Synthesis of *tert*-butyl chloride – Protocol S

$$(CH_3)_3COH + HCl \rightarrow (CH_3)_3CCl + H_2O$$

Reaction. In an Erlenmeyer flask, cool 17 mL (204 mmol) of concentrated hydrochloric acid (about 278% excess) with an ice-water bath to close to 0 ºC. Transfer the cold acid to a separatory funnel and carefully add 4 g (54 mmol) of *tert*-butyl alcohol. Shake the mixture well, carefully venting. Swirl it occasionally for 20 minutes.

Isolation. Allow the layers to cleanly separate and remove the aqueous acid layer. Wash the product layer first with 10 mL of water, and then with 10 mL of 5% sodium hydrogen carbonate solution. Finally, wash the product layer with 10 mL of saturated sodium chloride solution, always removing the aqueous layer. Dry the product over anhydrous sodium sulphate for at least 10 minutes. Decant the product.

Purification. Purify the product using distillation.

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.

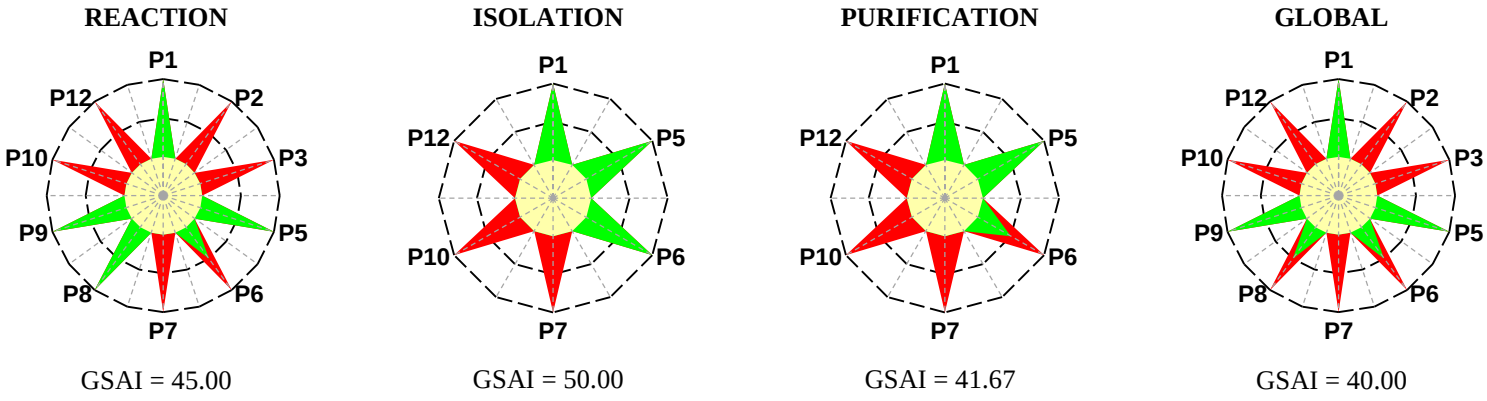

Figure 1. Greenness assessment (GS) for the synthesis of *tert*-butyl chloride

Construction of the GS

$$(CH_3)_3COH + HCl \rightarrow (CH_3)_3CCl + H_2O$$

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 *tert*-butyl chloride, protocol S[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
tert-Butyl alcohol (CAS 75-65-0)	✓			H225, H319, H332, H335	2	1	3
Auxiliary substances							
Solvents							
Sodium chloride (saturated solution)		✓		-	1	1	1
Sodium hydrogen carbonate (dilute solution)		✓		-	1	1	1
Water[a,b]		✓		-	1	1	1
Other auxiliary substances							
Anhydrous sodium sulphate (CAS 7757-82-6)		✓		-	1	1	1
Product							
tert-Butyl chloride (507-20-0)	✓	✓	✓	H225	1	1	3
Waste							
Carbon dioxide		✓		H280	1	1	2
Hydrochloric acid (dilute solution)		✓		-	1	1	1
Isobutylene	✓			H220, H280	1	1	3
Sodium chloride (aqueous solution)		✓		-	1	1	1
Sodium sulphate		✓		-	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 *tert*-butyl chloride, protocol S[α]

Green Chemistry Principle	Reaction		Isolation		Purification		Global	
	s	**Explanation**	**s**	**Explanation**	**s**	**Explanation**	**s**	**Explanation**
P1 Prevention	3	Isobutylene	3	Waste is innocuous	3	Waste is innocuous	3	Waste is innocuous
P2 Atom Economy	1	Excess of hydrochloric acid > 10%, formation of by-products		NA		NA	1	Excess of hydrochloric acid > 10%, formation of by-products
P3 Less hazardous chemical synthesis	1	Hydrochloric acid, H314		NA		NA	1	Hydrochloric acid, H314
P5 Safer solvents and auxiliary substances	3	Solvents and auxiliary substances are not used	3	Solvents and auxiliary substances are innocuous	3	Solvents and auxiliary substances are not used	3	Solvents and auxiliary substances are innocuous
P6 Increase energy efficiency	2	0 ºC ≤ T ≤ 100 ºC	3	Room temperature	2	0 ºC ≤ T ≤ 100 ºC	2	0 ºC ≤ T ≤ 100 ºC
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	Hydrochloric acid, H314, *tert*-butyl alcohol and *tert*-butyl chloride, H225, isobutylene, H220	1	*tert*-Butyl chloride, H225	1	*tert*-Butyl chloride, H225	1	Hydrochloric acid, H314, *tert*-butyl alcohol and *tert*-butyl chloride, H225, isobutylene, H220

[α]s – Score; NA – Not applicable

References

Georgia Regents University, *http://www.aug.edu/~tcrute/lab_experiments/3411%20lab%20SN1%20prep%20of%20tbutyl%20chloride.doc* (accessed April 2013).