SO-d_6): δ = 7.22–8.64 (m, 9H, Ar H); MS (70 eV): *m/z* (%) = 314 ($M^+ + 2$) (6), 312 (M^+) (12), 239 (100). Found: C, 61.62; H, 2.82; N, 8.76%. Calcd for $C_{16}H_9ClN_2OS$: C, 61.44; H, 2.90; N, 8.96%.

10c: Yield 0.38 g (58%), mp 292–294°C; IR (cm^{-1}): 1659s (polarized CO), 1619, 1597, 1552, 1529, 1352, 1304, 1207, 1185, 1145, 991, 975, 835, 816, 769, 719, 645; ^{1}H NMR (Me_2SO-d_6): δ = 7.45–8.62 (m, 12H, Ar H); MS (70 eV): *m/z* (%) = 330 ($M^+ + 2$) (8), 328 (M^+) (14), 255 (100). Found: C, 73.30; H, 3.78; N, 8.64%. Calcd for $C_{20}H_{12}N_2OS$: C, 73.15; H, 3.68; N, 8.53%.

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