Synthesis of manganese(III) acetylacetonate

Greenness optimization

The greenest procedures for each step are: R_8^1 for the reaction, I_3^{2-4} for the isolation, and Pu_8^1 for the purification. Combining these procedures it is possible to obtain greener procedures than those of the original protocols.

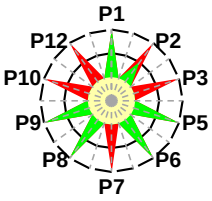
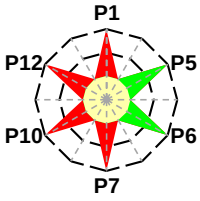
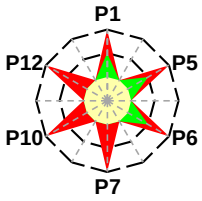
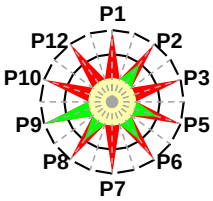
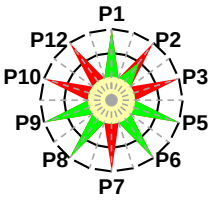
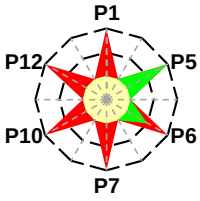
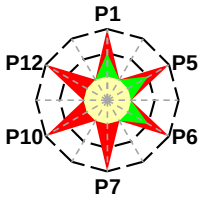
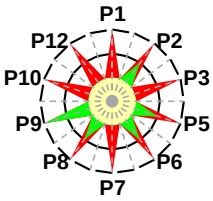
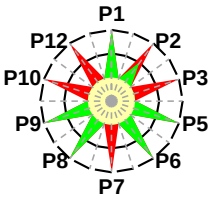
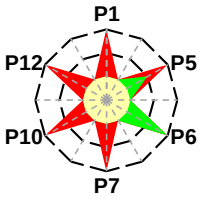
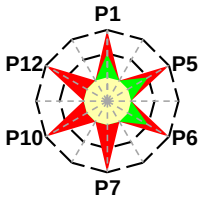
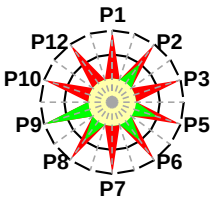
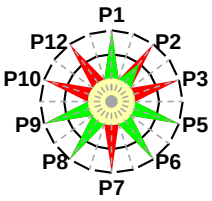
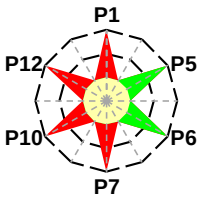
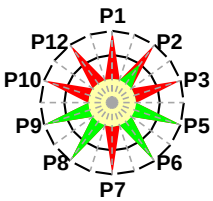
In Table 1 are presented four combinations (1-4), considering the greener procedures for the reaction and purification and different procedures for the isolation, with GSAI values between 25.00 and 33.33. Combination 3 coincides with protocol I^1 (GSAI = 30.00).

Combinations 1, 2 and 3 present all the same greenness (GSAI = 30.00). However, despite the global greenness being the same in all combinations, it should not be indifferent the choice of the procedures for the several steps, because the greenness in each step is itself relevant. In this case, one should choose the isolation procedure I_3.

Combination 4 is the greenest (GSAI = 45.00), because purification is not prescribed. This combination is greener than any of the analysed protocols.

Optimized protocols are described below.

Table 1. Green star obtained by combining the greenest procedures of each step

Combination	Reaction	Isolation	Purification	Global process
1	**R_8**  **GSAI = 55.00**	**I_3**  **GSAI = 33.33**	**Pu_8**  **GSAI = 25.00**	 **GSAI = 30.00**
2	**R_8**  **GSAI = 55.00**	**I_1, I_2, I_4**  **GSAI = 25.00**	**Pu_8**  **GSAI = 25.00**	 **GSAI = 30.00**
3 = Pr I	**R_8**  **GSAI = 55.00**	**I_6**  **GSAI = 25.00**	**Pu_8**  **GSAI = 25.00**	 **GSAI = 30.00**
4	**R_8**  **GSAI = 55.00**	**I_3**  **GSAI = 33.33**	Without purification	 **GSAI = 45,00**

Optimized protocol 1

Reaction. Add theoretical proportions of potassium permanganate and manganous sulfate in the presence of a slight excess of acetylacetone and at a regulated pH of about 5.0. *(No buffer is indicated, so it's considered the use of sodium acetate, which is greener.)*

Isolation. Cool the mixture to room temperature, collect the dark product by suction filtration, wash it with water and dry the solid at the pump.

Purification. Recrystallize the product from hot acetone.

Optimized protocol 2

Reaction. Add theoretical proportions of potassium permanganate and manganous sulfate in the presence of a slight excess of acetylacetone and at a regulated pH of about 5.0. *(No buffer is indicated, so it's considered the use of sodium acetate, which is greener.)*

Isolation. Cool the solution to room temperature, filter the solid and wash it with cold distilled water. Dry the precipitate in a dessicator over anhydrous calcium chloride.

Purification. Recrystallize the product from hot acetone.

Optimized protocol 3

Reaction. Add theoretical proportions of potassium permanganate and manganous sulfate in the presence of a slight excess of acetylacetone and at a regulated pH of about 5.0. *(No buffer is indicated, so it's considered the use of sodium acetate, which is greener.)*

Isolation. Wash the crystals with 0.1 M aqueous acetylacetone, then with small portions of acetone and ether to hasten the drying process.

Purification. Recrystallize the product from hot acetone.

Optimized protocol 4

Reaction. Add theoretical proportions of potassium permanganate and manganous sulfate in the presence of a slight excess of acetylacetone and at a regulated pH of about 5.0. *(No buffer is indicated, so it's considered the use of sodium acetate, which is greener.)*

Isolation. Cool the mixture to room temperature, collect the dark product by suction filtration, wash it with water and dry the solid at the pump.

Purification. Not prescribed.

References

(1) Cartledge, G.H. Equilibrium Between the Complexes of Tervalent Manganese with 2,4-Pentanedione. *J. Am. Chem. Soc.*, **1951**, *73 (9)*, 4416-4419.

(2) Geremia, S.; Demitri, N. Crystallographic Study of Manganese(III) Acetylacetonate: An Advanced Undergraduate Project with Unexpected Challenges. *J. Chem. Educ.*, **2005**, *82*, 460-465.

(3) University of Bristol, *http://www.chm.bris.ac.uk/teaching-labs/1AManual2005-6/Experiment7.pdf* (accessed April 2011).

(4) Szafran, Z.; Pike, R.M.; Singh, M.M. *Microscale Inorganic Chemistry – A Comprehensive Laboratory Experience*. Wiley: New York, 1991, pp. 224-229.