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A greener synthetic protocol for the preparation of carbodiimide

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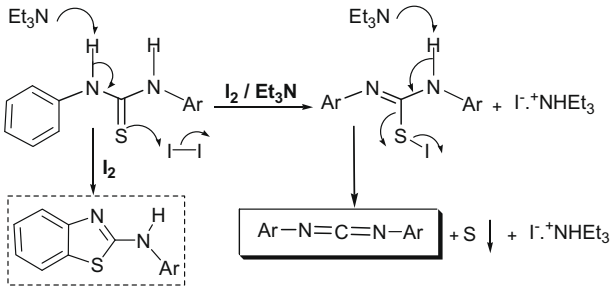
ABSTRACT

A new and facile preparation of symmetrical and unsymmetrical 1,3-diaryl and aryl-alkyl carbodiimides via a dehydrosulfurisation of their corresponding thioureas is described. Herein, the classical method of oxidative desulfurisation of thiourea to carbodiimide involving toxic heavy metal oxides (HgO) has been replaced with an easily available, cost-effective and environmentally benign reagent, iodine. Simple reaction conditions, easy purification of the products and high yields are important attributes of the present methodology and perhaps the best alternative from a green chemistry perspective. The only limitation to this method however, is in the preparation of 1,3-dialkyl substituted carbodiimide.

Carbodiimides rank as one of the most important class of reagent in synthetic organic chemistry, which are widely used as synthetic intermediates. They have found several applications such as synthesis of nucleotides, peptides and heterocycles, oxidation with dimethyl sulfoxide, permease inhibitors, polymer stabilisers, cycloaddition reactions etc.[1] The importance of carbodiimides can be judged from the earliest review by Khorana[1a] and subsequent three reviews[1b–d] where various methods of their preparation, properties and uses have been extensively discussed. Carbodiimides are normally constructed from a preformed N–C–N skeleton, addition of N to C–N and a N+C+N approach.[1a–d] Synthetic methods for carbodiimides employed before the year 1981 are covered in the above four reviews. Subsequent methods adopted also, falls into the above three categories which can again be broadly classified as, (i) thermolysis-decarboxylation of isocyanates,[2] (ii) dehydration of ureas[3] and (iii) dehydrosulfurisation of thioureas.[4] Following the N+C–N type approach, it has been prepared by the condensation of an amine and an isonitrile in the presence of oxygen and iodine using a palladium catalyst.[5] Although a large number of processes are available in the literature, there are limitations to these methods. Some of the drawbacks associated are the use of expensive palladium catalyst and strongly oxidising vanadium and phosphorous based reagents. The use of halogenated solvents, strong alkaline condition, the requirement of specialised reaction conditions, elevated temperature and longer reaction times are other drawbacks. Further, most of the reported methods for the preparation of carbodiimides are associated with the formation of urea, isothiocyanate and guanidine byproducts and the polymerisation, particularly for aromatic carbodiimides. Some of the reported methods, though interesting, are of no preparative value, because of the expensive and toxic nature of the reagents used. In spite of its known toxicity, yellow mercuric oxide (HgO) has remained as the most frequently used reagent till date.[1a]

We have been working on various aspects of green chemistry.[6] Our recent success on hypervalent iodine(III) mediated desulfurisation of dithiocarbamate salts to isothiocyanates further leading to heterocycles[7a] and cyanamides[7b] and the similar success using molecular iodine[8] prompted us to attempt an iodine mediated desulfurisation of 1,3-disubstituted thiourea for the preparation of carbodiimide. This approach is similar to the earlier desulfurisation strategy, where treatment of the 1,3-disubstituted thiourea with diacetoxyiodobenzene (DIB) gave carbodiimide as the intermediate which reacted with the liberated acetate from DIB giving N-acylated urea.[7c] In the absence of any external nucleophile, it should be possible to stop the reaction at the carbodiimide stage. When 1,3-diphenyl thiourea **1** (1 equiv) was treated with iodine (1.1 equiv) in the presence of a base, triethylamine (2 equiv) in ethyl acetate in an ice-cold condition, carbodiimide **1a** was obtained in good yield.[11] Among the various solvents tested, such as ethyl acetate, acetoni-



Scheme 1. Plausible mechanism for the formation of carbodiimide from 1,3-disubstituted thiourea.

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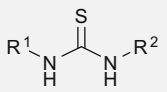
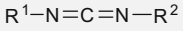
Table 1
Preparation of carbodiimide from 1,3-disubstituted thiourea and iodine[a]

	Substrate		Product[b]	
				
	R^1	R^2		Yield (%)[c]
1	C_6H_5–	C_6H_5–	**1a**	86
2	*p*-$CH_3C_6H_4$-	*p*-$CH_3C_6H_4$–	**2a**	93
3	*o,p*-$(CH_3)_2C_6H_3$-	*o,p*-$(CH_3)_2C_6H_3$–	**3a**	88
4	*p*-$OCH_3C_6H_4$-	*p*-$OCH_3C_6H_4$–	**4a**	76
5	*o*-$OCH_3C_6H_4$–	*o*-$OCH_3C_6H_4$–	**5a**	73
6	*p*-ClC_6H_4–	*p*-ClC_6H_4–	**6a**	70
7	*p*-BrC_6H_4–	*p*-BrC_6H_4–	**7a**	72
8	C_6H_5–	*p*-$CH_3C_6H_4$–	**8a**	94
9	C_6H_5–	*o,o'*-$(CH_3)_2C_6H_3$–	**9a**	58
10	C_6H_5–	*o*-ClC_6H_4–	**10a**	68
11	C_6H_5–	*m*-$NO_2C_6H_4$–	**11a**	81
12	C_6H_5–	*p*-BrC_6H_4–	**12a**	82
13	*p*-$CH_3C_6H_4$–	*p*-ClC_6H_4–	**13a**	90
14	C_6H_5–	C_6H_{11}–	**14a**	85
15	C_6H_5–	*m,p*-$(OMe)_2C_6H_3CH_2CH_2$–	**15a**	67

[a] Reaction were monitored by TLC.
[b] Confirmed by IR, ^1H, and ^{13}C NMR.[12]
[c] Isolated yield.

trile, dichloromethane, toluene and THF, ethyl acetate was found to be the most efficient solvent giving the highest yield. The reaction when performed at 0–5 °C gives better yields with fewer side products which otherwise is associated with a number of side products when carried out at room temperature. Further, a portion-wise addition of iodine over a period of 10–15 min furnished better yields compared to the addition in one go.

The proposed mechanism for the formation of carbodiimide is shown in Scheme 1. This is supported by the isolation of precipitated elemental sulfur. The requirement of 2 equiv of base triethylamine is essential for this reaction. It may be noted here that 1,3-diarylthiourea on treatment with iodine in the absence of triethylamine undergoes oxidative cyclisation to yield benzothiazole exclusively (Scheme 1).

To demonstrate the versatility of this methodology we synthesised a series of symmetrical and unsymmetrical 1,3-diaryl as well as aryl–alkyl thioureas which were subjected to a treatment with iodine and triethylamine in ethyl acetate. As can be seen from Table 1, symmetrical thioureas containing electron-donating groups at *o*- and *p*- positions or both the positions **2**–**5**, all gave their corresponding carbodiimides **2a**–**5a** in good to excellent yields (73–93%). This methodology was found to be equally efficient even when moderately electron-withdrawing substituents such as chloro **6** or bromo **7** groups are attached to the aromatic ring.

After the successful preparation of various symmetrical carbodiimides, we tested this strategy on some unsymmetrical 1,3-disubstituted thioureas. Unsymmetrical substrate, 1-phenyl-3-*p*-tolyl thiourea **8** afforded corresponding carbodiimide **8a** in high yield (94%) but 1-(2,6-dimethylphenyl)-3-phenylthiourea **9** gave much lower yield (58%) of the product **9a**. The lesser yield in the latter may possibly be due to the steric crowding imparted by the two bulky methyl substituents from the adjacent ortho positions which perhaps prevented the deprotonation by the hindered triethylamine base. Again, starting with 1-(2-chlorophenyl)-3-phenylthiourea **10**, the corresponding carbodiimide **10a** was obtained in satisfactory yield. In the case of thiourea **11** the conversion to carbodiimide **11a** was found to be excellent (81%). Other unsymmetrical thioureas **12**–**15** gave good to satisfactory yields of their corresponding carbodiimides **12a–15a** as shown in Table 1. It may be noted that substrates **14** and **15** are unsymmetrical thioureas having an aryl group on one side and an alkyl pendant on the other. When we applied this protocol to bis-alkyl thioureas such as 1,3-dicyclohexylthiourea, the method was not very successful in giving a number of side products. Earlier, we had observed a pK_a dependent regioselectivity for unsymmetrical thioureas.[6a,9] On the basis of our previous observations[6a,8,9] and mechanism proposed in Scheme 1, we have reasoned that this has to do with the acidity of the aliphatic amine protons attached to the thiourea. The acidity of the aromatic amines (pK_a in the range 3.8–5.6) are expected to be enhanced further when attached to the thiourea and are thus sufficiently acidic to be abstracted by triethylamine base (pK_a 10.78). On the other hand, the cyclohexylamine (pK_a 10.66), even when attached to the thiourea is probably not sufficiently acidic to be abstracted by triethylamine base and particularly so when two subsequent deprotection are to take place. This explains why the method is not feasible for the synthesis of 1,3-dialkyl substituted carbodiimide and is thus unsuccessful in synthesising the useful reagent dicyclohexylcarbodiimide (DCC). Indeed this is perhaps the only drawback associated with this methodology compared to the reported procedures.

In summary, we have developed a general, economical and environmentally acceptable method for the preparation of carbodiimides from their corresponding 1,3-disubstituted thioureas. In comparison to the reported methods for the preparation of carbodiimides, our procedure is perhaps the simplest and most convenient and thus has industrial implication.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.12.017.

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11. *General procedure for preparation of 1,3-diphenyl carbodiimide* **1a**[10a] *from 1,3-diphenyl thiourea* **1***:* To a stirred and ice-cooled solution of 1,3-diphenylthiourea **1** (457 mg, 2 mmol) in ethyl acetate (5 mL), was added triethylamine (556 μL, 4 mmol). To this was added iodine (558 mg, 2.2 mmol) portion-wise over a period of 30 min. A light yellow colour precipitate of sulfur started separating out during this period. The precipitated sulfur was filtered, the organic layer evaporated and then extracted with hexane (2 × 15 mL). The solution was concentrated under reduced pressure and purified by eluting through a short column of silica gel (100% hexane) to give **1a** (334 mg, 86%). Oily liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 (m, 6H), 7.31 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 124.4, 125.8, 129.7, 135.5, 138.5. IR (KBr): 2936 (w), 2139 (s), 2105 (m), 1588 (w), 1487 (m), 1202 (w), 757 (w). Calcd for $C_{13}H_{10}N_2$ (194.23): C, 80.39; H, 5.19; N, 14.42. Found: C, 80.45; H, 5.21; N, 14.38.
12. *Spectral data of compounds*:
    1,3-Di(p-tolyl)carbodiimide **2a**: white solid; mp 57–58 °C (Lit[10b] 55–58 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.31 (s, 6H, 2 × CH_3), 7.05 (d, 4H, J = 8.4 Hz), 7.10 (d, 4H, J = 8.4 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.1, 124.0, 130.2, 135.4, 135.9, 136.1. IR (KBr): 2922 (w), 2761 (w), 2678 (w), 2137 (s), 2108 (s), 1607 (w), 1504 (m), 1209 (w), 814 (m) cm^{-1}. Calcd for $C_{15}H_{14}N_2$ (222.29): C, 81.05; H, 6.35; N, 12.60. Found: C, 81.11; H, 6.32; N, 12.58.
    1,3-Di(2,4-dimethylphenyl)carbodiimide **3a**: white solid; mp 71.5–72.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.32 (s, 6H, 2 × CH_3), 2.36 (s, 3H, 2 × CH_3), 6.95–7.11 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 18.1, 20.8, 124.0, 127.4, 131.4, 131.9, 133.8, 134.5, 134.7. IR (KBr): 2920 (w), 2142 (s), 2116 (s), 1496 (m), 1209 (m), 1119 (w), 811 (w) cm^{-1}. Calcd for $C_{17}H_{18}N_2$ (250.34): C, 81.56; H, 7.25; N, 11.19. Found: C, 81.54; H, 7.28; N, 11.23.
    1,3-Di(p-methoxyphenyl)carbodiimide **4a**: oily liquid; (Lit.[2c] mp 52–53 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.7 (s, 6H), 6.82 (d, 4H, J = 8.0 Hz), 7.08 (d, 2H, J = 8.0 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 55.5, 114.8, 125.1, 131.3, 136.5, 157.4. IR (KBr): 2927 (w), 2126 (s), 2105 (s), 1501 (s), 1245 (m), 828 (w), 764 (s) cm^{-1}. Calcd for $C_{15}H_{14}N_2O_2$ (254.28): C, 70.85; H, 5.55; N, 11.02. Found: C, 70.88; H, 5.61; N, 11.08.
    1,3-Di(o-methoxyphenyl)carbodiimide **5a**: white solid; mp 71.5–72.5 °C; (Lit.[7c] 72–76 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.85 (s, 6H, 2 × CH_3), 6.90 (m, 4H), 7.14 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 56.2, 111.5, 121.1, 125.2, 126.0, 128.1, 137.6, 154.1. IR (KBr): 2938 (w), 2138 (s), 2102 (s), 1492 (m), 1454 (w), 1257 (m), 1024 (w), 754 (m) cm^{-1}. HRMS (ESI): MH^+, found 255.2929, $C_{15}H_{15}N_2O_2$ requires 255.2957. Calcd for $C_{15}H_{14}N_2O_2$ (254.28): C, 70.85; H, 5.55; N, 11.02. Found: C, 70.81; H, 5.65; N, 11.00.
    1,3-Di(p-chlorophenyl)carbodiimide **6a**: white solid; mp 51–52 °C; (Lit.[10a] 54–57 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09 (d, 4H, J = 8.8 Hz), 7.29 (d, 4H, J = 8.8 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 125.7, 129.9, 131.5, 134.8, 136.8. IR (KBr): 2924 (w), 2166 (s), 2137 (s), 1485 (s), 1209 (m), 1091 (s), 834 (s) cm^{-1}. Calcd for $C_{13}H_8Cl_2N_2$ (263.12): C, 59.34; H, 3.06; N, 10.65. Found: C, 59.33; H, 3.02; N, 10.59.
    1,3-Di(p-bromophenyl)carbodiimide **7a**: white solid; mp 69–70 °C; (Lit.[10c] 69–71 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.04 (d, 4H, J = 8.8 Hz), 7.45 (d, 4H, J = 8.8 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 119.1, 126.0, 132.8, 134.6, 137.2. IR (KBr): 2159 (w), 2159 (s), 2116 (s), 1578 (w), 1480 (m), 1209 (m), 1069 (w), 1009 (w), 822 (s) cm^{-1}. Calcd for $C_{13}H_8Br_2N_2$ (352.03): C, 44.36; H, 2.29; N, 7.96. Found: 44.39; H, 2.33; N, 7.90.
    Phenyl-p-tolyl-carbodiimide **8a**: clourless liquid (Lit.[10d] liquid); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.33 (s, 3H, CH_3), 7.09 (m, 7H), 7.28 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.7, 123.7, 123.8, 125.3, 129.3, 129.9, 135.1, 135.2, 135.3, 138.4. IR (KBr) 2921 (w), 2129 (s), 2104 (s), 1594 (m), 1519 (w), 1494 (m), 1281 (w), 1206 (m), 816 (m) cm^{-1}. Calcd for $C_{14}H_{12}N_2$ (208.26): C, 80.74; H, 5.81; N, 13.45. Found: C, 80.71; H, 5.78; N, 13.49.
    (2,6-Dimethyl-phenyl)-phenyl-carbodiimide **9a**: yellowish liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.38 (s, 6H, 2 × CH_3), 6.98 (m, 3H). 7.08–7.17 (m, 3H), 7.29 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 19.2, 123.9, 124.9, 125.3, 128.4, 129.6, 131.7, 133.0, 135.1, 140.0. IR (KBr): 2917 (w), 2151 (s), 2120 (m), 1590 (w), 1474 (w), 1198 (w), 754 (w) cm^{-1}. Calcd for $C_{15}H_{14}N_2$ (222.29): C, 81.05; H, 6.35; N, 12.60. Found: C, 81.10; H, 6.38; N, 12.61.
    (2-Chloro-phenyl)-phenyl-carbodiimide **10a**: clourless liquid (Lit.[10d] liquid); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.06 (m, 1H), 7.17 (m, 5H), 7.33 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 124.4, 125.7, 125.8, 126.4, 127.7, 129.6, 130.1, 133.0, 135.9, 138.0. IR (KBr): 2907 (w), 2145 (s), 2103 (s), 1584 (m), 1481 (m), 1215 (m), 1051 (w), 751 (m) cm^{-1}. Calcd for $C_{13}H_9ClN_2$ (228.68): C, 68.28; H, 3.97; N, 12.25. Found: C, 68.30; H, 3.98; N, 12.24.
    (3-Nitro-phenyl)-phenyl-carbodiimide **11a**: yellowish liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (m, 3H), 7.36 (m, 2H), 7.49 (m, 2H), 8.02 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 119.2, 120.3, 124.7, 126.6, 129.8, 130.2, 130.4, 133.8, 136.8, 140.8, 149.2. IR (KBr): 2140 (s), 2104 (m), 1638 (w), 1526 (w), 1349 (w), 1208 (w), 751 (s) cm^{-1}. Calcd for $C_{13}H_9N_3O_2$ (239.23): C, 65.27; H, 3.79; N, 17.56. Found: C, 65.33; H, 3.75; N, 17.55.
    (4-Bromophenyl)-phenyl-carbodiimide **12a**: oily liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.00 (d, 2H, J = 8.0 Hz), 7.15 (m, 3H), 7.29 (m, 2H), 7.38 (d, 2H, J = 8.00 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 118.8, 124.5, 125.9, 126.0, 129.7, 132.7, 134.9, 137.8, 137.9. IR (KBr): 3063 (w), 2137 (s), 2101 (s), 1595 (w), 1582 (m), 1485 (m), 1206 (m), 1069 (w), 825 (m), 755 (m) cm^{-1}. Calcd for $C_{13}H_9BrN_2$ (273.13): C, 57.17; H, 3.32; N, 10.26. Found: C, 57.21; H, 3.29; N, 10.27.
    (4-Chloro-phenyl)-p-tolyl-carbodiimide **13a**: yellowish liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30 (s, 3H, CH_3), 7.07 (m, 6H), 7.23 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.1, 124.2, 125.4, 129.7, 130.3, 130.8, 135.1, 135.3, 135.9, 137.7. IR (KBr) 2921 (w), 2135 (s), 2108 (s), 1591 (w), 1492 (m), 1209 (m), 1093 (w), 828 (m), 816 (m) cm^{-1}. Calcd for $C_{14}H_{11}ClN_2$ (242.70): C, 69.28; H, 4.57; N, 11.54. Found: C, 69.28; H, 4.54; N, 11.52.
    Cyclohexyl-phenyl-carbodiimide **14a**: yellowish liquid (Lit.[4a] liquid); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.20–1.37 (m, 3H), 1.42–1.56 (m, 3H), 1.75 (m, 2H), 1.98 (m, 2H), 3.44 (m, 1H), 7.07 (m, 3H), 7.26 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 24.4, 25.4, 35.0, 56.7, 123.4, 124.6, 129.4, 136.3, 141.0. IR (KBr): 2931 (m), 2855 (w), 2129 (s), 2049 (w), 1595 (m), 1500 (w), 1152 (m), 755 (m) cm^{-1}. Calcd for $C_{13}H_{16}N_2$ (200.28): C, 77.96; H, 8.05; N, 13.99. Found: C, 77.98; H, 8.01; N, 13.95.
    [2-(3,4-Dimethoxy-phenyl)-ethyl]-phenyl-carbodiimide **15a**: yellowish liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.92 (t, 2H, J = 6.8 Hz, NCH_2), 3.64 (t, 2H, J = 6.8 Hz, $ArCH_2$), 3.80 (s, 3H, CH_3), 3.82 (s, 3H, CH_3), 6.75 (m, 3H), 6.86 (d, 2H, J = 7.2 Hz), 7.06 (t, 1H, J = 7.2 Hz), 7.21 (t, 2H, J = 8.0 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 37.2, 48.1, 55.8, 55.9, 111.5, 112.2, 120.9, 123.6, 124.6, 129.2, 130.8, 136.4, 140.3, 147.9, 149.0. IR (KBr): 2936 (m), 2834 (w), 2125 (s), 1592 (m), 1505 (m), 1463 (w), 1261 (m), 1237 (m), 1028 (m), 804 (w), 760 (m) cm^{-1}. Calcd for $C_{17}H_{18}N_2O_2$ (282.34): C, 72.32; H, 6.43; N, 9.92. Found: C, 72.36; H, 6.41; N, 9.94.