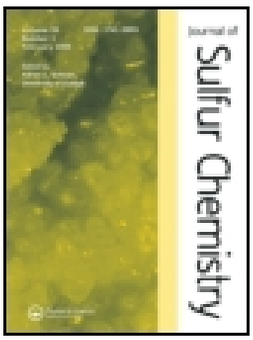

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Selective and facile oxidative desulfurization of thioureas and thiobarbituric acids with singlet molecular oxygen generated from *trans*-3,5-dihydroperoxy-3,5-dimethyl-1,2-dioxolane

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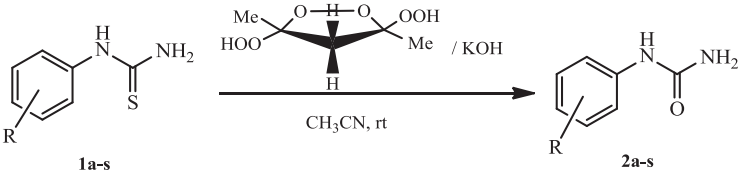
An efficient and facile procedure using *trans*-3,5-dihydroperoxy-3,5-dimethyl-1,2-dioxolane has been developed for oxidative desulfurization of thioureas and thiobarbituric acids. The reactions proceeded smoothly very fast under mild conditions in basic media at room temperature to afford the respective ureas in excellent yields. Simple procedure and work up, mild conditions, high yields, short reaction times, use of highly potent and non-toxic oxidant are the main merits of the present method.



Keywords: *trans*-3,5-dihydroperoxy-3,5-dimethyl-1,2-dioxolane; DHPODMDO; oxidation; desulfurization; thioureas; thiobarbituric acid; urea

1. Introduction

Thiourea and its derivatives are known as hazardous, highly toxic and carcinoma-inducing materials.[1] However, thioureas and many other thiocarbonyl compounds are of high industrial potential,[2–4] and are employed as versatile tools in multi-step synthesis of various natural products. Also, they are biologically active molecules, which involve transformation of thiocarbonyl group into the corresponding carbonyl group in final step.[5,6] On the other hand, the oxo analogs of thioureas are non-toxic and environmentally friendly compounds which can be oxidized to various nitrogen-containing heterocyclic products of pharmaceutical activities and used as synthones in cyanine dyes.[7]

Several methods have been developed for oxidative desulfurization of thioureas and other thiocarbonyl compounds into oxo analogs or other derivatives such as disulfides and heterocyclic products.[8–10] The reagents reported in the literature for oxidative desulfurization mainly include thionyl chloride,[11] phosgene,[12] t-butyl hypochlorite,[13] potassium superoxide,[14]

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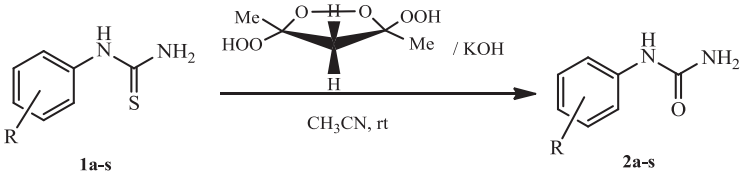


Scheme 1. Desulfurization of thioureas with DHPDMDO.

ceric ammonium nitrate,[15] m-chloroperbenzoic acid,[16] peracetic acid,[17] KBr/alkaline solution,[18] OsO_4,[19] $KMnO_4$,[20] dimethyldioxirane,[21] mercuric oxide,[22,23] alkaline peroxide,[24,25] N-bromosuccinimide,[26] oxone,[27] 3-carboxypyridinium and 2,2′-bipyridinium chlorochromates,[28,29] ozone,[30] H_2O_2,[31] I_2/Et_3N,[32] $n-Bu_4N^+IO_4^-$,[33] $(n\text{-}BuPPh_3)_2Cr_2O_7$,[34] and cetyltrimethyl ammonium dichromate.[35] In addition, desulfurization of 1,3-disubstituted thioureas with the hypervalent organoiodine (III) reagent, diacetoxyiodobenzene, to form N-acylated ureas via carbodiimide intermediates has been reported.[36] Pramod and co-workers have reported the o-iodoxybenzoic-acid-mediated desulfurization of thioureas to carbodiimides.[37] However, many of these methods suffer from certain drawbacks such as using noxious and toxic reagents, long reaction times, tedious work-up, and removal of harmful by-products such as phosphorous by-products.[38] As a result, to avoid these limitations, development of new and benign approaches for oxidative desulfurization of sulfur-containing compounds, including thioureas, appears as an interesting research challenge. In recent years, gem-dihydroperoxides have been extensively used as highly potent oxidants for a variety of functional group transformations in organic synthesis.[39–46] Herein, we report the hitherto unexplored efficient and convenient oxidative desulfurization of mono- and disubstituted ureas and their related compounds such as thiobarbituric acids with *trans*-3,5-dihydroperoxy-3,5-dimethyl-1,2-dioxolane (DHPODMDO).

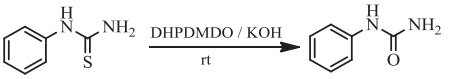
In continuation of our ongoing research on the synthesis of various hydroperoxides,[47–52] and their applications as highly potent oxidants for various organic transformations,[53–60] we were encouraged to investigate the hitherto unexplored oxidative potential of DHPDMDO for oxidative desulfurization of different sulfur-containing compounds such as thioureas into the corresponding oxo analogs. As shown in Scheme 1, various substituted thioureas (**1a–1s**) were reacted with DHPDMDO as an efficient oxidant. The reactions proceeded smoothly in aqueous alkaline solution at room temperature to afford the corresponding ureas (**2a–2s**) in excellent yields (Scheme 1).

2. Results and discussion

To establish the reaction conditions, we preliminarily reacted phenylthiourea **1a** with DHPDMDO in aqueous KOH solution at room temperature as the model reaction. The effects of solvent and the oxidant loading on the reaction rate and yield were screened by using different solvents such as EtOAc, CH_2Cl_2, H_2O, EtOH, AcOH and CH_3CN, with various amounts of the oxidant (Table 1).

First, a separate reaction was set up for each solvent using constant 1 mmol amount of the oxidant and 5 mL of 5% aqueous KOH solution at room temperature (Table 1, Entries 1–6). As shown in Table 1, the best solvent appeared to be CH_3CN among the other solvents examined in terms of the reaction time (20 min) and the yield (70%) (Entry 6). In the next stage, in order to evaluate the effect of the oxidant concentration using CH_3CN as the solvent of choice, the reaction was repeated for different amounts of the oxidant with constant reaction time of 1

Table 1. Screening the conditions for the model desulfurization reaction of phenylthiourea with DHPDMDO/KOH at room temperature[a].



1a **2a**

Entry	Solvent	Oxidant (mmol)	Time (min)	Yield[b] (%)
1	EtOAc	1	60	0
2	CH_2Cl_2	1	60	20
3	H_2O	1	90	Trace
4	EtOH	1	90	0
5	CH_3COOH	1	50	Trace
6	CH_3CN	1	20	70
7	CH_3CN	1	1	62
8	CH_3CN	0.5	1	45
9	CH_3CN	1.5	1	82
10	CH_3CN	2	1	95
11	CH_3CN	3	1	95
12	CH_3CN	2	20	95
13	CH_3CN	2	30	95
14	CH_3CN	0	1	0
15	CH_3CN	0	120	0
16[c]	CH_3CN	2	1	Trace
17[c]	CH_3CN	2	120	Trace

[a]Conditions: phenyl thiourea (1 mmol), 5% aq. KOH (5 mL), solvent (5 mL), r.t.
[b]Isolated pure yield.
[c]No base was used in the reaction.

min (Entries 7–11) and the best oxidant loading was found to be 2 mmol, as resulted in almost complete desulfurization of phenylthiourea (Entry 10). It was noticed that, the yield of the reaction was diminished when lower amounts of the oxidant are used (Entries 7–9), and no further improvement of the yield was observed for higher amounts of the oxidant (Entry 11) with constant reaction time of 1 min. More experiments were carried out (Entries 12, 13) using the best oxidant concentration of 2 mmols at different reaction times to determine the best reaction time, which appeared to be 1 min (Entry 10). In addition, the crucial role of the oxidant in the reaction was approved by conducting the reaction in the absence of the oxidant under the optimized conditions that ended with almost complete recovery of the starting materials even after a long reaction time of 120 min (Entries 14, 15). Moreover, the importance of the presence of KOH base in the reaction was evaluated when the reaction was carried out using 1,3-diphenylthiourea as the substrate under neutral condition, which produced no detectable amount of the expected product **2o** (Entries 16, 17), but instead, diphenylcarbodiimide was obtained as the only product which was identified on the basis of its spectral (FT-IR and NMR) data as given below. Finally, the possible occurrence of the reaction in acidic media was examined by conducting the reaction in acetic acid as solvent, which resulted in only trace amount of the expected product (Entry 5).

Spectral data of diphenylcarbodiimide: oily liquid. ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = 7.20$ (m, 6 H), 7.31 (m, 4 H). ^{13}C-NMR (75 MHz, $CDCl_3$): $\delta = 124.3, 125.7, 129.6, 135.4, 138.4$. FT-IR (nujol): 2135, 2105, 1587, 1207, 755, 691 cm^{-1}.

In summary, according to the experimental results summarized in Table 1, the optimum conditions found for this reaction is using CH_3CN as the solvent with 2 mmols of the oxidant in basic solution of KOH at room temperature.

To establish the generality of the reaction, a variety of mono- and 1,3-disubstituted thioureas (**1a–1q**) and thiobarbituric acids (**1r–1s**) were subjected to the optimized conditions and the

results are summarized in Table 2. In general, the reactions proceeded very fast and smoothly to furnish the products in excellent and comparable yields (80–98%) irrespective of the nature of the substituent groups on the aromatic rings.

All the products obtained were characterized on the basis of their physical and spectral (IR, NMR) analysis as presented in experimental section.

3. Conclusion

In summary, an efficient and environmentally friendly method based on oxidative desulfurization of mono- and 1,3-disubstituted thiourea derivatives and barbituric acids to the corresponding oxo analogs employing DHPDMDO in aqueous KOH solution at room temperature has been developed. Use of highly potent and non-toxic oxidant, avoiding any expensive and/or toxic catalyst, mild reaction conditions, improved reaction rates and yields make this approach superior over many other reported methods.

4. Experimental

FT-IR spectra were taken on a Perkin Elmer GX FT IR spectrometer in KBr pellets. ^{1}H- and ^{13}C-NMR spectra were recorded on a 300 MHz and 400 MHz BRUKER instrument in DMSO-d_6 solutions using TMS as internal standard. Melting points were measured on an SMPI apparatus.

Caution: Although we did not encounter any problem with DHPDMDO, it is potentially explosive and should be handled with precautions; all reactions should be carried out behind a safety shield inside a fume hood and transition metal salts or heating should be avoided.

4.1. *Preparation of DHPDMDO*

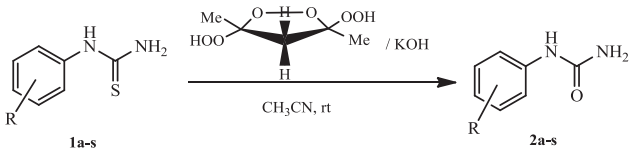
Following our previously reported procedure,[55] this compound was prepared from acetyl acetone upon treatment with 30% aqueous H_2O_2 under the catalytic effect of $SnCl_2{\cdot}2H_2O$ as described below.

To a stirred solution of acetylacetone (100 mg, 1 mmol) in CH_3CN (5 mL) was added $SnCl_2.2H_2O$ (45 mg, 0.2 mmol) and the resulting mixture was stirred for 5 min at room temperature. Then, aqueous 30% H_2O_2 (5 mmol) was added to the reaction mixture and let to stir for 12 h at room temperature. After completion of the reaction as monitored by TLC, water (15 mL) was added and the product was extracted with ethyl acetate (2 × 10 mL). The combined organic layer was dried over anhydrous $MgSO_4$ and evaporated under reduced pressure to leave an almost pure white crystalline product in 85% yield (140 mg); mp 98–100°C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm): 8.43 (bs, 2H, OOH), 2.67 (s, 2H, CH_2-4), 1.59 (s, 6H, CH_3). ^{13}C-NMR (75 MHz, D_2O) δ: 16.5 (CH_3), 50.7 (CH_2-4), 112.7 (C-3, C-5); IR (KBr pellet) ν(cm^{-1}): 3389 (w), 1433, 1380, 1333, 1173, 848, 790, 470.

4.2. *Typical procedure for desulfurization of thiourea derivatives 1a–1s to oxo analogs 2a–2s*

To a stirred solution of phenylthiourea **1** (1 mmol) and 5% aq. KOH (5 mL) in acetonitrile (5 mL) was added DHPDMDO (0.332 g, 2 mmol). The resulting mixture was allowed to stir at room temperature for an appropriate time (Table 2). After completion of the reaction as monitored

Table 2. Desulfurization of thioureas and barbituric acids with DHPDMDO/aq. KOH in CH_3CN at room temperature[a].



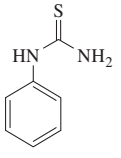
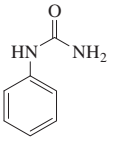
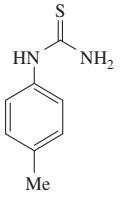
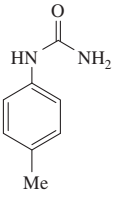
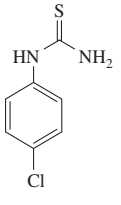
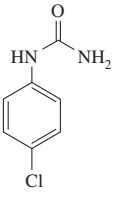
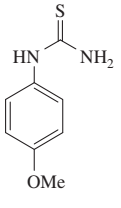
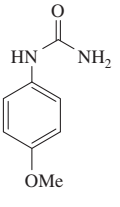
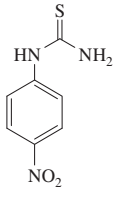
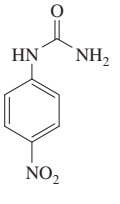
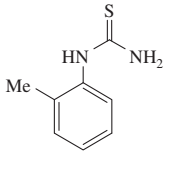
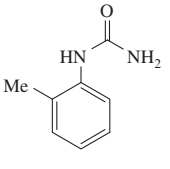
Entry	Substrate **1**	Product **2**	Time (min)	Yield (%)[b]	Mp (°C) Found	Mp (°C) Reported [34,61]
A			1	95	141–144	142
B			10	93	180–183	180
C			2	89	205–208	204
D			10	84	165–168	168
E			1	91	226–228	228
F			15	81	192–194	190–195

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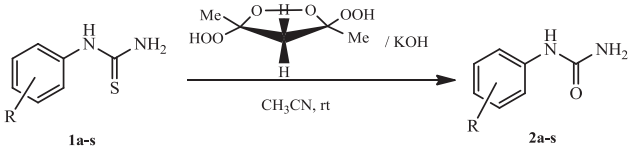
Table 2. Continued.



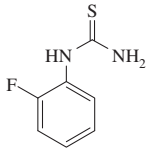
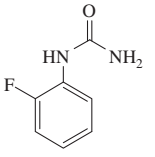
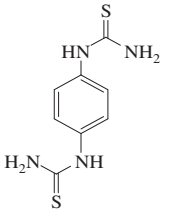
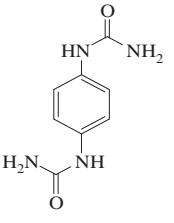
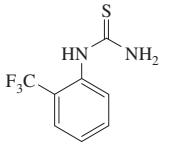
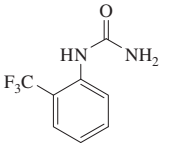
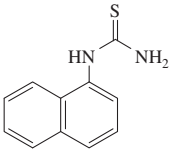
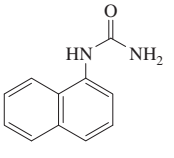
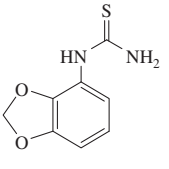
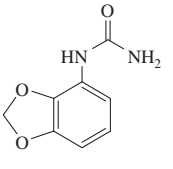
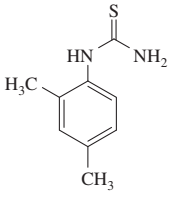
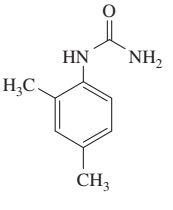
Entry	Substrate **1**	Product **2**	Time (min)	Yield (%)[b]	Mp (°C) Found	Mp (°C) Reported [34,61]
G			10	83	186	186–188
H			20	89	358	–
I			10	87	100–102	101–103
J			5	95	218–221	222
K			5	96	182	179–181
L			15	87	202–204	204–205

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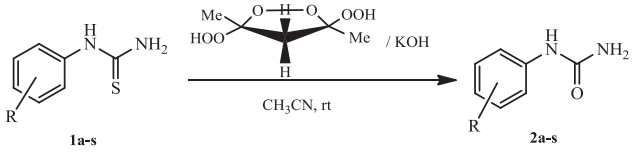
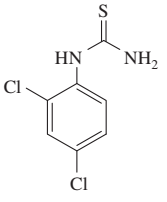
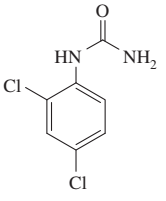
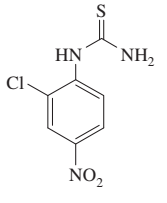
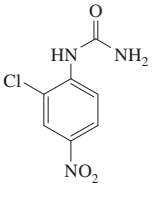
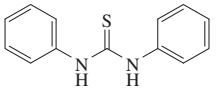
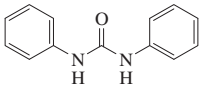
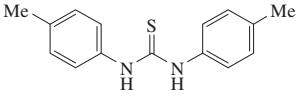
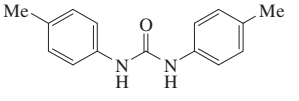
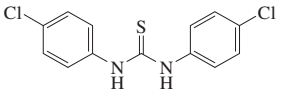
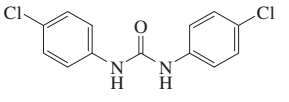
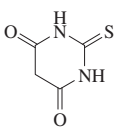
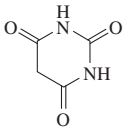
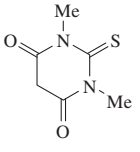
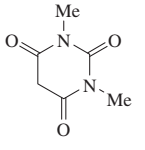
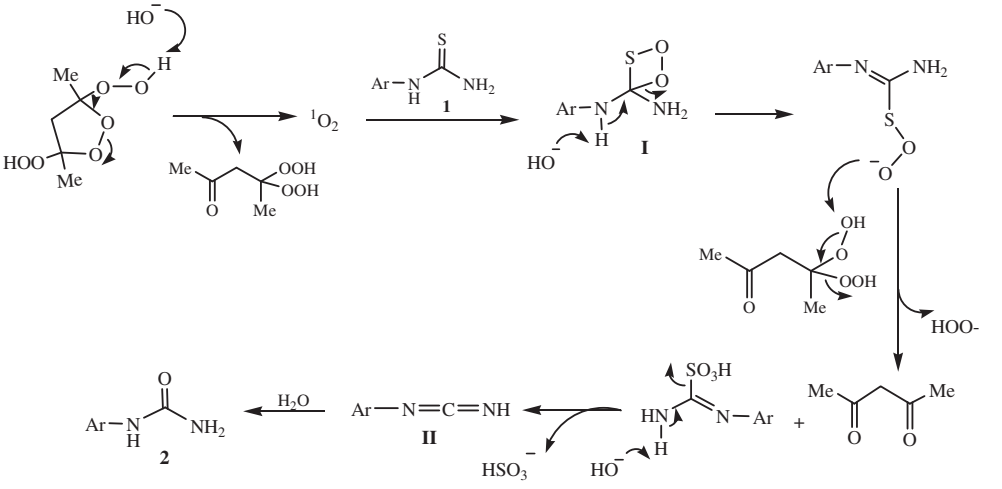
Table 2. Continued.



Entry	Substrate **1**	Product **2**	Time (min)	Yield (%)[b]	Mp (°C) Found	Mp (°C) Reported [34,61]
M			10	89	220–221	220–223
N			10	94	248–251	248
O			1	98	238–240	242
P			2	93	235–236	236
Q			1	92	234	235–236
R			10	85	248–251	252
S			15	80	121–123	123

[a]Condition: substrate (1 mmol), oxidant (2 mmol), 5% aq. KOH (5 mL), CH_3CN (5 mL), r.t.
[b]Isolated pure yield.



Scheme 2. Proposed mechanism for desulfurization of thioureas with the oxidant DHPDMDO in aqueous KOH solution.

by TLC, the reaction mixture was diluted with water (10 mL) and the product was extracted in dichloromethan (3 × 5 mL). The combined organic layer was washed with water (2 × 5 mL) and dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure gave almost pure products. Structures of the known products were established on the basis of their physical and spectroscopic (IR, ^{1}H-NMR and ^{13}C-NMR) data, which were consistent with those reported.[34,61]

Based on the formation of carbodiimide II as the intermediate, which was detected in the course of the reaction, and also according to the $^1O_2$-based mechanisms proposed for the oxidative desulfurization of thioureas in the literature,[61–66] a plausible reaction mechanism proposed to explain the desulfurization of thioureas **1a–1s** to the respective oxo analogs **2a–2s** with DHPDMDO in aqueous KOH solution is depicted in Scheme 2. Based on our previously reported evidence,[57] it is likely that the reaction initially involves the generation of singlet oxygen molecule via ring-opening decomposition of the oxidant, which acts as the main source of oxidant to produce a four-membered 1,2,3-dioxathietane intermediate **I**. To provide evidence for the involvement of $^1O_2$ in the reaction, and in virtue of prolonged liftime of $^1O_2$ in deuterated solvents, we repeated the reaction for 1,1′-(1,4-phenylene)bis(thiourea) **1h** in CD_3CN solvent under the same optimized conditions and noticed substantial improvements of the reaction time and the yield as well.

4.3. *Characterization data for the products 2 [34,61]*^{lit}*:*

4.3.1. *1-Phenyl urea (2a)*

White solid; m.p. 141–144 °C. IR (KBr).3429, 3314, 3268, 1656, 1614, 1597, 1553, 1497, 1357, 751, 697 cm^{-1}. ^{1}H-NMR (DMSO-d_6): δ(ppm) 8.55 (s, 1H), 7.38 (d, 2H), 7.20 (t, 2H), 6.87 (t, 1H), 5.84 (s, 2H). ^{13}C-NMR (DMSO-d_6): δ(ppm) 156.5, 141.0, 129.0, 121.5, 118.2.

4.3.2. *p-Tolylurea (2b)*

White solid; m.p. 180–183°C.IR (KBr).3430, 3311, 3216, 1654, 1620, 1591, 1549, 1407, 1256, 1109, 1024, 824, 811, 779 cm^{-1}. ^{1}H-NMR (DMSO-d_6): δ(ppm) 8.35 (s, 1H), 7.24 (d, 2H), 7.00

(d, 2H), 5.73 (s, 2H), 2.20 (s, 3H). ^{13}C-NMR (DMSO-d_6): δ(ppm) 156.7, 138.0, 130.4, 129.9, 118.2, 25.4.

4.3.3. *2-Fluorophenylurea (2 g)*

White solid; m.p. 186°C. IR (KBr). 3424, 3322, 3217,1657, 1624, 1600, 1552, 1492, 1456, 1359, 1257, 754 cm^{-1}. ^{13}C-NMR (DMSO-d_6): δ(ppm) 156.1, 154.0, 150.2, 128.8, 128.6, 124.7, 122.0, 121.9, 120.8, 120.8, 115.3, 115.0.

4.3.4. *1,1′-(p-Phenylene)bis(thiourea) (2 h):*[new]

Purple solid; m.p. > 345°C. IR (KBr). 3464, 3430, 3336, 1645, 1604, 1552, 1409, 1340, 813, 644 cm^{-1}. ^{1}H-NMR (DMSO-d_6): δ(ppm) 8.46 (s, 2H), 7.18 (s, 4H), 5.76 (s, 4H); ^{13}C-NMR (DMSO-d_6): δ(ppm) 156.6, 134.8, 118.9. *m/z* (EI): 52, 81, 108, 157, 194 (M^+).

4.3.5. *2-Trifluoromethylphenylurea (2i)*

White solid; m.p. 100–102°C. IR (KBr). 3479, 3440, 3339, 3186, 1742, 1708, 1689, 1657, 1617, 1590, 1543, 1461, 1363, 1322, 1285, 1108, 760 cm^{-1}. ^{1}H-NMR (DMSO-d_6): δ(ppm) 8.94 (s, 1H), 7.99–8.00 (d, 1H), 7.67–7.69 (d, 1H), 7.41–7.44 (t, 1H), 7.31–7.34 (t, 1H), 5.97 (s, 2H). ^{13}C-NMR (DMSO-d_6): δ(ppm) 156.4, 156.2, 152.4, 137.6, 135.7, 133.6, 133.1, 126.4, 126.3, 126.2, 125.7, 125.5, 125.0, 124.5, 123.3, 123.2, 122.3, 119.3.

4.3.6. *1-Naphthylurea (2j)*

Purple solid; m.p. 218–221°C. IR (KBr). 3443, 3304, 3208, 1651, 1608, 1555, 1530, 1505, 1359, 784, 760 cm^{-1}. ^{1}H-NMR (DMSO-d_6): δ(ppm) 8.65 (s, 1H), 8.15 (s, 1H), 7.96 (d, 1H), 7.84 (s, 1H), 7.75–7.35 (m, 4H), 6.19 (s, 2H). ^{13}C-NMR (DMSO-d_6): δ(ppm) 156.2, 135.7, 133.5, 128.6, 126.3, 16.1, 125.7, 123.3, 123.2, 117.0, 109.2

4.3.7. *1,3-benzodioxol-4-yl urea (2k):*[new]

Black solid; m.p. 182–183°C. IR (KBr). 3416, 3360, 3214, 2909, 2797, 1647, 1608, 1547, 1500, 1486, 1447, 1366, 1280, 1247, 1197, 1042, 857, 790 cm^{-1}. ^{1}H-NMR (DMSO-d_6): δ(ppm) 8.33 (s, 1H), 7.66–7.68 (d, 1H), 6.98–7.02 (t, 1H), 6.33–6.35 (d, 1H), 5.95 (s, 1H), 5.85 (s, 1H), 5.17 (s, 2H). ^{13}C-NMR (DMSO-d_6): δ(ppm) 156.5, 147.7, 141.8, 135.4, 110.7, 108.4, 101.0, 100.9. *m/z* (EI): 79, 108, 109, 136, 137, 180 (M^+).

4.3.8. *2-Chloro-4-nitrophenylurea (2n)*

Yellow solid; m.p. 248–251°C. IR (KBr). 3500, 3392, 3324, 1676 cm^{-1}. ^{1}H-NMR (DMSO-d_6): δ(ppm) 6.88 (s, 2H), 7.43–8.66 (d, 1H).^{13}C-NMR (DMSO-d_6): δ(ppm) 155.6, 147.8, 132.0, 122.9, 119.0, 114.0.

4.3.9. *1,3-Diphenylurea (2o)*

White solid; m.p. 238–240 °C. IR (KBr). 3299, 1649, 1558, 1544, 1474, 1385, 1292, 1098, 818 cm^{-1}. ^{1}H-NMR (DMSO-d_6): δ(ppm) 8.63 (br, 2H), 7.46 (d, 4H), 7.29 (d, 4H), 6.98 (t, 2H). ^{13}C-NMR (DMSO-d_6): δ(ppm) 152.4, 134.9, 129.1, 127.9, 123.7.

4.3.10. *1,3-Bis(4-chlorophenyl)urea (2q)*

White solid; m.p. 234 °C [28, 43][lit]. IR (KBr). 3296, 1633, 1591, 1492, 1290, 1086, 823, 639 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ(ppm) 8.05 (br, 2H), 7.55 (d, 4H), 7.48 (d, 4H). ^{13}C-NMR ($CDCl_3$): δ(ppm) 152.2, 134.0, 129.9, 129.1, 123.0.

4.3.11. *N,N′-Dimethylbarbituric acid (2s)*

White solid; m.p. 121–123 °C. IR (KBr). 3168, 3082, 1766, 1718, 1679 cm^{-1}. ^{1}H-NMR (DMSO-d_6): δ(ppm) 3.06 (s, 6H), 3.63 (s, 2H). ^{13}C-NMR (DMSO-d_6): δ(ppm) 173.4, 150.2, 31.5, 9.5.

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Supplemental data

Supplemental data for this article can be accessed at doi:10.1080/17415993.2015.1082181 description of location.

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