Synthesis of ethyl acetate

Greenness optimization

The greenest procedures for each step are: R_1,[1,2] R_2[2] and R_8[3] for the reaction, I_7[4] for the isolation, and Pu_1[1,2,5-9] for the purification. Combining these procedures it is possible to obtain greener procedures than those of the original protocols.

In Table 1 are presented six combinations (1-6), considering the greener procedures for the reaction and purification and different procedures for the isolation, with GSAI values between 33.33 and 50.00.

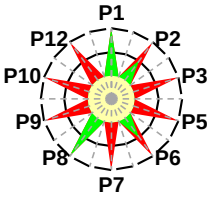
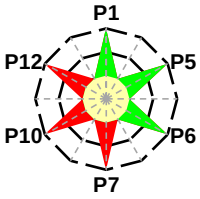
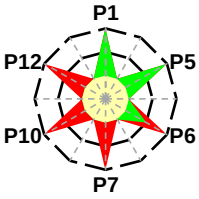
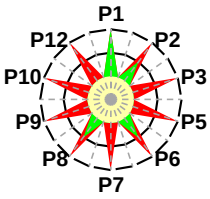
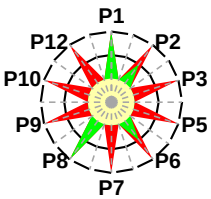
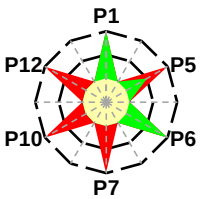
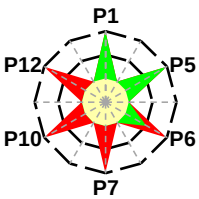
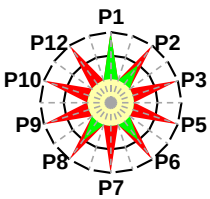
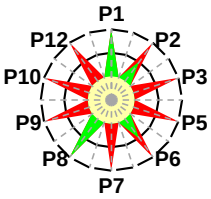
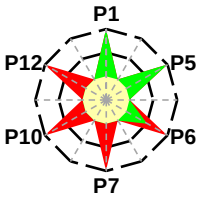
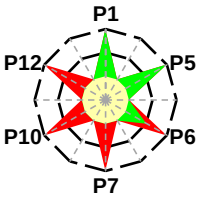
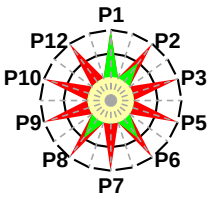
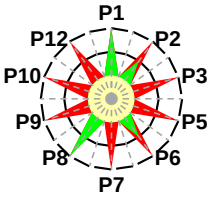
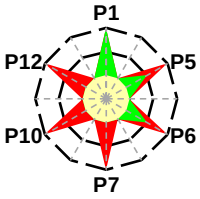
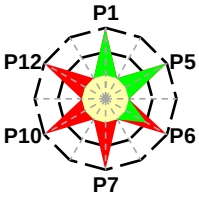
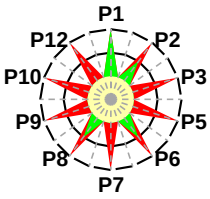
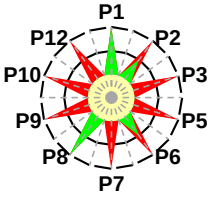
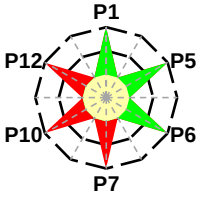
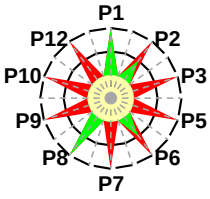
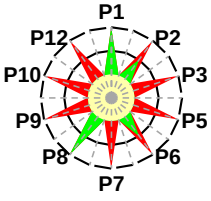
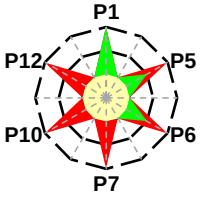
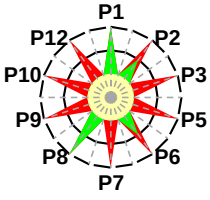
The combinations 1, 2, 3 and 4 present all the same greenness (GSAI = 25.00). However, despite the global greenness being the same in all combinations, it should not be indifferent the choice of the procedures for the several steps, because the greenness in each step is itself relevant. In this case, one should choose the purification procedure I_7. In these cases, a greener protocol than any of the analysed where the three steps are carried out is obtained.

Combination 5 is the greenest (GSAI = 30.00), because purification is not prescribed. This combination presents the same greenness of the protocol I^3 (the greenest of the analysed protocols).

Combination 6 does not result from the greener procedures of each step, since it uses I_5[10] for the isolation of the product, but has the same greenness of combination 5 (GSAI = 30.00). However, contrary to what happens with the combination 5, in 6 is performed a simple distillation to isolate the product.

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_1, R_2 or R_8  GSAI = 30.00	I_7  GSAI = 50.00	Pu_1  GSAI = 41.67	 GSAI = 25.00
2	R_1, R_2 or R_8  GSAI = 30.00	I_6  GSAI = 41.67	Pu_1  GSAI = 41.67	 GSAI = 25.00
3	R_1, R_2 or R_8  GSAI = 30.00	I_8  GSAI = 41.67	Pu_1  GSAI = 41.67	 GSAI = 25.00
4	R_1, R_2 or R_8  GSAI = 30.00	I_5, I_{10}  GSAI = 33.33	Pu_1  GSAI = 41.67	 GSAI = 25.00
5	R_1, R_2 or R_8  GSAI = 30.00	I_7  GSAI = 50.00	Without purification	 GSAI = 30.00
6	R_1, R_2 or R_8  GSAI = 30.00	I_5, I_{10}  GSAI = 33.33	Without purification	 GSAI = 30.00

Optimized protocol 1

Reaction. Mix 25 mL (428 mmol) of ethanol and 25 mL (437 mmol) of glacial acetic acid (stoichiometric proportions) in a 250 mL round-bottomed flask, and add slowly, cooling (ice bath) and shaking, 5 mL of concentrated sulfuric acid. Ensure that the liquid is homogeneous, then fit the flask with a water-condenser and boil the mixture gently for 10 minutes.

Isolation. Agitate the distillate in an open flask with dilute sodium carbonate solution until neutral to litmus, then separate the oil in a separatory funnel.

Purification. Prepare an apparatus for distillation and collect the fraction boiling between 74 e 79 ºC.

Optimized protocol 2

Reaction. Mix 25 mL (428 mmol) of ethanol and 25 mL (437 mmol) of glacial acetic acid (stoichiometric proportions) in a 250 mL round-bottomed flask, and add slowly, cooling (ice bath) and shaking, 5 mL of concentrated sulfuric acid. Ensure that the liquid is homogeneous, then fit the flask with a water-condenser and boil the mixture gently for 10 minutes.

Isolation. Prepare a saturated solution of sodium carbonate by combining 4.5 g of sodium carbonate with 15 mL of distilled water. Shake well, and allow any undissolved solid to settle. Pour the clear sodium carbonate solution into a separatory funnel, and add the reaction mixture. Shake vigorously and allow the layers to separate. Discard the aqueous layer. Transfer the ethyl acetate layer to a round bottom flask.

Purification. Prepare an apparatus for distillation and collect the fraction boiling between 74 e 79 ºC.

Optimized protocol 3

Reaction. Mix 25 mL (428 mmol) of ethanol and 25 mL (437 mmol) of glacial acetic acid (stoichiometric proportions) in a 250 mL round-bottomed flask, and add slowly, cooling (ice bath) and shaking, 5 mL of concentrated sulfuric acid. Ensure that the liquid is homogeneous, then fit the flask with a water-condenser and boil the mixture gently for 10 minutes.

Isolation. Allow the system to cool down. Remove the reflux column and replace it with the distillation column. Distil the product which boils at 76.5-77.5 ºC.

Purification. Prepare an apparatus for distillation and collect the fraction boiling between 74 e 79 ºC.

Optimized protocol 4

Reaction. Mix 25 mL (428 mmol) of ethanol and 25 mL (437 mmol) of glacial acetic acid (stoichiometric proportions) in a 250 mL round-bottomed flask, and add slowly, cooling (ice bath) and shaking, 5 mL of concentrated sulfuric acid. Ensure that the liquid is homogeneous, then fit the flask with a water-condenser and boil the mixture gently for 10 minutes.

Isolation. Cool the mixture. Set up the apparatus for distillation and heat the bottom of the distilling flask in the hot water bath until no more distillate is coming over (b.p. = 77 ºC). Pour about 10 mL of saturated sodium carbonate solution into a separatory funnel. Add the distillate, stopper and shake vigorously. Allow the layers to separate and discard the aqueous layer. Collect the product.

Purification. Prepare an apparatus for distillation and collect the fraction boiling between 74 e 79 ºC.

Optimized protocol 5

Reaction. Mix 25 mL (428 mmol) of ethanol and 25 mL (437 mmol) of glacial acetic acid (stoichiometric proportions) in a 250 mL round-bottomed flask, and add slowly, cooling (ice bath) and shaking, 5 mL of concentrated sulfuric acid. Ensure that the liquid is homogeneous, then fit the flask with a water-condenser and boil the mixture gently for 10 minutes.

Isolation. Agitate the distillate in an open flask with dilute sodium carbonate solution until neutral to litmus, then separate the oil in a separatory funnel.

Purification. Not prescribed.

Optimized protocol 6

Reaction. Mix 25 mL (428 mmol) of ethanol and 25 mL (437 mmol) of glacial acetic acid (stoichiometric proportions) in a 250 mL round-bottomed flask, and add slowly, cooling (ice bath) and shaking, 5 mL of concentrated sulfuric acid. Ensure that the liquid is homogeneous, then fit the flask with a water-condenser and boil the mixture gently for 10 minutes.

Isolation. Cool the mixture. Set up the apparatus for distillation and heat the bottom of the distilling flask in the hot water bath until no more distillate is coming over (b.p. = 77 ºC). Pour about 10 mL of saturated sodium carbonate solution into a separatory funnel. Add the distillate, stopper and shake vigorously. Allow the layers to separate and discard the aqueous layer. Collect the product.

Purification. Not prescribed.

References

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(2) Mann, F.G.; Saunders, B.C. *Practical Organic Chemistry – 4th edition.* Longmans, Green and Co: London, 1960, pp. 96-97.

(3) Goffs School, *http://www.goffs.herts.sch.uk/Subjects/MWA/A2%20CHEM/F324/CarboxylicAcids&Esters/CarboxylicAcidsWS/CarboxylicAcidsPractical2.pdf* (accessed April 2013).

(4) Moore, F.J. *Experiments in Organic Chemistry – 1st edition.* John Wiley & Sons: New York, 1911, pp. 12-13.

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