Res Chem Intermed (2012) 38:2479–2489
DOI 10.1007/s11164-012-0563-4

An improved method for the preparation of alkyl/arylurea derivatives using chlorocarbonylsulfenyl chloride as carbonylating agent

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Received: 11 January 2012 / Accepted: 18 April 2012 / Published online: 8 May 2012

Abstract A convenient procedure has been developed for preparation of amine-substituted or monomethylamine-substituted alkyl/arylurea derivatives. The method comprises two steps—reaction of an alkyl/aryl amine with chlorocarbonylsulfenyl chloride in a non-polar solvent to produce an alkyl/arylcarbonylsulfenyl chloride, then reaction of this alkyl/arylcarbonylsulfenyl chloride with ammonia or monomethylamine in a two-phase reaction with a phase-transfer catalyst, to produce the corresponding alkyl/aryl-substituted urea.

Keywords Aryl ureas · Cyclohexylamine · Chlorocarbonylsulfenyl chloride · Carbonylation

Introduction

Alkyl/aryl ureas (**3**) are well known commercial intermediates used for preparation of drugs and fine chemicals. Some of these ureas, shown in Fig. 1 (**3a–h**), have been produced industrially on a large scale.

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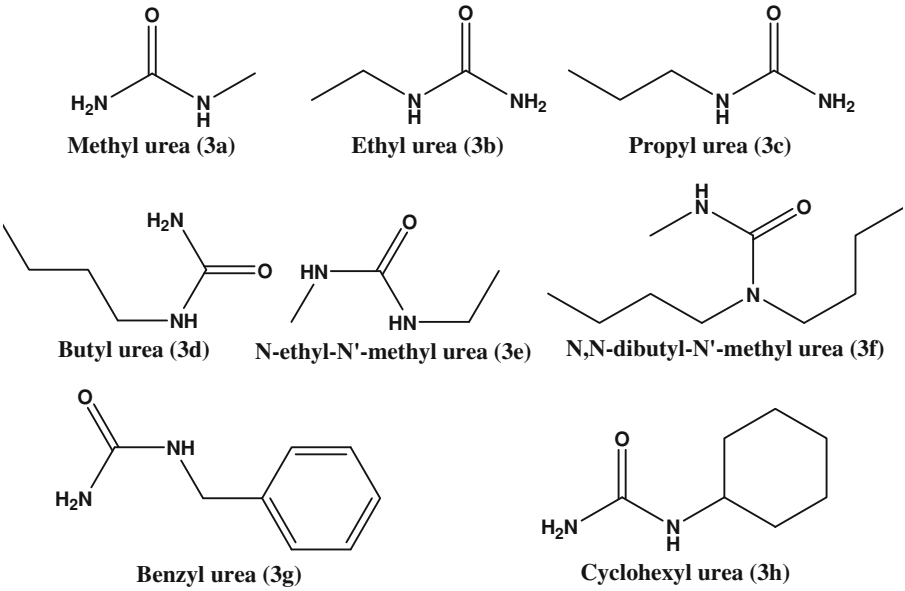


Fig. 1 Some commercially available alky/arylurea derivatives

Alkyl/aryl ureas are a family of well-known compounds. They are important intermediates [1] in the production of isocyanate drugs, phytomedicines, and herbicides, and are used in coloring agents. Several methods for synthesis of mono alkyl/aryl ureas have been reported in the literature. Much literature is available, dealing with a wide variety of procedures for the preparation of alkyl/arylurea derivatives; most of the procedures entail:

1 reaction of ammonia with a suitable carbamoyl chloride obtained by phosgenation of the corresponding amine [2, 3];
2 reaction of salts of suitable amines with the cyanate of an alkaline metal [4–8];
3 reaction of suitable isocyanates with ammonia [9–12];
4 reaction of a suitable amine with nitrourea then transamidation of the resulting products with dimethylamine [13, 14];
5 transamidation of diaryl ureas with dimethylamine [15–18]; and
6 oxidative–reductive carbonylation of nitroarenes and dimethylamine with carbon monoxide as catalyst [11, 19, 20].

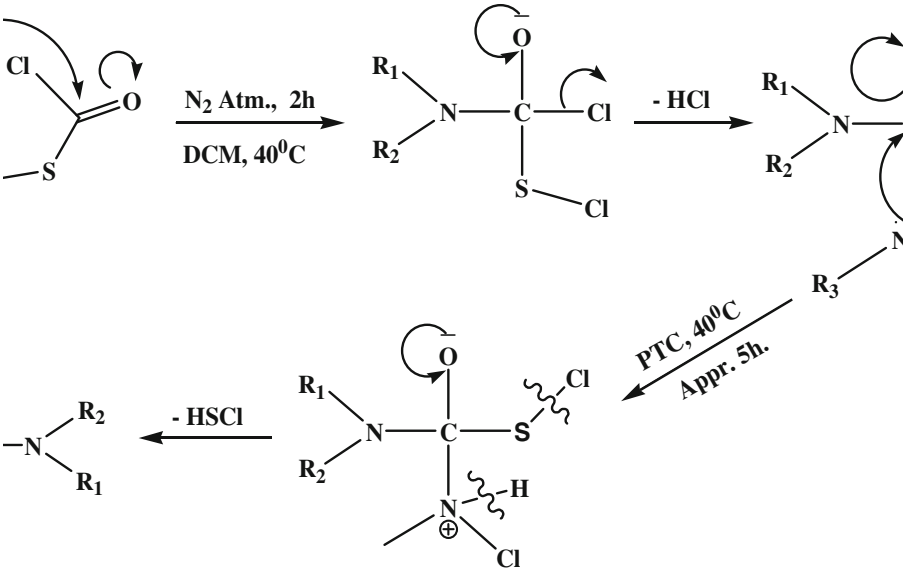
The starting materials used in the first four procedures are fairly expensive, highly toxic, and difficult to obtain. The fifth process does not have the same disadvantages as the first four processes. For example, in methods 1 and 2 the raw materials are toxic, difficult to obtain, and very expensive. Phosgene is a potentially toxic chemical, an environmental hazard, a source of accidents, and is difficult to handle, thus posing a risk not only to workers but also to the health of nearby inhabitants as a result of environmental pollution. In method 5, the urea used in transamidation is an innocuous non-toxic, and inexpensive compound, but yields of the reaction products are fairly low, and purity, as indicated by melting point, is very low.

The objective of this study was to elaborate a economical, commercially viable process for preparation of alkyl/arylurea derivatives of general formula **3**. In this communication, the corresponding amines are first reacted with chlorocarbonylsulfenyl chloride (CCSC) in dichloromethane under a nitrogen atmosphere. The resulting alkyl/arylcarbonylsulfenyl chlorides are then further reacted with ammonia or monomethylamine in a two phase reaction using a phase-transfer catalyst (PTC) to produce the corresponding alkyl/aryl ureas.

Results and discussion

In this work, carbonylation of the corresponding amine with the carbonylating agent CCSC under an N_2 atmosphere was followed by condensation with ammonia or monomethylamine in aqueous solution in a two-phase reaction using different non-polar solvents and different PTCs.

Because carbonylation of the corresponding amine with CCSC is a very fast reaction initiated by nucleophilic substitution of the loan pair of electrons present on the nitrogen of the amine with a positively charged carbonyl carbon to form *N*-alkyl/arylcarbonylsulfenyl chloride, a further loan pair of electrons present on the nitrogen of ammonia or methylamine can undergo nucleophilic substitution with the positively charged carbonyl carbon of the alkyl/arylcarbonylsulfenyl chloride to form the corresponding alkyl/arylurea derivatives. The detailed reaction mechanism is shown in Scheme 1.



Scheme 1 General method for the preparation of monomethylamine/amine substituted alkyl/arylurea derivatives (**3a**–**h**): **3a**: Methylurea; **3b**: Ethylurea; **3c**: Propylurea; **3d**: Butylurea; **3e**: *N*-ethyl-*N'*-methylurea; **3f**: *N*,*N*-dibutyl-*N'*-methylurea; **3g**: Benzylurea; **3h**: Cyclohexylurea

The factors that affect completion of the second stage of the reaction include the two-phase system, the catalyst, the sequence of addition of the starting materials, and the quantity of solvent used.

Alkyl/arylcarbonylsulfenyl chloride in solvent was added dropwise to a solution of the PTC, sodium chloride, sodium hydroxide, boric acid, and monomethylamine or ammonia in water and triethylamine in organic solvent (dichloromethane).

The total amount of water and organic solvent used were optimized. Use of smaller amounts of water and organic solvent increased the viscosity of the mixture at the beginning of the reaction and affected the rate of stirring and the separation of the organic phase.

The purity and yield of the synthesized urea derivatives depend on different factors, for example the PTC, triethylamine, their respective concentrations, reaction temperature and time, and stirring rate. Considering these factors, the types of catalyst and their concentrations were first optimized.

To follow the reaction, GC with flame-ionization detection (FID) was chosen as the most appropriate technique for analysis of the composition of the alkyl/arylcarbonylsulfenyl chloride present in the organic phase.

In the first five experiments (Table 1, entries 1–5) the reaction was performed in H_2O–DCM at 40 °C in the presence of the PTC. In the absence of TEBA (Table 1, entry 5), most of starting alkyl/arylcarbonylsulfenyl chloride was found to be unreacted with organic phase after 3 h whereas on addition of TEBA the rate of conversion was increased (Table 1, entries 1–4).

Among the trialkylamines used in the literature, 4-dimethylaminopyridine (4-DMAP), a more sterically hindered amine, was successfully applied in our next experiments (Table 1 entry 6). Replacement of triethylenediamine (TEDA) by

Table 1 Effect of PTC and solvents in the synthesis of alkyl/aryl ureas **3a–h**

Entry	Tertiary amine	PTC	Solvent	Yield (%)
1	TEDA (0.11 mM)	Triethylbenzylammonium chloride (0.22 mM)	Dichloromethane–water	95
2	TEA (0.11 mM)	Triethylbenzylammonium chloride (0.15 mM)	Dichloromethane–water	72
3	TEDA (0.11 mM)	Triethylbenzylammonium chloride (0.05 mM)	Dichloromethane–water	55
4	TEDA (0.11 mM)	Triethylbenzylammonium chloride (0.10 mM)	Dichloromethane–water	88
5	TEDA (0.22 mM)	–	Dichloromethane–water	45
6	4-DMAP (0.11 mM)	Triethylbenzylammonium chloride (0.22 mM)	Dichloromethane–water	85
7	TEDA (0.11 mM)	Triethylbenzylammonium chloride (0.22 mM)	Ethylene dichloride	75
8	TEDA (0.11 mM)	Triethylbenzylammonium chloride (0.22 mM)	Tetrahydrofuran	52
9	TEDA (0.11 mM)	Triethylbenzylammonium chloride (0.22 mM)	Dimethyl sulfoxide	28

Reaction using alkyl/arylamine:CCSC 1.0 M:1.20 M

4-dimethylaminopyridine (4-DMAP) caused urea yield to decrease by 6–12 %. To eliminate byproduct formation by alky/arylcarbonylsulfenyl chloride hydrolysis, the concentration of unreacted alky/arylcarbonylsulfenyl chloride was kept as low as possible.

As indicated in Table 1, 0.22 mM TEBA, 0.11 mM TEDA, and a 5 h reaction time enabled maximum conversion of alky/arylcarbonylsulfenyl chloride with minimum hydrolysis at 40 °C using H_2O–DCM as solvent system (Table 1, entry 1).

In summary, both yield and purity of alkyl/arylurea derivatives produced by reaction of alky/arylcarbonylsulfenyl chloride with aqueous ammonia/monomethylamine using the PTC system are affected by different factors, for example the catalyst, temperature, and stirring of the reaction mixture.

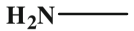
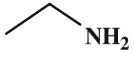
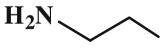
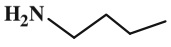
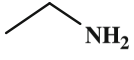
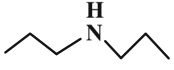
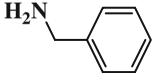
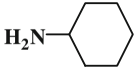
The tertiary amine catalyst should act as a protecting agent to prevent hydrolysis of the alky/arylcarbonylsulfenyl chloride and, at the same time, act as a suitable leaving group to enhance the reaction of alky/arylcarbonylsulfenyl chloride with ammonia/monomethylamine. TEDA was a good protecting agent, alky/arylcarbonylsulfenyl chloride was not hydrolyzed. Both DMAP and triethylamine (TEA) were suitable as temporary protecting agents and better leaving groups facing ammonia/monomethylamine. Therefore, in the presence of DMAP or TEDA. The reaction time must be minimized to prevent hydrolysis of alky/arylcarbonylsulfenyl chloride.

Use of 0.22 mM TEBA and 0.11 mM TEDA resulted in a reasonable rate of reaction with minimum hydrolysis of alky/arylcarbonylsulfenyl chloride. Performing the reaction under the optimized conditions resulted in conversion of the alky/arylcarbonylsulfenyl chloride to the urea derivative at 40 °C (using CH_2Cl_2/H_2O as solvent system) after 2 h with 90–95 % purity. The final optimized reaction conditions used for preparation of the alkyl/arylurea derivatives starting from the amine are listed in Table 2. Yields of the alkyl/arylurea derivatives formed by conducting the reaction under different conditions are compared in Table 3.

Conclusion

The method described is a simple efficient one-pot process for synthesis of commercially important urea derivatives by reaction of amines with CCSC followed by reaction with ammonia/monomethylamine. A notable feature of the method of preparation is that the process is economically viable, i.e. high rate of reaction, negligible byproducts, and cleaner reaction profiles, which makes it a useful and attractive process, especially for commercial synthesis. The general nature of the procedure is another important benefit, and producing a method requiring no phosgene is a major achievement. Simple experimental and product-isolation procedures are certainly important in the development of greener and more efficient procedures for synthesis of the urea derivatives used as commercially important intermediates in the synthesis of different products, specifically drugs and herbicides. This is an important improvement over phosgenation and other costlier methods currently being used.

Table 2 Reaction conditions for synthesis of alky/arylurea derivatives **3a–h**

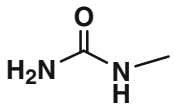
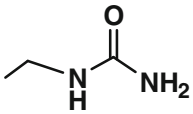
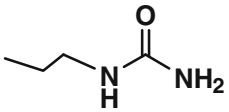
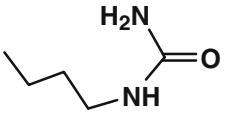
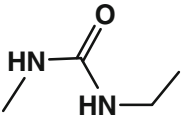
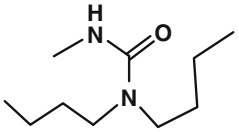
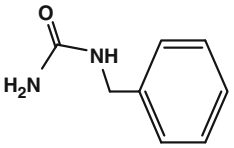
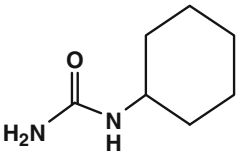
No.	Amine	1	Ratio (1/CCSC)	Time (h)	2	Ratio (2/MMA or NH_3)	Time (h)	3	Yield (%)[a] (purity, %)[b]	mp (°C)
1		**1a**	1:1.05	2	**2a**	1:1.10	6	**3a**	92 (97.00)	102–102.5
2		**1b**	1:1.10	4	**2b**	1:1.20	5	**3b**	93.5 (95.8)	92.0–92.5
3		**1c**	1:1.15	2	**2c**	1:1.25	4	**3c**	92 (95.40)	93.0–96.0
4		**1d**	1:1.15	4	**2d**	1:1.20	6	**3d**	91 (94.50)	95.0–96.5
5		**1e**	1:1.10	3	**2e**	1:1.25	5	**3e**	88 (94.00)	50–50.5
6		**1f**	1:1.05	5	**2f**	1:1.20	7	**3f**	85 (92.00)	45.5–46.0
7		**1g**	1:1.10	3	**2g**	1:1.15	6	**3g**	88 (93.50)	148.0–149.0
8		**1h**	1:1.15	5	**2h**	1:1.15	5	**3h**	86 (95.00)	193.0–194.5

[a] Yields of the isolated products

[b] Purity determined by GC

3a: methylurea, **3b**: ethylurea, **3c**: propylurea, **3d**: butylurea, **3e**: *N*-ethyl-*N'*-methyl urea, **3f**: *N*,*N*-dibutyl-*N'*-methyl urea, **3g**: benzylurea, **3h**: cyclohexylurea

Table 3 Comparison of the yields of alkyl/arylurea derivatives obtained by conducting the reaction under different conditions

No.	Product	Yield (%), this method	Yield (%) of methods reported in the literature			
			A [24]	B [25]	C [26]	D [27]
1		92.00	91.20	–	79.00	–
2		93.50	89.93	–	83.00	–
3		92.00	–	78.43	81.00	–
4		91.00	95.13	03.50	–	–
5		88.00	97.70	–	–	–
6		85.00	90.25	–	–	–
7		88.00	93.10	40.66	–	–
8		86.00	94.57	–	–	90.95

Experimental

All chemicals (ammonia, monomethylamine, benzylamine, ethylamine, propylamine, butylamine, dibutylamine, cyclohexylamine, DCM, TEBA, TEDA, 4-DMAP, and TEA) were purchased from Merck, India. Perchloromethyl mercaptan was donated by India Pesticides Limited, India. Melting points were determined on a Paramount digital melting point instrument. Gas chromatographic (GC) analysis was performed on a Thermo Fisher GC model, GC-1000. ^{1}H NMR spectra were obtained on a AVAN DMX 400 (Brukerspectrometer). Mass and exact-mass spectra were recorded on a Perkin–Elmer mass spectrometer.

General procedure for synthesis of the urea derivatives

A 2,000 ml four-necked double-glass-walled reactor (with water at the desired temperature circulating between the walls) was equipped with a mechanical stirrer (made up of one four-blade turbine), a condenser, a dropping funnel, and a thermometer. Anhydrous amine (0.5 mol) in 600 ml dichloromethane was placed in the reactor, then CCSC solution (1.05–1.25 M) was added dropwise over a period of 60–90 min under vigorous reflux in a nitrogen atmosphere. The reaction was mildly exothermic. The progress of the reaction was monitored by GC. After the addition, the reaction was further maintained at reflux temperature for an additional 2 h, by which time evolution of HCl had ceased. Partial distillation of dichloromethane ($\sim$250 ml) was conducted to remove any dissolved HCl. The alkyl/arylcarbonylsulfenyl chloride was removed from the flask and placed in a pressure-equalizing addition funnel. Then, 10.55 g (0.17 mol) boric acid, 58.5 g (1.0 mol) NaCl, 5.73 g (0.145 mol) NaOH, and 250 mg (4.55 mM) TEBA were dissolved in 600 ml water. The pH of the solution was maintained between 10.0 and 10.5 at 25 °C. This solution and 62 mg (0.11 mM) TEDA in 300 ml dichloromethane were then placed in the stirred reaction flask. The temperature of the reaction mixture was stabilized at 30 °C, by use of water circulation, while stirring at 1,600 rpm, and the solution of alky/arylcarbonylsulfenyl chloride in dichloromethane was added dropwise during 25 min while the reaction mixture temperature was maintained at 40 °C, and vigorous stirring was continued. The reaction mixture, especially the organic layer, became a milky viscous suspension within 30 min. Stirring was continued for a further 2 h until the mixture became completely clear. The aqueous layer pH was maintained above 9.0 throughout the reaction. The lower organic layer was removed after settling for 15 min and the reflux condenser was replaced by a distillation head connected to a condenser and collector. The water and volatile impurities were removed by vacuum distillation. The residue obtained was extracted with 200 ml dimethylformamide followed by crystallization to obtain the urea as a 98.5 % pure product (GC area %).

Methylurea (**3a**)

Yield: 34.10 g (92 %); 97.0 % purity (GC), colorless needles from chloroform, mp: 102–102.5 °C (Lit[24]).

^{1}H NMR (400 MHz): δ ppm = 2.46 (d, J = 5.0 Hz, 3 H, CH_3), 5.49 (s, 2H, NH_2), 5.85 (s, H, NH).

MS (E1, 70 eV): m/z (%) = 75.8.

Ethylurea (**3b**)

Yield: 41.10 g (93.5 %); 95.80 % purity (GC), colorless needles from ethyl acetate, mp: 92.0–92.5 °C (Lit[24]).

^{1}NMR (400 MHz): δ ppm = 1.16 (t, J = 7.00, 2H, –CH_3),3.20 (d, J = 7.0 Hz, 2 H, N–CH_2), 5.01 (br s, 2H, NH_2).

MS (E1, 70 eV): m/z (%) = 89.1.

Propylurea (**3c**)

Yield: 45.65 g (92 %) 95.4 % purity (GC), colorless needles, mp: 173–174 °C (Lit[25]).

^{1}NMR (400 MHz): δ ppm = 1.06 (t, J = 7.00, 3H, –CH_3), 1.68(m, 2H, J = 7.00, –CH_2), 3.40 (t, J = 7.0 Hz, 2H, N–CH_2), 5.51 (br s, 2H, NH_2).

MS (E1, 70 eV): m/z (%) = 103.1.

Butylurea (**3d**)

Yield: 52.80 g, (91 %), 94.5 % purity (GC), colorless needles, mp: 95–96.5 °C (Lit[24]).

^{1}NMR (400 MHz): δ ppm = 1.1 (t, 3H, CH_2–$\underline{CH_3}$), 1.32 (m, 2H, CH_2–($\underline{CH_2}$)–CH_3), 1.5 (m, 2H, –CH_2), 2.9 (t, 2H, –N–CH_2–), 5.50 (br s, 2H, NH_2), 5.89 (br s, 1 H, NH).

MS (E1, 70 eV): m/z (%) = 117.2.

N-ethyl-*N*′-methylurea (**3e**)

Yield: 38.70 g, (88 %), 94 % purity (GC), colorless needles, mp: 50–51.5 °C (Lit[24]).

^{1}NMR (400 MHz): δ ppm = 1.12 (t, J = 7.00, 3H, CH_2–$\underline{CH_3}$), 2.75 (d, J = 5.00, 3H, NH–CH_3), 3.17 (dq, J = 7.00, 2H, CH_2), 5.53 (br s, 2H, NH_2).

MS (E1, 70 eV): m/z (%) = 103.2.

N,*N*-dibutylurea (**3f**)

Yield: 67 g, (85 %), 92 % purity (GC), colorless needles, mp: 45.5–46.0 °C (Lit[24]).

^{1}NMR (400 MHz): δ ppm = 1.12–1.75 (m, 8H, CH_2–($\underline{CH_2}$)$_2$–CH_3), 2.84 (d, J = 5.00, 3H, NH–$\underline{CH_3}$), 3.20 (t, J = 7.20, 4H, N[CH_2–(CH_2)$_2$–CH_3], 4.35 (br s, 1 H, NH).

MS (E1, 70 eV): m/z (%) = 173.2.

Benzylurea (**3g**)

Yield: 66 g, (88 %), 93.5 % purity (GC), organic layer was washed with water followed by concentration under vacuum the crude product was further recrystallized in diethyl ether. mp: 148–149 °C (Lit[21]).

^{1}NMR (400 MHz): δ ppm = 4.15(d, J = 6.00, 2H, CH_2), 5.42 (br s, 2H, NH_2), 6.35 (br s, 1H, NH), 7.05–7.25 (m, 5H, phenyl).

MS (E1, 70 eV): m/z (%) = 151.2

Cyclohexylurea (**3h**)

Yield: 61 g, (86 %), 95 % purity (GC), colorless needles, mp: 193–194.5 °C (Lit[24]).

^{1}NMR (400 MHz): δ ppm = 0.51–1.30 (5 m, 10H, 5 × CH_2), 2.75–2.89 (m, 1H, CH), 4.88 (br s, 2H, NH_2), 5.39 (d, 1H, NH).

MS (E1, 70 eV): m/z (%) = 143.2.

Chlorocarbonylsulfenyl chloride (CCSC) [21–23]

Trichloromethanesulfenyl chloride (PCMM) (294 ml, 500 g, 2.7 mol) was placed in a 2-l reaction flask equipped with reflux condenser, thermometer, and stirrer. A mixture of water (54 ml, 3.0 M) in concentrated sulfuric acid (620 ml) was added dropwise over 3 h. The heterogenous mixture was vigorously stirred for 6 h at 45–50 °C as HCl evolved and was then stirred overnight at 25 °C to ensure complete conversion of PCMM to CCSC. The progress of the reaction was monitored by GC. The upper phase (280 g, 80 %) was separated and distilled through a column, b.p. 98–101 °C (Lit[21], b.p. 98 °C) to provide, typically, 230 g (65 %) CCSC as a clear light yellow liquid.

Acknowledgments The authors gratefully acknowledge the Center for Biomedical Magnetic Resonance (CBMR; SGPGIMS), Lucknow, for NMR spectra, and the Central Drug Research Institute (CDRI), Lucknow, for mass spectra. One of the authors (K. Adeppa) wishes to convey his grateful feelings of gratitude to India Pesticides Ltd, Lucknow, India, for providing all laboratory facilities and financial support, which made it possible to complete this work successfully.

References

1. Ulmann's Encyclopaedia of Industrial Chemistry, vol A 27, 5th edn., p. 355
2. C.W.E.I. Todd, Preparation of 3-(halophenyl)-1-(methyl or ethyl) urea and herbicidal composition and application, U.S. Patent 2764478 (1953)
3. N.E.E.I. Searle, Weed control composition and method of preparation, U.S. Patent 2764478 (1956)
4. O. Scherer, G. Horlein, H. Schonowsky, Preparation of urea derivatives and their use as herbicides, U.S. Patent 3937726 (1976)
5. D.M. Spatz, B. Cross, Preparation of *para*-phenylalkoxy phenyl urea and thiourea compound and their herbicidal use, U.S. Patent 4289903 (1981)
6. K.H. Koenig, V. Schwendemann, U. Schirmer, M. Liesner, B. Wuerzer, Process for the preparation of halogenoalkylphenyl ureas and their use in combating undesired plant growth, DE Patent 3213375 (1983)
7. N. Haeberle, H. Oeltze, L. Brader, Process for the preparation of urea derivatives, DE Patent 3638753 (1988)

8. M. Haug, H.J. Santel, R.R. Schmidt, H. Strang, Process for the preparation of difluorophenyl urea derivatives and their use as herbicides, DE Patent 3800269 (1989)
9. A.G. Ciba Geigy, Method of selectively combating weeds with 4-isopropyl phenyl ureas, GB. Patent 1407587, 1975. Chem. Abstr. **84**, 4711 (1976)
10. R. Sales, L. Barquets, R. Perez Esteban, A. Martin Recio, G. Hervas, ES Patent 520096 (1984)
11. X. Wang, J. Mei, S. Lu, C.N. Patent 1597663, 2005. Chem. Abstr. 144, 191981 (2006)
12. W. Schroth, J. Andersch, H.D. Schaedler, R. Spitzner, Chem. Ztg. **113**, 261–271 (1989)
13. R.L. Jones, Preparation of alkyl–aryl urea, U.S. Patent 2768971 (1956)
14. Z. Wu, D. Guo, Z. Zou, Synthetic method of herbicide isoproturon, C.N. Patent 1063279 (1992)
15. R.H. Werther, H. Korntner, E. Auer, K. Thoonhofer, Process for the preparation of pure asymmetric disubstituted ureas, Patent Application EP 427963 (1991)
16. Y. Yang, S. Lu, Substitution reaction of *N*,*N*′-diphenylurea by amines to unsymmetric phenylureas. Org. Prep. Proc. Int. **31**, 559–576 (1999)
17. Y. Yang, S. Lu., C.N. Patent 1276368 (2000)
18. X. Wang, P. Li, X. Yuan, S. Lu, Selenium catalyzed carbonylation of nitroarenes to symmetrical 1,3-diaryl ureas under solvent free condition. J. Mol. Catal. A. Chem **253**, 261–264 (2006)
19. H. Tietz, K.L. Schwetlick, H.L. Schoebel, H. Herbig, H.J. Lankau, Process for the preparation of phenyl urea, D.D. Patent 227700 (1985)
20. Chemie, Georg Thieme Verlag, Stuttgart, Process for the preparation of *N*-aryl-*N*′-(mono-or di substituted)-urea derivatives, vol. 8, pp. 119–128 (1952)
21. W. Weiss, Process for the preparation of chlorocarbonylsulfenyl chloride, German Patent 1224720 (1964)
22. K. Adeppa, D.C. Rupainwar, M. Krishna, An improved cost effective synthesis of *N*,*N*-disubstituted carbamoyl halides and their derivatives. Can. J. Chem. **88**(12), 1277–1280 (2010)
23. K. Adeppa, D.C. Rupainwar, M. Krishna, An improved method for the preparation of some herbicidal 1,1-dimethyl-3-aryl ureas using chlorocarbonylsulfenyl chloride as a carbonylating agent. Synth. Commun. **42**(5), 714–721 (2012)
24. P. Edoardo, D. Jacopo, S. Anna Maria, Process to prepare alkyl ureas from *O*,*S*-dimethyl dithio carbonate, European Patent 1334965A1 (2003)
25. J. Kenson Simens, T. Ohio, Production of urea derivatives, U.S. Patent 2673859 (1950)
26. K. Findeisen, R. Freimuth, K. Wagner, Process for the preparation of alkyl ureas, U.S. Patent 4310692 (1982)
27. R. Fauss, K. Findelsen, U. Dobereiner, Process for the preparation of monocyclohexyl urea, U.S. Patent 4740618 (1988)