



Evaluation of Synthesis of Methyl 3-Chloro-5-(4,6-dimethoxypyrimidin-2-ylcarbamoylsulfamoyl)-1-methylpyrazole-4-carboxylate Using Green Metrics

ROHIDAS GILBILE^{1,2,*}, RAM BHAVANI² and RITU VYAS¹

¹Department of Chemistry, Pacific Academy of Higher Education and Research University, Udaipur-313 024, India

²Green Evolution Laboratories, Wangapally Village, Nalgonda-500 085, India

*Corresponding author: E-mail: rohidasgilbile2017@gmail.com

Received: 20 January 2017;

Accepted: 9 March 2017;

Published online: 13 May 2017;

AJC-18377

A modified synthesis of methyl 3-chloro-5-(4,6-dimethoxypyrimidin-2-ylcarbamoylsulfamoyl)-1-methylpyrazole-4-carboxylate (halosulphuron) is described. The merits of the synthesis are (i) one pot chlorination of methyl 1-methyl-1H-pyrazole-4-carboxylate (**1**) in presence of sulphuryl chloride resulting in methyl 3,5-dichloro-1-methyl-1H-pyrazole-4-carboxylate (**2**) (ii) conversion of 3-chloro-5-mercapto-1-methyl-1H-pyrazole-4-carboxylate (**3**) to 3-chloro-1-methyl-5-sulfamoyl pyrazole-4-carboxylate (**4**) under mild reaction conditions utilizing tetrabutyl ammonium chloride, N-chlorosuccinimide and ammonium carbonate (iii) condensation of sulphonamide (**4**) with carbamate (**6**) by microwave irradiation. Efforts were made to calculate, atom economy, reaction mass efficiency and E-factor for all the reaction steps involved in the synthesis of halosulfuron. The E-factor values in step 2 and step 4 reaction is lower, indicating that these reactions are greener (generation of less waste) when compared to the remaining steps in the synthesis.

Keywords: Halosulphuron, Synthesis, Sulphonylureas, Atomic economy, E-factor, Green metrics.

INTRODUCTION

Sulfonyl ureas are a series of environmentally well-suited herbicides that were discovered by DuPont Crop Protection in 1975 and first commercialized for wheat and barley crops in 1982. They have now been urbanized and commercialized worldwide in all main agronomic crops and for a lot of forte uses (e.g., range land/pasture, forestry, vegetation management). Sulfonyl ureas stand for a most important move ahead in global crop protection technology and have occupied a prominent key position in weed control by introducing a exclusive mode of action. Particularly, these compounds hinder with a key enzyme required for weed cell growth-acetolactate synthase. In addition, sulfonyl ureas are well-matched with the global drift toward post emergence weed control and integrated pest management.

Sulfonyl ureas, a characteristic group of herbicides, were broadly applied to scheming a selection of weeds in a assortment of crops and vegetables [1]. These herbicides reveal a simple but effectual biological mode of action through inhibiting acetolactate synthase (ALS). Because there was no acetolactate synthase balance in mammals, they were capable at ultra-low application rates while exhibiting extremely low acute and chronic mammalian toxicities in assessment with other herbicides [2]. The structure of the yeast acetolactate

synthase-chlorimuronethyl complex discloses that the two substituent on the heterocyclic ring made hydrophobic contact with certain specific protein [3]. Previous literature precedence demonstrates that monosulfuron (Fig. 1) with a mono-substituent on the pyrimidine ring also displace higher active herbicidal effects [4-8].

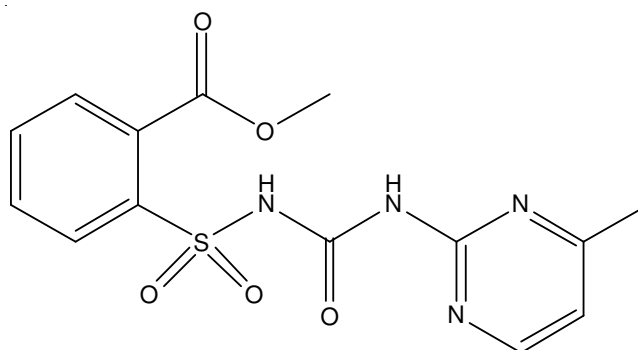


Fig. 1. Structure of monosulphuron

Some sulfonyl urea residues might survive in soil longer than that people expected, which would bring unfavourable effect to other following crops. For example, chlorsulfuron has been used in wheat and barley, but could stay vigorous in the soil for more than a few years and harm legumes and

oilseeds [9]. Flupyr-sulfuron methyl-sodium which was reported as a new 5-substituted sulfonylurea herbicide used to control grasses and broadleaf weeds in cereals [10] it has less than one month residual life [11]. Since then, several other 5-substituted sulfonylureas which show similar characteristics have been reported [12-14].

Attempts and efforts to decrease the environmental crash of a synthetic process should begin in the initial stage of the product/process development. Some tools have been established and further developed to tolerate fewer argumentative processes [15-23], such as choosing of solvents considering environmental, health and safety feature as well as the life cycle assessment (LCA) and economic measure. Kralisch and co-workers [24,25] evaluated and optimized an approach considering ecological and economic aspects of the production of some reactants and solvents used in synthesis, workup, recycling and disposal. To appraise the greenness of a product or process the authors used three main criteria: energy factor (EF), environmental and human health factor (EHF) and cost factor (CF). Such criteria describe the energy demand, toxicity and the cost of chemicals, auxiliaries and equipment used during a product or process of life cycle stages. There are some other metrics which can also be used such as atom economy (AE) [26,27], reaction mass efficiency (RME) [28], environmental factor (E-factor) [29-32], effective mass yield [33], mass intensity [34] and the process profile [35].

Thus, the present aim of this study was to evaluate the atom economy, reaction mass efficiency and environmental factor of the improved synthesis of methyl 3-chloro-5-(4,6-dimethoxy-pyrimidin-2-ylcarbamoylsulfamoyl)-1-methylpyrazole-4-carboxylate (Halosulphuron) using green metrics.

EXPERIMENTAL

The uncorrected melting points of compounds were taken in an open capillary in a paraffin bath. All reagents used were commercial and laboratory grade, melting points were determined in open capillaries and are uncorrected. IR spectra were recorded on potassium bromide disks on a Perkin-Elmer 383 spectrophotometer. ^1H NMR spectra were obtained on Varian 400 MHz instrument and Varian 300 MHz, with TMS as internal Standard and chemical shifts are expressed in δ ppm solvent used in CDCl_3 and $\text{DMSO}-d_6$ and mass spectrum on a Hewlett Packard mass spectrometer operating at 70 eV, purity of the compounds were checked by TLC, which is performed with E. Merck pre coated silica gel plates (60 F-254) with iodine as a developing agent.

Step-1: Preparation of methyl 3,5-dichloro-1-methyl-1H-pyrazole-4-carboxylate (2): Sulphuryl chloride (14.4 mL, 178.35 mmol) was added to a solution of compound **1** (5 g, 35.68 mmol) in dichloromethane (100 mL) and the resulting mixture was stirred at room temperature for 12 h. The reaction mixture was poured into saturated aqueous solution of sodium bicarbonate (40 mL) and extracted with dichloromethane (2×20 mL). The combined extracts were washed with brine solution (3×25 mL), dried over sodium sulphate (22 g), filtered and evaporated *in vacuo* to obtain the crude product. The crude compound was crystallized using cyclohexane (30 mL) to afford compound **1**. White powder; Yield: 7g, 94 %; m.p.: 58-

59 °C. ^1H NMR (300 MHz, CDCl_3): δ 3.85 (s, 3H, -OMe), 3.82 (s, 3H, -NMe); ESI-MS: m/z , 209 ($\text{M}+1$) $^+$.

Step-2: Preparation of methyl 3-chloro-5-mercapto-1-methyl-1H-pyrazole-4-carboxylate (3): To a solution of compound **2** (5 g, 23.92 mol) in DMF (11 mL) was added portion wise 70 % sodium hydrogen sulphide (4.78 g, 59.79 mmol) at room temperature. After stirring for 30 min at 60 °C, the mixture was cooled to room temperature, poured into water (90 mL) and the insoluble solid was filtered off. The filtrate was acidified with 35 % HCl (6 mL). The resultant solid was gathered, washed with water and dried *in vacuo* to obtain compound **3**. Off white solid; Yield: 4.74 g, 96 %; m.p.: 84-85 °C; ^1H NMR (300 MHz, CDCl_3): δ 6.64 (s, 1H, -SH), 3.88 (s, 3H, -OMe), 3.74 (s, 3H, -NMe); ESI-MS: m/z , 207 ($\text{M}+1$) $^+$.

Step-3: Preparation of methyl 3-chloro-1-methyl-5-sulfamoyl pyrazole-4-carboxylate (4): To a stirred mixture of compound **3** (4g, 19.35 mmol), tetrabutyl ammonium chloride (21.5 g, 77.36 mmol) and water (0.87 g, 48.33 mmol) in MeCN (25 mL) at 0 °C, N-chloro succinimide (7.75 g, 58.04 mmol) was added as a solid in portions over 1-2 min. After 30 min, ammonium carbonate (1.95g, 20.30 mmol) was added to the mixture over 1-2 min. The resulting mixture was stirred at room temperature for 12 h (until TLC showed complete disappearance of starting material). The mixture was filtered and rinsed with acetonitrile (20 mL). The filtrate was evaporated to obtain compound **4**. Recrystallization from a mixture of EtOH and water resulted in pure product. White solid, Yield: 4.41 g, 90 %; m.p.: 125-126 °C; ^1H NMR ($\text{DMSO}-d_6$, 300 MHz): δ 8.10 (brs, 2H, NH_2), 4.05 (s, 3H, NMe), 3.88 (s, 3H); ESI-MS: m/z , 254 ($\text{M}+1$);

Step-4: Preparation of phenyl 4,6-dimethoxypyrimidin-2-yl carbamate (6): To a stirred solution of compound **5** (1g, 6.45 mmol) in acetonitrile (10 mL) was added triethylamine (0.85 g, 8.40 mmol) followed by phenyl chloroformate (1.31 g, 8.37 mmol) at room temperature. The reaction mixture was heated to 60 °C for 6 h. The reaction mixture was cooled to room temperature and diluted with water (6 mL) and the precipitated solids were filtered and dried under vacuum to obtain compound **6**. White solid, Yield: 1.48 g, 83 %; m.p.: 119 °C; ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 7.65 (s, 1H), 7.42-7.40 (m, 2H), 7.18-7.14 (m, 3H), 5.80 (s, 1H), 3.96 (s, 6H); ESI-MS: m/z , 276.1 ($\text{M}+1$);

Step-5: Preparation of methyl 3-chloro-5-(4,6-dimethoxy-pyrimidin-2-yl carbamoylsulfamoyl)-1-methylpyrazole-4-carboxylate (7): A mixture of compound **6** (0.32 g, 1.16 mmol), compound **4** (0.25 g, 0.98 mmol) and triethylamine (0.12 g, 1.18 mmol) in acetonitrile (5 mL) was irradiated in a microwave at 60 °C for 10 min. After completion of the reaction (checked by TLC), the reaction mixture was diluted with water (10 mL) and extracted with dichloromethane (10 mL). The organic layer was washed with 1 M HCl (2×5 mL) and then with water (20 mL) followed by brine solution (10 mL). The organic layer was dried over anhydrous sodium sulphate (6.2 g), filtered and evaporated under reduced pressure to obtain the crude product. The crude product was re-crystallized in acetonitrile (10 mL) to obtain the pure compound **7**. Off-white powder; Yield: 0.410 g, 96 %; m.p.: 176 °C (Lit. m.p.: 175.5-177.2 °C); ^1H NMR (400 MHz, CDCl_3): δ 7.56 (s, 1H), 5.64

(s, 1H), 4.17 (s, 1H), 3.86 (s, 6H), 3.71 (s, 3H); ESI-MS: m/z , 435.1 (M+1)⁺.

RESULTS AND DISCUSSION

The synthesis of methyl 3-chloro-5-(4,6-dimethoxypyrimidin-2-yl carbamoylsulfamoyl)-1-methylpyrazole-4-carboxylate (**7**, halosulphuron) is illustrated in **Scheme-I**. The present synthetic sequence is a modified version of the previously literature reported method [36]. Ring chlorination of methyl 1-methyl-1H-pyrazole-4-carboxylate (**1**) was carried out in presence of sulphuryl chloride in dichloromethane at room temperature for 12 h gave methyl 3,5-dichloro-1-methyl-1H-pyrazole-4-carboxylate (**2**). Reaction of dichloro compound **2** with 70 % NaSH in DMF at 60 °C for 30 min gave methyl 3-chloro-5-mercapto-1-methyl-1H-pyrazole-4-carboxylate (**3**). Treatment of thiol **3** with tetrabutyl ammonium chloride, N-chloro-succinimide, water [37] and subsequent reaction with ammonium carbonate in acetonitrile at room temperature for 12 h resulted in the formation of the key intermediate methyl 3-chloro-1-methyl-5-sulfamoyl pyrazole-4-carboxylate (**4**). This method offers an *in situ* generation of sulphonyl chloride under mild reaction condition, than the previous reported literature precedence (commonly by bubbling of chlorine gas, although this methodology is comparatively general, issues related with the use of excess oxidant and/or aqueous acid have prompted the development of alternative methods). Treatment of 4,6-dimethoxypyrimidin-2-amine (**5**) with phenylchloroformate in presence of triethyl amine in acetonitrile at 60 °C for 6 h gave phenyl 4,6-dimethoxypyrimidin-2-ylcarbamate (**6**). Condensation of sulphonamide **4** with carbamate **6** by microwave irradiation at 60 °C for 10 min gave the desired methyl 3-chloro-5-(4,6-dimethoxypyrimidin-2-ylcarbamoylsulfamoyl)-1-methylpyrazole-4-carboxylate (**7**, Halosulphuron). All the compounds were characterized by ¹H NMR and mass spectroscopic techniques. ¹H NMR and mass spectral data of the Halosulphuron is in agreement with the desired structure. Inspired by and following the green metrics evaluation procedure reported by Martins *et al.* [38,39], we have evaluated the

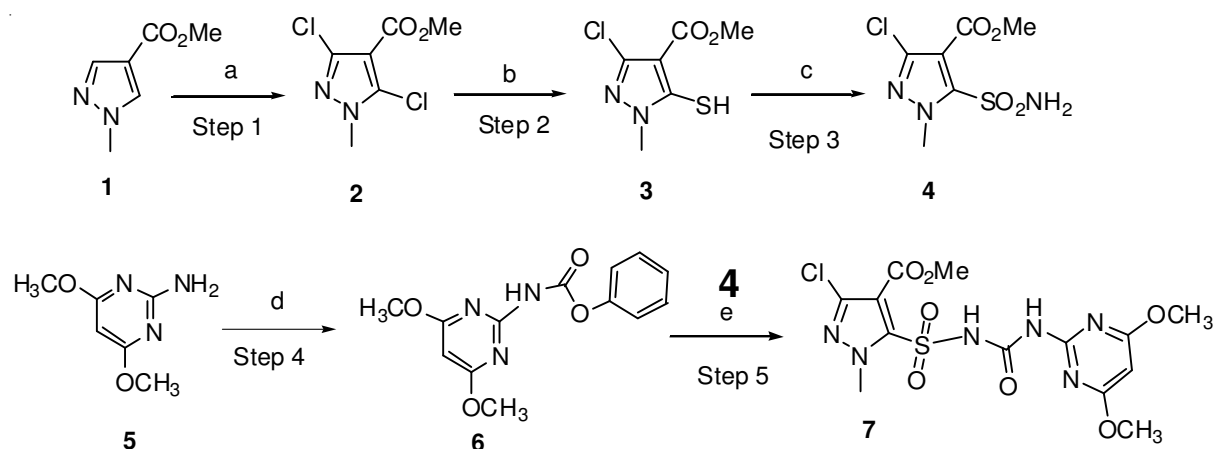
atom economy, reaction mass efficiency and environmental-factor (Fig. 2) for all the steps that are involved in the synthesis of halosulphuron (**Scheme-I**). To the best of our knowledge, these calculation procedures have not been reported for the synthesis of halosulphuron in the literature until now.

Atom economy (AE), reaction mass efficiency (RME):

The technique to compute atom economy ignores the reaction yield, molar excess of reactions, auxiliaries and utilization of solvents. Atom economy is a calculation of how much of the reactant remains in the desired product despite of the steps to obtain it. Therefore, atom economy is the ratio of the molecular weight of the final product to the sum total of the molecular weights of all reactants/substances produced in the stoichiometric equation for the reaction involved [28]. An ideal reaction has an atom economy of 100 %. For most reactions, a 100 % economy can never be reached owing to the nature of the reaction.

On the other hand, reaction mass efficiency takes into account the actual molar quantities of reactants, yields and the concepts of atom economy. In other words, reaction mass efficiency is the percentage of the mass of the reactants that remains in the product [28]. In eqn. 1, MW_P is the molecular weight of product P, MW_{R1} is the molecular weight of reactant R1 and MW_{R2} is the molecular weight of reactant R2. In eqn. 2, m_p (g) is the mass of the product isolated in grams and m_{R1} and m_{R2} are the mass of reactants R1 and R2, respectively, input to obtain mass of product.

Computational data of atom economy and reaction mass efficiency for the various steps involved in the synthesis is tabulated in Table-1. From Table-1, it is observed that, there is a major variation in the atom economy for all the reaction steps that are involved in the synthesis of halosulphuron. In all the steps, atom economy is less than the 100 % due to the formation of different by-products in the individual steps. In case of step 4 and step 5: atom economy is 88 % and 82 %, due to the formation of only one byproduct such as triethylamine.HCl and phenol respectively, while in the case of step 1 and step 2: atom economy is 75 % and 78 % due to the formation of byproduct *viz.*, HCl + H₂SO₄ and NaCl. The atom



Reaction conditions: a) Sulphuryl chloride, DCM, room temperature, 12 h; b) 70 % NaSH, DMF, 60 °C, 30 min; c) tetra-butyl ammonium chloride, N-chloro-succinimide, water, acetonitrile, ammonium carbonate, room temperature, 12 h; d) phenyl chloroformate, triethyl amine, acetonitrile, 60 °C, 6 h; e) compound **4**, triethyl amine, acetonitrile, microwave, 60 °C, 10 min

Scheme-I: Synthesis of methyl 3-chloro-5-(4,6-dimethoxypyrimidin-2-yl carbamoylsulfamoyl)-1-methyl pyrazole-4-carboxylate

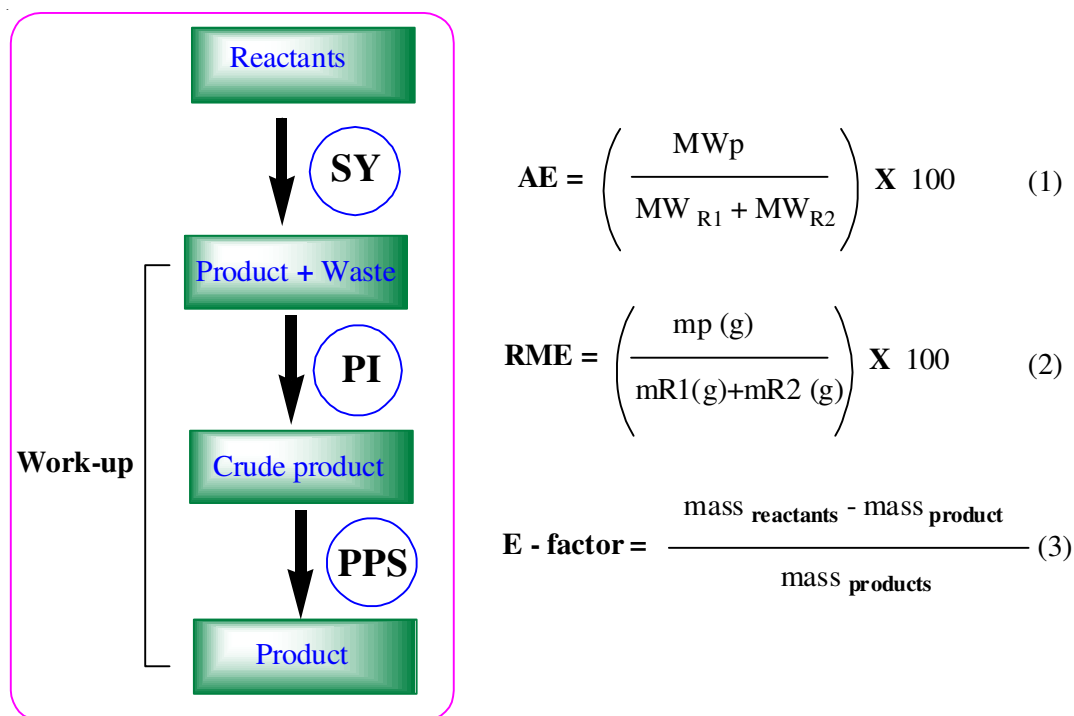


Fig. 2. Calculations to obtain atom economy, reaction mass efficiency and environmental-factor [procedure to obtain products: synthesis step (SYS), product isolation steps (PIS) and product purification step (PPS)]

TABLE-1
ATOM ECONOMY AND REACTION MASS EFFICIENCY
FOR THE VARIOUS STEPS INVOLVED IN THE
SYNTHESIS OF HALOSULPHURON

Compd.	Step	Atom economy (%)	Yield (%)	Reaction mass efficiency (%)
2	1	75	94	24
3	2	78	96	48
4	3	34	90	12
6	4	88	83	47
7	5	82	96	59

economy is least in case of Step 1 due the formation of more than one byproduct during the reaction (*viz.*, succinimide, HCl and tetrabutyl ammonium hydroxide).

The calculation of reaction mass efficiency, offers a more practical evaluation of the synthetic procedures, it takes into account the yield of reaction and molar excess of the reactants/reagents requisite for the total conversion of the product. From the results in Table-1, in case of steps 2, 4 and 5, although the reactions occurs with 78, 88 and 82 % atom economy respectively, the reaction mass efficiency percentage is 48, 47 and 59, while in the case of step 1 and step 3, the reaction mass efficiency percentage is much lower *i.e.*, 24 and 12. This variation in reaction mass efficiency is attributed to the factors such as number of reactants involved in the reaction, usage of excess molar equivalents of reactants and poor yields of the products.

Environmental-factor: The environmental-factor is the ratio of generated waste weight and end product total weight. It is a useful tool for the evaluation of rapid processes and is based on generated waste [29-32]. The environmental-factor may be obtained for (a) the synthesis step (SYS); (b) for the synthesis and product isolation steps (SYS + PIS); and (c) for the synthesis and workup steps (SYS + PIS + PPS) [39] (Fig.

2). Environmental-factor was calculated on the basis of amount of reactant and the volume of solvent used in the synthesis (SYS) and synthesis and isolation (SYS + PIS), where purification was needed, environmental-factors were calculated for synthesis, isolation and purification (SYS + PIS + PPS). The environmental-factor was calculated by eqn. 3. Water was not computed in the environmental-factor because they can be recovered after the separation of the product [29-31]. The values of the environmental-factors for the various steps involved in the synthesis of halosulphuron are shown in Table-2. When SYS calculation is taken into account, from Table-2 it is evident that the best environmental-factor value is assigned to the reactions step 2 and step 4, this is attributed to easy isolation of the products through simple acidic wash followed by water washings of the precipitated solids. When isolation and purification (SYS + PIS, SYS + PIS + PPS calculations) is taken into account, it is noticed that environmental-factor in case of step 1, step 3 and step 5 increased radically in comparison to step 2 and step 4 reaction steps. This increase in environmental-factor value is ascribed to the usage of voluminous amounts of solvent (during work up of the reactions), purification techniques (crystallization or column chromatography) and drying agents.

TABLE-2
E-FACTOR FOR THE VARIOUS STEPS INVOLVED IN
THE SYNTHESIS OF HALOSULPHURON

Compd. No.	Yield (%)	Step	SYS	SYS + PIS	SYS + PIS + PPS
2	94	1	22.1	32.9	36.2
3	96	2	3.1	—	—
4	90	3	25.0	28.5	29.2
6	83	4	6.44	—	—
7	96	5	10.2	57.8	77.0

It is noteworthy to mention that, irrespective of the high yields obtained in the various steps, there is a huge variation in the reaction mass efficiency and environmental-factor value; this is due to the inclusion of solvents and drying agent while computing the environmental-factor. Environmental-factor values give us an in hand information of various steps in generating waste on the laboratory scale. In the present case step 2 and step 4 are considered greener than step 1, 3 and 5.

Conclusion

In conclusion, the present paper evaluates the atom economy, reaction mass efficiency and environmental-factor for the various steps involved in the modified synthesis of methyl 3-chloro-5-(4,6-dimethoxypyrimidin-2-ylcarbamoyl-sulfamoyl)-1-methylpyrazole-4-carboxylate (halosulphuron). The important modification in the synthesis involves one pot chlorination reaction, preparation of sulphonamide intermediate derivative under mild reaction condition and microwave synthesis of halosulphuron. Based on the green metrics evaluation technique, it is inferred that the environmental-factor values in step 2 and step 4 reaction is lower, indicating that these reactions are greener (generation of less waste), when compared to the remaining steps in the synthesis.

REFERENCES

1. J.V. Hay, *Pestic. Sci.*, **29**, 247 (1990); <https://doi.org/10.1002/ps.2780290303>.
2. H.M. Brown, *Pestic. Sci.*, **29**, 263 (1990); <https://doi.org/10.1002/ps.2780290304>.
3. J.G. Wang, Z.M. Li, N. Ma, B.L. Wang, L. Jiang, S.S. Pang, Y.T. Lee, L.W. Guddat and R.G. Duggleby, *J. Comput. Aided Mol. Des.*, **19**, 801 (2005); <https://doi.org/10.1007/s10822-005-9028-9>.
4. S.S. Pang, R.G. Duggleby and L.W. Guddat, *J. Mol. Biol.*, **317**, 249 (2002); <https://doi.org/10.1006/jmbi.2001.5419>.
5. S.S. Pang, L.W. Guddat and R.G. Duggleby, *J. Biol. Chem.*, **278**, 7639 (2003); <https://doi.org/10.1074/jbc.M211648200>.
6. J.A. McCourt, S.S. Pang, L.W. Guddat and R.G. Duggleby, *Biochemistry*, **44**, 2330 (2005); <https://doi.org/10.1021/bi047980a>.
7. Z.M. Li, G.F. Jia and L.X. Wang, CN 1106393 (1995).
8. L.X. Wang, Z.M. Li, G.F. Jia and J.P. Chen, CN 1223791 (1999).
9. K.H. Horsham, *Avoiding Crop Damage from Residual Herbicides*, Department of Primary Industries, Victoria, vol. 1 (2008).
10. S.R. Teaney, L. Armstrong, K. Bentley, D. Cotterman, D. Leep, P.H. Liang, C. Powley, J. Summers and S. Cranwell, *Brighton Crop Prot. Conf. Weeds*, **1**, 49 (1995).
11. J. Rouchaud, C. Moulard, H. Eelen and R. Bulcke, *Weed Res.*, **42**, 14 (2002); <https://doi.org/10.1046/j.1365-3180.2002.00258.x>.
12. O. Ort, K. Bauer and H. Bieringer, WO 9213845 (1992).
13. K. Lorenz, H.J. Ressel and L. Willms, WO 2002008176 (2002).
14. G. Schnabel, L. Willms, K. Bauer and H. Bieringer, US 5747421 (1998).
15. A.D. Curzons, D.J.C. Constable and V.L. Cunningham, *Clean Prod. Process.*, **1**, 82 (1999); <https://doi.org/10.1007/s100980050014>.
16. K. Alfonsi, J. Colberg, P.J. Dunn, T. Fevig, S. Jennings, T.A. Johnson, H.P. Kleine, C. Knight, M.A. Nagy, D.A. Perry and M. Stefaniak, *Green Chem.*, **10**, 31 (2008); <https://doi.org/10.1039/B711717E>.
17. G. Fleischer and W.P. Schmidt, *Int. J. Life Cycle Assess.*, **2**, 20 (1997); <https://doi.org/10.1007/BF02978711>.
18. R. Gani, C. Jimenez-Gonzalez and D.J.C. Constable, *Comput. Chem. Eng.*, **29**, 1661 (2005); <https://doi.org/10.1016/j.compchemeng.2005.02.021>.
19. M. Li, P.F. Harten and H. Cabezas, *Ind. Eng. Chem. Res.*, **41**, 5867 (2002); <https://doi.org/10.1021/ie010574s>.
20. S. Elgue, L. Prat, P. Cognet, M. Cabassud, M. Le Lann and J. Cezerac, *J. Sep. Purif. Technol.*, **34**, 273 (2004); [https://doi.org/10.1016/S1383-5866\(03\)00200-4](https://doi.org/10.1016/S1383-5866(03)00200-4).
21. C. Jimenez-Gonzales, A.D. Curzons, J.C. Constable and V.L. Cunningham, *Clean Technol. Environ. Policy*, **7**, 42 (2005); <https://doi.org/10.1007/s10098-004-0245-z>.
22. C. Capello, U. Fischer and K. Hungerbühler, *Green Chem.*, **9**, 927 (2007); <https://doi.org/10.1039/b617536h>.
23. S. Elgue, L. Prat, M. Cabassud and J. Cezerac, *Chem. Eng. J.*, **117**, 169 (2006); <https://doi.org/10.1016/j.cej.2005.11.017>.
24. D. Kralisch, A. Stark, S. Körsten, G. Kreisel and B. Ondruschka, *Green Chem.*, **7**, 301 (2005); <https://doi.org/10.1039/b417167e>.
25. D. Kralisch, D. Reinhardt and G. Kreisel, *Green Chem.*, **9**, 1308 (2007); <https://doi.org/10.1039/b708721g>.
26. B.M. Trost, *Science*, **254**, 1471 (1991); <https://doi.org/10.1126/science.1962206>.
27. B.M. Trost, *Acc. Chem. Res.*, **35**, 695 (2002); <https://doi.org/10.1021/ar010068z>.
28. D.J.C. Constable, A.D. Curzons and V.L. Cunningham, *Green Chem.*, **4**, 521 (2002); <https://doi.org/10.1039/B206169B>.
29. R.A. Sheldon, *Chem. Ind.*, 903 (1992).
30. R.A. Sheldon, *Chemtech*, 38 (1994).
31. R.A. Sheldon, *J. Chem. Technol. Biotechnol.*, **68**, 381 (1997); [https://doi.org/10.1002/\(SICI\)1097-4660\(199704\)68:4<381::AID-JCTB620>3.0.CO;2-3](https://doi.org/10.1002/(SICI)1097-4660(199704)68:4<381::AID-JCTB620>3.0.CO;2-3).
32. P.J. Dunn, S. Galvin and K. Hettenbach, *Green Chem.*, **6**, 43 (2004); <https://doi.org/10.1039/B312329D>.
33. T. Hudlicky, D.A. Frey, L. Koroniak, C.D. Claeboe and L.E. Brammer Jr., *Green Chem.*, **1**, 57 (1999); <https://doi.org/10.1039/a901397k>.
34. A.D. Curzons, D.N. Mortimer, D.J.C. Constable and V.L. Cunningham, *Green Chem.*, **3**, 1 (2001); <https://doi.org/10.1039/b007871j>.
35. C.E. Berkoff, K. Kamholz, D.E. Rivard, G. Wellman and H. Winicov, *Chemtech*, 552 (1986).
36. K. Morimoto, T. Sato, S. Yamamoto and H. Takeuchi, *J. Heterocycl. Chem.*, **34**, 537 (1997); <https://doi.org/10.1002/jhet.5570340231>.
37. H. Veisi, R. Ghorbani-Vaghei, S. Hemmati and J. Mahmoodi, *Synlett.*, 2315 (2011); <https://doi.org/10.1055/s-0030-1261232>.
38. M.A.P. Martins, P.H. Beck, L. Buriol, C.P. Frizzo, D.N. Moreira, M.R.B. Marzari, M. Zanatta, P. Machado, N. Zanatta and H.G. Bonacorso, *Monatsh. Chem.*, **144**, 1043 (2013); <https://doi.org/10.1007/s00706-013-0930-x>.
39. M.A.P. Martins, C.P. Frizzo, D.N. Moreira, L. Buriol and P. Machado, *Chem. Rev.*, **109**, 4140 (2009); <https://doi.org/10.1021/cr9001098>.