Synthesis of vanadyl acetylacetonate – Protocol Q

$$2V_2O_5 + 9(Hacac) \rightarrow 4[VO(acac)_2] + (CH_3CO)_2CO + 5H_2O$$

Reaction. Place 5 g (27 mmol) of vanadium pentoxide in a 200 mL round-bottomed flask and add 100 mL (969 mmol) of acetylacetone (about 698% excess). Reflux the mixture gently for 24 hours.

Isolation. Filter the suspension while hot, and cool the filtrate. Remove the remaining acetylacetone by evaporation in a stream of air. Wash the solid product with acetone and ethyl ether and dry it at 110 ºC.

Purification. Recrystallize the solid from acetylacetone.

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 Figures 1 and 2. As no SDS file was found for pentan-2,3,4-trione, two alternatives were considered: one takes into account the maximum hazard of this substance and the other does not consider the pentan-2,3,4-trione for greenness assessment.

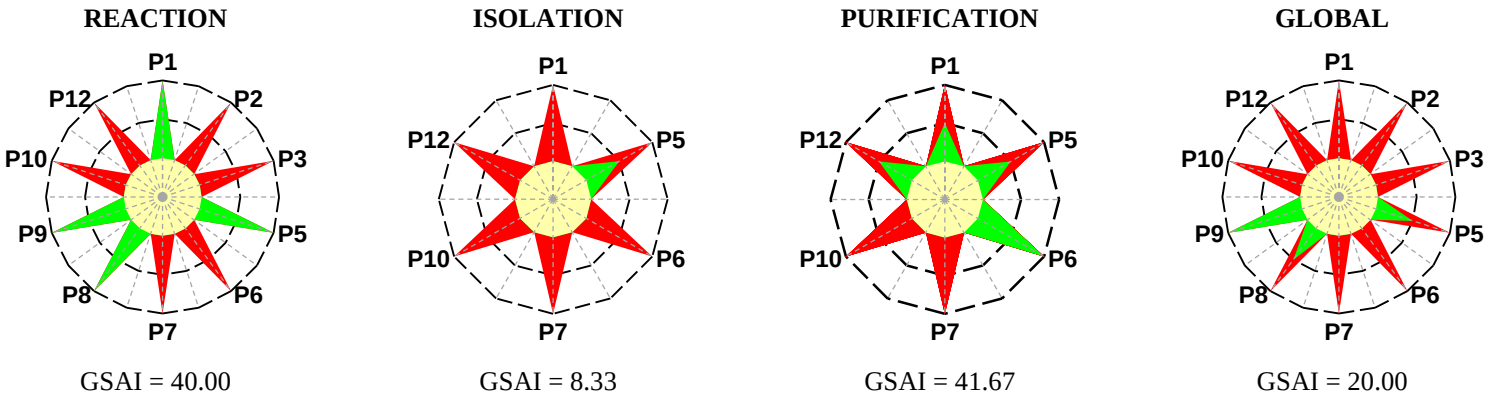

Figure 1. Greenness assessment (GS) for the synthesis of vanadyl acetylacetonate (considering maximum hazard of the pentan-2,3,4-trione)

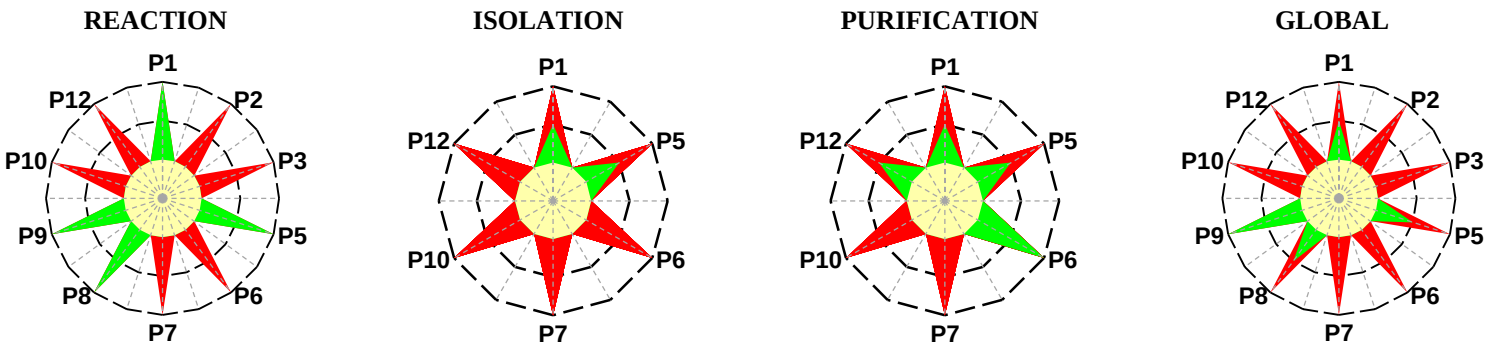

Figure 2. Greenness assessment (GS) for the synthesis of vanadyl acetylacetonate (not considering the pentan-2,3,4-trione)

Construction of the GS

$$2V_2O_5 + 9(Hacac) \rightarrow 4[VO(acac)_2] + (CH_3CO)_2CO + 5H_2O$$

Table 1 presents the hazards and scores associated with the substances involved and Tables 2 and 3 present the scores used to construct the green stars.

Table 1. Hazards for the synthesis of vanadyl acetylacetonate, protocol Q[α]

Substances involved	Step			Hazard code	Score: hazards to...		
	R	I	Pu		HH	E	P
Stoichiometric reagents							
Acetylacetone[c] (CAS 123-54-6)	✓			H226, H302	2	1	2
Vanadium pentoxide (CAS 1314-62-1)	✓			H302, H332, H335, H341, H361, H372, H411	3	3	1
Auxiliary substances							
Solvents							
Acetone (CAS 67-64-1)		✓		H225, H319, H336	2	1	3
Acetylacetone[c] (CAS 123-54-6)			✓	H226, H302	2	1	2
Ethyl ether (CAS 60-29-7)		✓		H224, H302, H336, EUH019, EUH066	2	1	3
Product							
Vanadyl acetylacetonate (3153-26-2)	✓	✓	✓	H302, H315, H319, H335	2	1	1
Waste							
Acetone		✓		H225, H319, H336	2	1	3
Acetylacetone[c] (excess)		✓	✓	H226, H302	2	1	2
Ethyl ether		✓		H224, H302, H336, EUH019, EUH066	2	1	3
Pentan-2,3,4-trione		✓		No data available			
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; [c] Degradable

Table 2. Scores used to construct the green star for the synthesis of vanadyl acetylacetonate, protocol P (considering maximum hazard of the pentan-2,3,4-trione) [α]

Green Chemistry Principle	Reaction		Isolation		Purification		Global	
	s	**Explanation**	**s**	**Explanation**	**s**	**Explanation**	**s**	**Explanation**
P1 Prevention	3	Without waste	1	Pentan-2,3,4-trione	2	Acetylacetone, H302	1	Pentan-2,3,4-trione
P2 Atom Economy	1	Excess of acetylacetone > 10%, formation of by-products		NA		NA	1	Excess of acetylacetone > 10%, formation of by-products
P3 Less hazardous chemical synthesis	1	Vanadium pentoxide, H341, H361, H372, H411, and pentan-2,3,4-trione		NA		NA	1	Vanadium pentoxide, H341, H361, H372, H411, and pentan-2,3,4-trione
P5 Safer solvents and auxiliary substances	3	Solvents and auxiliary substances are not used	2	Acetone, H319, H336 and ethyl ether, H302, H336, EUH066	2	Acetylacetone, H302	2	Acetone, H319, H336 and ethyl ether, H302, H336, EUH066, acetylacetone, H302
P6 Increase energy efficiency	1	T > 100 ºC	1	T > 100 ºC	3	Room temperature	1	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	Vanadium pentoxide, H341, H361, H372, and pentan-2,3,4-trione	1	Acetone, H225, ethyl ether, H224, and pentan-2,3,4-trione	2	Acetylacetone, H302 and vanadyl acetylacetonate, H302, H315, H319, H335	1	Vanadium pentoxide, H341, H361, H372, acetone, H225, ethyl ether, H224, and pentan-2,3,4-trione

[α] s – Score; NA – Not applicable

Table 3. Scores used to construct the green star for the synthesis of vanadyl acetylacetonate, protocol P (not considering the pentan-2,3,4-trione) [α]

Green Chemistry Principle	Reaction		Isolation		Purification		Global	
	s	**Explanation**	**s**	**Explanation**	**s**	**Explanation**	**s**	**Explanation**
P1 Prevention	3	Without waste	2	Excess of acetylacetone, H302, acetone, H319, H336 and ethyl ether, H302, H336, EUH066	2	Acetylacetone, H302	2	Acetylacetone, H302 acetone, H319, H336 and ethyl ether, H302, H336, EUH066
P2 Atom Economy	1	Excess of acetylacetone > 10%, formation of by-products		NA		NA	1	Excess of acetylacetone > 10%, formation of by-products
P3 Less hazardous chemical synthesis	1	Vanadium pentoxide, H341, H361, H372, H411		NA		NA	1	Vanadium pentoxide, H341, H361, H372, H411
P5 Safer solvents and auxiliary substances	3	Solvents and auxiliary substances are not used	2	Acetone, H319, H336 and ethyl ether, H302, H336, EUH066	2	Acetylacetone, H302	2	Acetone, H319, H336 and ethyl ether, H302, H336, EUH066, acetylacetone, H302
P6 Increase energy efficiency	1	T > 100 ºC	1	T > 100 ºC	3	Room temperature	1	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	Vanadium pentoxide, H341, H361, H372	1	Acetone, H225, and ethyl ether, H224	2	Acetylacetone, H302 and vanadyl acetylacetonate, H302, H315, H319, H335	1	Vanadium pentoxide, H341, H361, H372, acetone, H225, and ethyl ether, H224

[α]s – Score; NA – Not applicable

References

Moeller, T. *et al*. *Inorganic Synthesis – vol. V*. McGraw-Hill Book Company, Inc: New York, 1957, pp. 113-116.