Synthesis of 1*H*-quinazoline-4-ones using intramolecular aromatic nucleophilic substitution

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Dedicated to Professor Roberto R. Rossi on his 60th birthday and Professor Edmundo A. Rúveda on his 70th birthday

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Abstract

The anions of 1-(2-bromobenzoyl)-3-phenylthiourea **1**, 1-(2-chlorobenzoyl)-3-phenylthiourea **2** and 1-(2-bromobenzoyl)-3-phenylurea **8** undergo intramolecular nucleophilic substitution (putative S_NAr mechanism), and not intramolecular $S_{RN}1$ substitution, to yield 1-phenyl-2-thioxo-2,3-dihydro-1*H*-quinazolin-4-one **6** and 1-phenyl-1*H*-quinazoline-2,4-dione **9** respectively. Under the same reaction conditions with the addition of copper(I) iodide, phenylthioureas **1** and **2** gave a rearrangement to the respective 2-halogeno-*N*-phenyl-benzamides.

Keywords: Intramolecular S_NAr, intramolecular $S_{RN}1$, 2-thioxo-2,3-dihydro-1*H*-quinazolin-4-ones, 1*H*-quinazoline-2,4-diones, Cu(I)-catalyzed rearrangement

Introduction

Aromatic $S_{RN}1$ substitutions have been extensively researched over the last twenty years and have become a useful synthetic protocol as well as a fascinating area of organic mechanism.[1] Surprisingly, intramolecular $S_{RN}1$ reactions are difficult to carry out and have not been widely used.[1-3] We have shown that benzothiazoles can be synthesized by intramolecular $S_{RN}1$ substitution but we were only able to initiate the single electron transfer chain (SET) reaction using the process on entrainment with enolate anions of acetone and diethyl phosphite.[2] Substitution of side chain anions onto *o*-halogenoarenes is a good synthetic procedure and we sought to extend our $S_{RN}1$ studies[2,4] to the synthesis of 1*H*-quinazolin-4-ones.

The synthesis of a range of 1*H*-quinazoline-4-ones is shown in Scheme 1. We quickly realized that the cyclizations were S_NAr reactions and not $S_{RN}1$ substitutions. $S_{RN}1$ substitutions

are formally aromatic nucleophilic substitutions but are able to take place on non-'activated' arenes because of activation by SET to yield intermediate radical anions which are able to dissociate under the reaction conditions. In contrast, S_NAr substitutions are not chain reactions and require strong electron withdrawing groups to lower the electron density on the arenes to facilitate attack by nucleophiles. The presence of the carbonyl in the *ortho*-position to the halogen in our precursors obviously lowers the electron density sufficiently to allow intramolecular S_NAr substitution. This facet of S_NAr reactions has not been widely identified in the literature[5,6] although we suspect that many examples have been studied but not mechanistically identified.

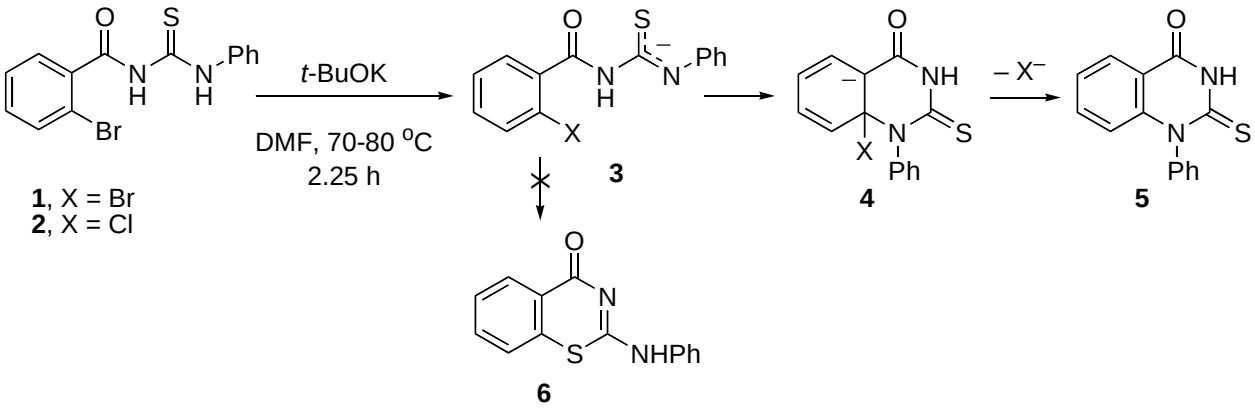
Our paper is a further example of taking care in not assuming $S_{RN}1$ mechanisms because the starting materials suggest that SET will be favourable. We have changed our initial mechanistic assignment in several studies.[4,7,8] For instance, the reaction between phenylthiolate anions and α-halogenonitroalkanes gives substitution to α-(phenylsulfanyl)nitroalkanes in dipolar aprotic solvent by an $S_{RN}1$ mechanism but switches to yielding disulfides in protic solvents by nucleophilic attack on the halide.[4,8] In a further example of apparent $S_{RN}1$ substitution, reactions between 2,6-diiodophenols and their phenolates anions to yield dityrosines, proceed by a non-SET nucleophilic substitution.[7] The diagnostic tests for the $S_{RN}1$ chain reaction are well worked out and should always be used to assign the $S_{RN}1$ mechanism.[1,2,4,7,8]

Results and Discussion

The *ortho*-carbonyl group in the precursors was used for simplicity of synthesis and to assist SET. Electron deficient arenes accept electrons more easily from nucleophiles in SET and the carbonyl group was an easy method of lowering arene electron density. Our earlier studies had used side chain thioamides and amides to generate the nucleophiles so we decided to do the same again. The starting materials, 1-(2-bromobenzoyl)-3-phenylthiourea 3-phenylureas **1**, 1-(2-chlorobenzoyl)-3-phenylthiourea 3-phenylureas **2** and 1-(2-bromobenzoyl)-3-phenylurea **7**, were prepared from the respective *o*-halogenobenzoic acids using literature procedures.[9,10] The starting materials were reacted under conditions shown to favour $S_{RN}1$,[2] *i.e.* potassium *tert*-butoxide (*t*-BuOK), DMF, heat and light catalysis. To our surprise, the nucleophilic substitution took place *via* the *N*-anion to yield 1-phenyl-2-thioxo-2,3-dihydro-1*H*-quinazolin-4-one **5** in high yield (100% crude, 29% purified) and not *via* the *S*-anion to yield the benzo[*e*]-[1,3]thiazin-4-one **6**.

The yield of **5** was not significantly altered using $S_{RN}1$ diagnostic tests. Carrying out the reaction in the dark (no light catalysis) gave an isolated yield of 29%. The use of *p*-dinitrobenzene as a strong electron acceptor to inhibit the SET step in the chain gave an isolated yield of 46%. Both reactions gave high yields of the crude product. The nature of the intermediate anion is unknown, either a mixture of mono-anions and/or the dianion. The most acidic proton is the 'imide' hydrogen but the anion must reside on the aniline-nitrogen (*i.e.* **3** as

shown in Scheme 1). A large excess of base was used (5 equiv.) and when the amount was cut to one equivalent, the yield dropped to 37% with unchanged starting material (29%). The dianion is unlikely to be the reactive species because the electron withdrawing effect of the carbonyl would be lost in the S_NAr reaction. When no base was used only starting material was recovered (80%) thereby eliminating the thiourea as the nucleophile. Light catalysis was not further used in the studies.

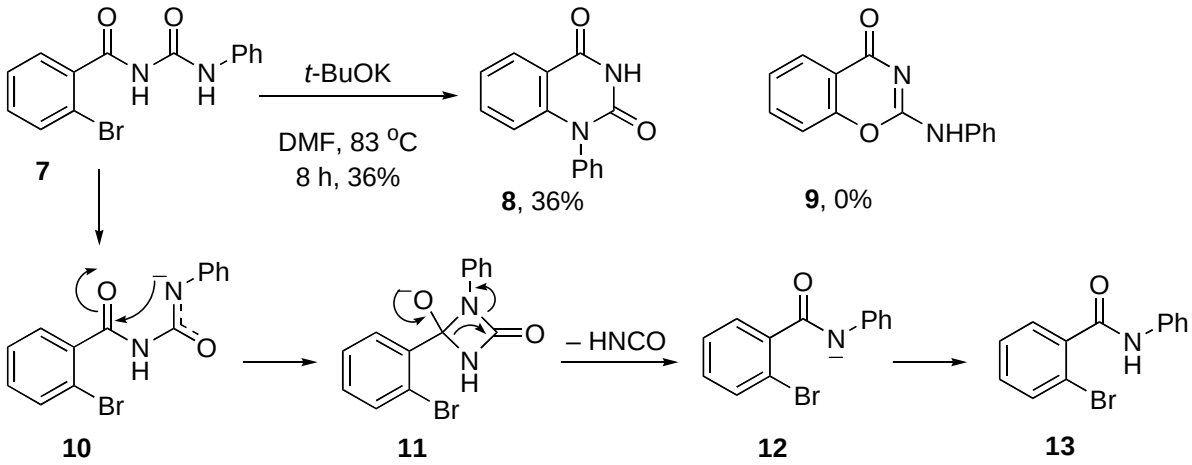


Scheme 1. Synthesis of the quinazolin-4-one **5** by a possible S_NAr mechanism.

A mechanism proceeding *via* a benzyne intermediate cannot be ruled out. Our earlier studies with the related compounds, *N*-(3-bromophenyl)-thiobenzamide and *N*-(3-chlorophenyl)-thiobenzamide, under the same reactions conditions only yielded unaltered starting material, whereas the corresponding 2-halogeno compounds yielded 2-phenylbenzothiazole by an $S_{RN}1$ mechanism.[2] This evidence ruled out benzyne intermediates for the latter reactions,[2] but does not necessarily rule out benzyne intermediates in the present study.

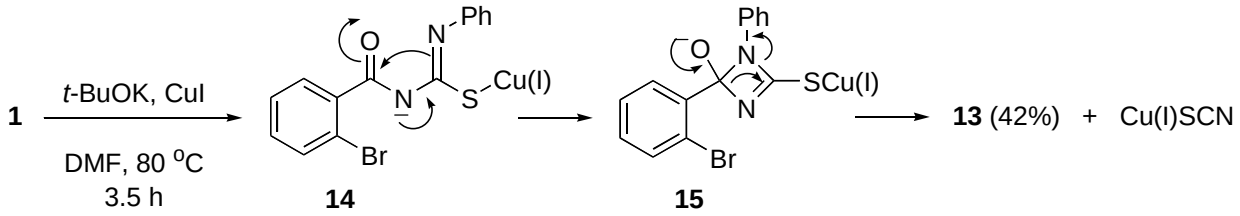
The nature of the leaving group is important in $S_{RN}1$ reactions because the lower the energy of the unpaired electron in the Ar-hal bond the faster the reaction (I > Br >> Cl >> F), *i.e.* very slow for X = Cl.[1,3] In contrast, the order for S_NAr is F >> Cl, Br, I. When the chloro starting material **2** was used the yield was also high with an isolated yield of **5** of 58%, *i.e.* not significantly lower. This result again strongly indicates a S_NAr mechanism. It is possible that a $S_{RN}1$ substitution is favourable for these precursors but that the S_NAr reaction is faster.

When 1-(2-bromobenzoyl)-3-phenylurea **7** was reacted under the same conditions, 1-phenyl-1*H*-quinazoline-2,4-dione **8** was formed in high yield as expected. None of the product 2-phenylamino-benzo[*e*][1,3]oxazin-4-one **9** due to S_NAr *via* the *O*-centre of the anion was observed. Small amounts of 2-bromo-*N*-phenyl-benzamide **13** were isolated. The reaction conditions were variable and repeat reactions (4.5 – 6.7 h) gave varying amounts of the quinazoline-2,4-dione **8** and 2-bromo-*N*-phenyl-benzamide **13** (51-63%). We suggest that the intermediate anion **10** undergoes a novel rearrangement *via* a 4-membered ring intermediate **11** which extrudes isocyanic acid to yield the anion of 2-bromo-*N*-phenyl-benzamide **12**. The driving force is provided by the irreversible extrusion of a neutral molecule of isocycanic acid.



Scheme 2. Synthesis of the quinazolin-2,4-dione **8** and rearrangement.

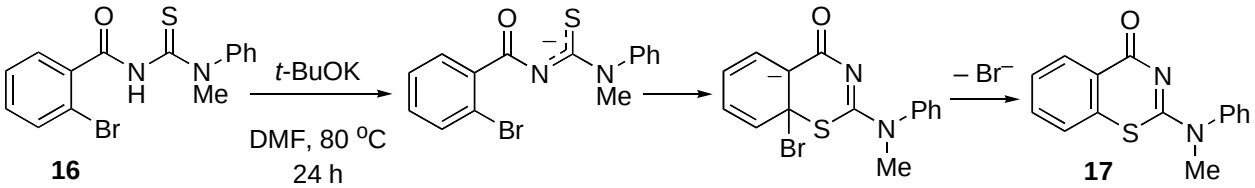
In our earlier studies we found that Cu-mediated reactions gave good yields for intramolecular reactions.[11] We therefore also studied the cyclization of 1-(2-halogenobenzoyl)-3-phenylthioureas **1** and **2** using Cu(I)I which gave rearrangement to 2-bromo-*N*-phenyl-benzamide **13** and 2-chloro-*N*-phenyl-benzamide respectively rather than S_NAr cyclization (Scheme 3). We propose a similar rearrangement with the *S*-atom complexed (*e.g*. intermediates **14** and **15**) by the Cu(I) which hinders S_NAr. The nature of the intermediate anion is not clear. The formation of copper(I) thiocyanate would be a driving force for the rearrangement. When the amount of Cu(I) was lowered from one equiv. to 0.2 equiv. some of the 1-phenyl-2-thioxo-2,3-dihydro-1*H*-quinazolin-4-one **5** (9%) was formed along with the benzanilide **13** indicating that full complexation by copper is required to prevent S_NAr. The chloro analogue **2** also gave rearrangement to 2-chloro-*N*-phenyl-benzamide (46%). 1-Benzoyl-3-phenyl-thiourea also gave rearrangement in a poor reaction (14%) and 1-(2-bromobenzoyl)-3-phenylurea **7** gave an intractable mixture of products.



Scheme 3. Cu(I) mediated rearrangement.

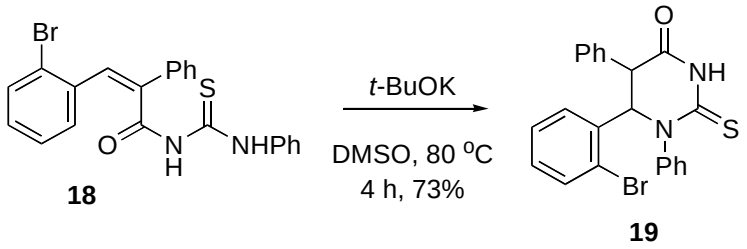
The *N*-methyl analogue **16** which is not able to cyclize *via* the *N*-atom of the intermediate anion was reacted under the same conditions and gave good yields of cyclization (65%) to the benzo[*e*][1,3]thiazin-4-one **17** *via* the *S*-atom of the anion. Therefore, in the reactions with **1** the

N-centre of the ambident anion cyclizes faster than the *S*-centre. When copper(I) (one equiv.) was added the yield dropped to 26%. The oxygen analogue, 3-(2-bromobenzoyl)-1-methyl-1-phenyl-urea, did not cyclize and starting material was recovered. Use of Cu(I) or $S_{RN}1$ conditions with entrainment also failed.



Scheme 4. Synthesis of 2-methyl-2-phenylamino-benzo[*e*][1,3]thiazin-4-one **17**.

Finally, we investigated the equivalent cyclization in the vinylogous thiourea **18** with the hope that 8-membered ring, albeit unfavourable, may be formed by S_NAr but the expected conjugate addition onto the β-position of the α,β-unsaturated acryloyl-thiourea yielded the 6-membered ring 2-thioxo-tetrahydro-pyrimidin-4-one **19** in good yield.



Scheme 5. Intramolecular conjugate addition.

Conclusions

2-Thioxo-2,3-dihydro-1*H*-quinazolin-4-one **5**, 1*H*-quinazoline-2,4-dione **8** and 2-methyl-2-phenylamino-benzo[*e*][1,3]thiazin-4-one **17** can be synthesized in reasonable yield using S_NAr from simple precursors. The presence of a carbonyl group *ortho* to the leaving halide in the precursors facilitates the putative S_NAr reactions as reported in the literature.[5] Interestingly, the anion (or dianion) of benzoylthioureas **1** and **2** and the phenylacryloyl-thioureas **18** undergo S_NAr and nucleophilic conjugate addition via the *N*-centre of the ambident anion rather than the *S*-center as commonly observed for thioureas and thioamides. The use of added Cu(I) leads to a novel rearrangement of the side chain thiourea and urea and blocks S_NAr .

Experimental Section

General Procedures. Melting points were determined with a Koffler block. Column chromatography was performed on silica gel (Merck 60, 70–230 mesh and 230-400 for flash chromatography) with the indicated eluent. TLC was carried out using aluminum backed TLC plates of silica gel 60 F254 (Merck, 0.2 mm). ^{1}H NMR spectra were recorded on a Perkin Elmer R32 spectrometer at 90 MHz and ^{13}C NMR spectra using a Bruker WP-80 spectrometer. All spectra were recorded in $CDCl_3$ with TMS as the internal standard. Chemical shifts were recorded in ppm and coupling constants *J* are given in Hz. Mass spectra (HRMS) at 70 eV using electron impact mode were performed on a Kratos MS 80 spectrometer. Irradiation of putative $S_{RN}1$ reactions was carried out using a Photophysics MLV18 irradiator with 12 lamps (25 W) emitting at 350 nm. All reactions were carried out under an atmosphere of nitrogen. Light petroleum refers to the bp 60-80 ˚C fraction.

Synthesis of thioureas

1-benzoyl-3-phenylthiourea was prepared by a literature procedure.[9]

1-(2-Bromobenzoyl)-3-phenylthiourea (1). General procedure for thiourea synthesis. 2-Bromobenzoic acid (25 g, 0.124 mol) and thionyl chloride (59 g, 0.496 mol) were refluxed for 3 h. The excess thionyl chloride was removed by distillation *in vacuo* to give a clear oil (27 g, 99%). The acid chloride was added dropwise to a mixture of ammonium thiocyanate (10.3 g, 0.135 mol) and dry acetone (75 mL). The mixture was stirred and heated under reflux for 5 min. Aniline (11.45 g, 0.123 mol) in dry acetone (25 mL) were added dropwise at a rate sufficient to maintain reflux. The resulting mixture was poured into cold water. The resulting crystals were filtered, washed with water, dried and recrystallized from ethanol to yield the thiourea **1** as orange crystals (27.39 g, 67%) mp 154-156 ˚C. Anal. Calcd. for $C_{14}H_{11}BrN_2OS$: C, 50.2; H, 3.3; N, 8.4; S, 9.55%. Found: C, 49.9; H, 3.3, N, 8.4; S, 9.9; ν_{max}(Nujol)/cm^{-1} 3160, 1685, 1540, 770, 745 and 700; δ_H 7.19-7.79 (9 H, m), 9.14 (1 H, brs, NH, exchangeable in D_2O) and 12.32 (1 H, brs, NH, exchangeable in D_2O); *m/z* 336/334, 255, 201/199, 157/155, 135 and 93.

1-(2-Chlorobenzoyl)-3-phenylthiourea (2). 2-Chlorobenzoic acid (20 g, 0.128 mol) was reacted as above to yield **2** as orange crystals (17.12 g, 46%) mp 154.5-156.5 ˚C. Anal. Calcd. for $C_{14}H_{11}ClN_2OS$: C, 57.85; H, 3.8; N, 9.65; Cl, 12.2%. Found: C, 57.5; H, 3.7, N, 9.4; Cl, 12.1; ν_{max}(Nujol)/cm^{-1} 3170, 1685, 1545, 770, 748 and 705; δ_H 7.00-7.88 (9 H, m), 9.30 (1 H, brs, NH, exchangeable in D_2O) and 12.40 (1 H, brs, NH, exchangeable in D_2O); *m/z* 225, 156, 152, 135, 93 and 77.

3-(2-Bromobenzoyl)-1-methyl-1-phenylthiourea (16). *N*-Methylaniline was used in place of aniline to yield **17** (85%) as orange crystals, mp 91-93 ˚C. Anal. Calcd. for $C_{15}H_{13}BrN_2OS$: C, 51.59; H, 375; Br, 22.88; N, 8.02. Found: C, 51.25; H, 3.6; Br, 22.8; N, 8.1; ν_{max}(Nujol)/cm^{-1} 3150, 1700, 1515, 760 and 735; δ_H 3.74 (3 H, s, Me), 7.23-7.56 (9 H, m), 8.35 (1 H, brs, CON*H*CS, exchangeable in D_2O); *m/z* 350/348, 270, 269, 185/183, 157/155, 107 and 106.

1-[3-(2-Bromophenyl)-2-phenylacryloyl]-3-phenylthiourea (18). 2-Bromobenzaldeyde (1.5 g, 8.11 mmol), phenylacetic acid (1.6 g, 11.75 mmol), triethylamine (0.85 g, 8.11 mmol) and acetic anhydride (25 mL) were heated under reflux for 6 h. The mixture was cooled and water added. The resulting crystals were filtered and recyrstallised (toluene) to yield colourless needles of 3-(2-bromophenyl)-2-phenyl-acrylic acid (2.2 g, 89%) mp 180-181 ˚C; ν_{max}(Nujol)/cm^{-1} 3410, 1685, 1600, 1440, 760, 735 and 695; δ_H 7.40-7.70 (9 H, m), 7.85 (1 H, s, 3-H) and 10.80 (1 H, brs, CO_2H); *m/z* 304/302, 223, 178, 177, 77 and 76.

3-(2-Bromophenyl)-2-phenylacrylic acid (1.0 g, 3.29 mmol) gave 1-[3-(2-bromophenyl)-2-phenyl-acryloyl]-3-phenylthiourea **18** as yellow crystals (1.32 g, 90%) mp (ethanol) 156.157 ˚C. Anal. Calcd. for $C_{22}H_{17}BrN_2OS$: C, 60.4; H, 3.9; N, 6.4; S, 7.3%. Found: C, 60.3; H, 3.9, N, 6.5; S, 7.4; ν_{max}(Nujol)/cm^{-1} 3490, 3350, 1660, 760, 735 and 695; δ_H 6.4-6.7 (14 H, m), 8.0 (1 H, s, 3-H), 8.3 (1 H, brs, NHPh) and 12.45 (1 H, brs, CONHCS); *m/z* 438/436, 357, 264, 222, 178, 135, 93, 88 and 77.

Synthesis of ureas

1-(2-Bromobenzoyl)-3-phenylurea (7). A literature procedure was used.[13] Oxalyl chloride (2.38 g, 18.7 mmol) was added to a stirred solution of 2-bromobenzamide (3.0 g, 15.0 mmol) in CH_2Cl_2 (30 mL) and heated under reflux for 23 h. Aniline (1.4 g, 14.5 mmol) was added and the reaction stirred for 20 min. The mixture was poured into water, the crystals filtered and recrystallized from ethanol to yield the urea **7** (2.56 g, 54%) mp 168.5-170.5 ˚C. Anal. Calcd. for $C_{14}H_{11}BrN_2O_2$: C, 52.7; H, 3.5; N, 8.8%. Found: C, 52.9; H, 3.5, N, 8.9; ν_{max}(Nujol)/cm^{-1} 3210, 3120, 1705 and 1560; δ_H 7.10-7.73 (9 H, m), 9.63 (1 H, brs, NH, exchangeable in D_2O) and 10,55 (1 H, brs, NH, exchangeable in D_2O); *m/z* 227/225, 201/199, 185/183, 157/155, 121, 120, 119, 93 and 77.

3-(2-Bromobenzoyl)-1-methyl-1-phenylurea. The above procedure was used except that the aniline was replaced by *N*-methylaniline to yield the urea as pale yellow crystals (60%) mp 237-240 ˚C (water/ethanol). Anal. Calcd. for $C_{15}H_{13}BrN_2O_2$: C, 54.1; H, 3.95; N, 8.4%. Found: C, 53.8; H, 3.8, N, 8.1; ν_{max}(Nujol)/cm^{-1} 3210, 1687 and 1590; δ_H 3.24 (3 H, s, Me) and 7.06-7.83 (10 H, m); *m/z* 227/225, 201/199, 185/183, 157/155, 107, 106, 77 and 76.

1-Phenyl-2-thioxo-2,3-dihydro-1*H*-quinazolin-4-one (6). General method for cyclization of ureas. 1-(2-Bromobenzoyl)-3-phenylthiourea **1** (1.0 g, 3.0 mmol), potassium *tert*-butoxide (1.67 g, 14.9 mmol) and dry DMF (20 mL) were stirred at 70-80 ˚C under an atmosphere of nitrogen for 2.25 h. The reaction mixture was diluted with water and extracted with CH_2Cl_2. The organic layers were washed with water, dried and evaporated to dryness to yield crude 1-phenyl-2-thioxo-2,3-dihydro-1*H*-quinazolin-4-one **5** (0.76 g, 100%). Recrystallisation from EtOAc gave pale yellow crystals of **6** (29%) mp 237-240 ˚C. Anal. Calcd. for $C_{14}H_{10}N_2OS$: C, 66.1; H, 4.0; N, 11.0, S, 12.6%. Found: C, 66.2; H, 4.0, N, 11.0, S, 12.4; ν_{max}(Nujol)/cm^{-1} 3270, 1697, 1590, 1450, 765 and 695; δ_H 6.51 (1 H, d, *J* 8.5, H-8) 7.23-7.70 (7 H, m, Ph-H and 6,7-H), 8.26 (1 H, dd, *J* 7.4, 1.7, H-5) and 10.30 (1 H, brs, NH, exchangeable in D_2O); δ_C 176.2 (2-C),158.7 (4-C),

143.3 and 139.4 (8a-C, Ph-1-C),135.3 (7-C), 135.3 and 128.9 (Ph *o*- and *m*-*C*H), 129.6, 128.2 and 124.8 (5,6-C and Ph-*p*-CH), 117.4 (4a-C) and 117.0 (8-C); *m/z* 253, 196, 195, 167, 166, 119, 90, 106, 77 and 76.

1-Phenyl-1*H*-quinazoline-2,4-dione (8). 1-(2-Bromobenzoyl)-3-phenylurea **7** (1.0 g, 3.13 mmol) was reacted using the general procedure for S_NAr reactions to yield **8** (0.27 g, 36%) mp 297-299 ˚C (from CH_2Cl_2/light petroleum) (lit.[12] 299 ˚C). ν_{max}(Nujol)/cm^{-1} 3170, 3120, 1710, 1690, 755, 750 and 705; δ_H 6.42 (1 H, d, *J* 8.3, H-8) 7.16-7.80 (7 H, m, Ph-H and 6,7-H), 8.05 (1 H, dd, *J* 7.4, 1.7, H-5) and 11.68 (1 H, brs, NH, exchangeable in D_2O); δ_C 162.07 (2-C),149.88 (4-C), 142.66 and 136.32 (8a-C, Ph-1-C),134.85 (7-C), 129.98 and 129.38 (Ph *o*- and *m*-*C*H), 128.94, 127.30 and 122.60 (5,6-C and Ph-*p*-CH), 115.33 (4a-C) and 115.30 (8-C); *m/z* 238, 195,167 and 77.

2-Chloro-*N*-phenyl-benzamide. General method for Cu(I) reactions. 1-(2-Chlorobenzoyl)-3-phenylthiourea **2** (0.2 g, 0.69 mmol) was reacted using the general method for S_NAr reactions. Cu(I)I (131 mg, 0.69 mmol, 1.0 equiv.) was added prior to the addition of *tert*-BuOK. The crude product containing largely pure 2-chloro-*N*-phenyl-benzamide (110 mg, 76%) was purified using flash column chromatography with diethyl ether and light petroleum as eluents to yield pure 2-chloro-*N*-phenyl-benzamide (73 mg, 46%). The mp and spectroscopic data were identical with authentic material.

2-(*N*-Methyl-*N*-phenylamino)-benzo[*e*][1,3]thiazin-4-one (17). 3-(2-Bromobenzoyl)-1-methyl-1-phenylthiourea **16** (1.0 g, 2.86 mmol) was reacted using the general procedure for S_NAr reactions. Flash column chromatography with diethyl ether and CH_2Cl_2 as eluents gave unaltered starting material **16** (0.24 g, 24%) and the thiazin-4-one **17** (0.5 g, 65%). Recrystallisation from EtOAc gave pale yellow crystals of **17** (36%) mp 146.5-149 ˚C (lit.[14] 145-147.5 C). Anal. Calcd. for $C_{15}H_{12}N_2OS$: C, 67.1; H, 4.5; N, 10.4, S, 11.95%. Found: C, 66.95; H, 4.6, N, 10.5, S, 11.9; ν_{max}(Nujol)/cm^{-1} 3060, 1640, 1595, 1580, 770, 750 and 690; δ_H 3.63 (3 H, s, Me), 7.05-7.22 (1 H, m, 8-H), 7.28-7.65 (7 H, m, Ph-H, 6,7-H) and 8.36-8.60 (1 H, m, 5-H); δ_C 169.54 (2-C),149.13 (4-C), 141.60 (Ph-1-*C*),133.84 (8a-C), 131.05, 130.39, 129.68. 127.77 and 125.41 (5,6,7,8-C and Ph-*p*-*C*H), 130.52 and 128.37 (Ph-*o*,*m*-*C*H), 122.52 (4a-C) and 40.35 (Me).

6-(2-Bromophenyl)-1,5-diphenyl-2-thioxo-tetrahydropyrimidin-4-one (19). 1-[3-(2-bromophenyl)-2-phenylacryloyl]-3-phenylthiourea **18** (0.26 g, 0.46 mmol) was reacted using the general procedure for S_NAr reactions except that DMSO replaced DMF. Recrystallisation of the crude product from ethanol gave **19** (0.16 g, 73%) as yellow needles, mp 186-188 ˚C. Anal. Calcd. for $C_{22}H_{17}BrN_2OS$: C, 60.4; H, 3.9; N, 6.4, S, 7.3%. Found: C, 60.1; H, 3.8, N, 6.4, S, 7.3; ν_{max}(Nujol)/cm^{-1} 3050, 1750, 770, 750 and 700; δ_H 3.5-4.3 (2 H, m, 5,6-H) and 6.4-8.6 (15 H, m); *m/z* 438/436, 357, 267,280, 103, 90 and 77. A ^{13}C spectrum was not measured, therefore it is possible that both diastereomers were present.

Acknowledgments

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