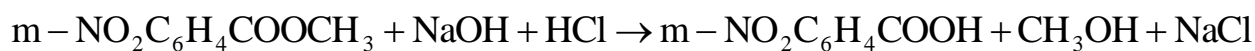


Synthesis of 3-nitrobenzoic acid – Protocol B



Reaction. In a 2 L round-bottomed flask fitted with a reflux condenser, place a solution of 80 g (2 mol) of sodium hydroxide (about 100% excess) in 320 mL of water and 181 g (1 mol) of methyl m-nitrobenzoate. Heat the mixture to boiling during 5 to 10 minutes or until saponification is complete as shown by the disappearance of the ester. Dilute the reaction mixture with an equal volume of water and when cool, pour with stirring into 250 mL (3 mol) of concentrated hydrochloric acid (about 200% excess).

Isolation. Cool the solution to room temperature and filter off the 3-nitrobenzoic acid by means of suction.

Purification. Recrystallize the product from 1% aqueous hydrochloric acid.

Safety. See hazards associated with the reagents in Table 1.

Greenness Assessment. The evaluation was performed using the Green Star (GS) and the results are shown in Figure 1.

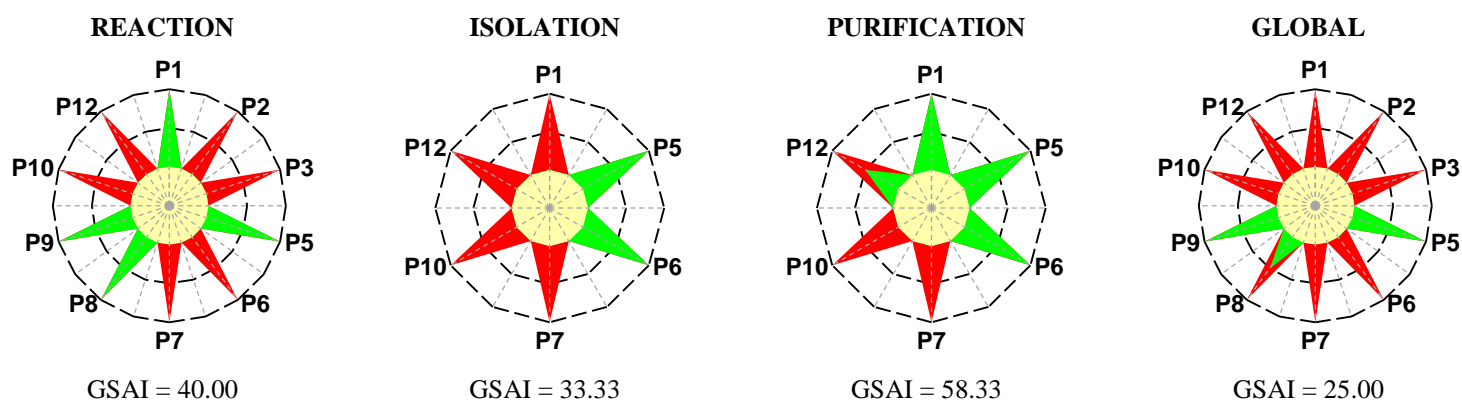


Figure 1. Greenness assessment (GS) for the synthesis of 3-nitrobenzoic acid

Construction of the GS

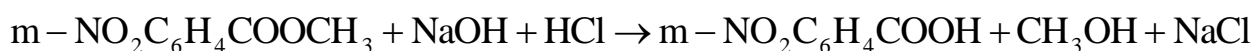


Table 1 presents the hazards and scores associated with the substances involved and Table 2 presents the scores used to construct the green stars.

Table 1. Hazards for the synthesis of 3-nitrobenzoic acid, protocol B^α

Substances involved	Step			Hazard code	Score: hazards to...		
	R	I	Pu		HH	E	P
Stoichiometric reagents							
Hydrochloric acid (CAS 7647-01-0)	✓			H314, H335	3	1	1
Methyl m-nitrobenzoate(CAS 618-95-1)	✓			-	1	1	1
Sodium hydroxide (CAS 1310-73-2)	✓			H314	3	1	1
Auxiliary substances							
Solvents							
Hydrochloric acid (1% solution)			✓	-	1	1	1
Water ^{a,b}	✓			-	1	1	1
Product							
3-nitrobenzoic acid (121-92-6)	✓	✓	✓	H302, H315, H319, H335, H412	2	2	1
Waste							
Hydrochloric acid (dilute solution)			✓	-	1	1	1
Methanol		✓		H225, H301, H311, H331, H370	3	1	3
Sodium chloride (aqueous solution)		✓		-	1	1	1
Sodium hydroxide (dilute solution)		✓		-	1	1	1
Water ^{a,b}		✓		-	1	1	1

^α R – Reaction; I – Isolation; Pu – Purification; HH – Human Health; E – Environment; P – Physical

^a Renewable; ^b Degradable to innocuous products

Table 2. Scores used to construct the green star for the synthesis of 3-nitrobenzoic acid, protocol B^a

Green Chemistry Principle	Reaction		Isolation		Purification		Global	
	s	Explanation	s	Explanation	s	Explanation	s	Explanation
P1 Prevention	3	Without waste	1	Methanol, H301, H311, H331, H370	3	Waste is innocuous	1	Methanol, H301, H311, H331, H370
P2 Atom Economy	1	Excess of sodium hydroxide and hydrochloric acid > 10%, formation of by-products		NA		NA	1	Excess of sodium hydroxide and hydrochloric acid > 10%, formation of by-products
P3 Less hazardous chemical synthesis	1	Sodium hydroxide and hydrochloric acid, H314, and methanol, H301, H311, H331, H370		NA		NA	1	Sodium hydroxide and hydrochloric acid, H314, and methanol, H301, H311, H331, H370
P5 Safer solvents and auxiliary substances	3	Water	3	Solvents and auxiliary substances are not used	3	1% aqueous hydrochloric acid	3	Water and 1% aqueous hydrochloric acid
P6 Increase energy efficiency	1	T > 100 °C	3	Room temperature	3	Room temperature	1	T > 100 °C
P7 Use renewable feedstocks	1	Substances not renewable	1	Substances not renewable	1	Substances not renewable	1	Substances not renewable
P8 Reduce derivatives	3	One stage		NA		NA	2	Two stages
P9 Catalysts	3	Without catalysts		NA		NA	3	Without catalysts
P10 Design for degradation	1	Substances not degradable	1	Substances not degradable	1	Substances not degradable	1	Substances not degradable
P12 Safer chemistry for accident prevention	1	Sodium hydroxide and hydrochloric acid, H314, and methanol, H225, H301, H311, H331, H370	1	Methanol, H225, H301, H311, H331, H370	2	3-nitrobenzoic acid, H302, H315, H319, H335	1	Sodium hydroxide and hydrochloric acid, H314, and methanol, H225, H301, H311, H331, H370

^as – Score; NA – Not applicable

References

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Fourneau, M.E. *et al. Synthèses Organiques*. Masson et C^{ie}, Éditeurs: Paris, 1935, pp. 63-64.