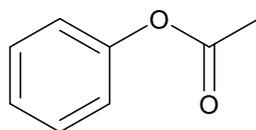
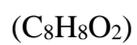


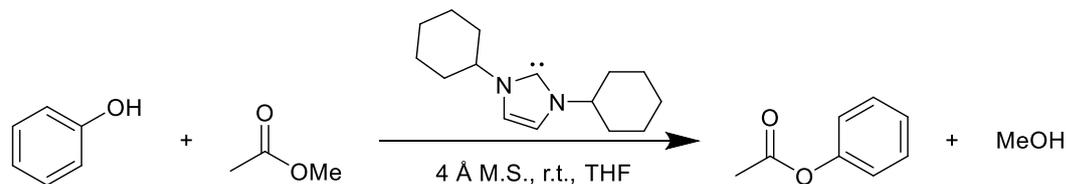
Organic chemistry practical course

Synthesis of phenyl acetate (Transesterification)



Hand over: X

I. Reaction: ^[1]



$$M(C_6H_6O) = 94.11 \text{ g/mol}$$

$$M(C_3H_6O_2) = 74.08 \text{ g/mol}$$

$$M(C_8H_8O_2) = 136.15 \text{ g/mol}$$

$$M(CH_4O) = 32.04 \text{ g/mol}$$

$$D(C_6H_6O) = 1.071 \text{ g/cm}^3$$

$$D(C_3H_6O_2) = 0.9342 \text{ g/cm}^3$$

$$D(C_8H_8O_2) = 1.073 \text{ g/cm}^3$$

$$D(CH_4O) = 0.810 \text{ g/cm}^3$$

Scheme 1: Reaction overview and stoichiometrics.

II. Theory: ^{[1] [2]}

This report describes the synthesis of phenyl acetate *via* a transesterification process between phenol and methyl acetate. As seen on the reaction scheme above, this process involves the exchange of the alkyl group of the previously existing ester. That way, the corresponding ester of the alcohol starting material is formed. This synthesis is usually facilitated by the presence of an acidic or basic catalyst.^[2] In this synthesis, a *N*-heterocyclic carbene was used as the catalyst.

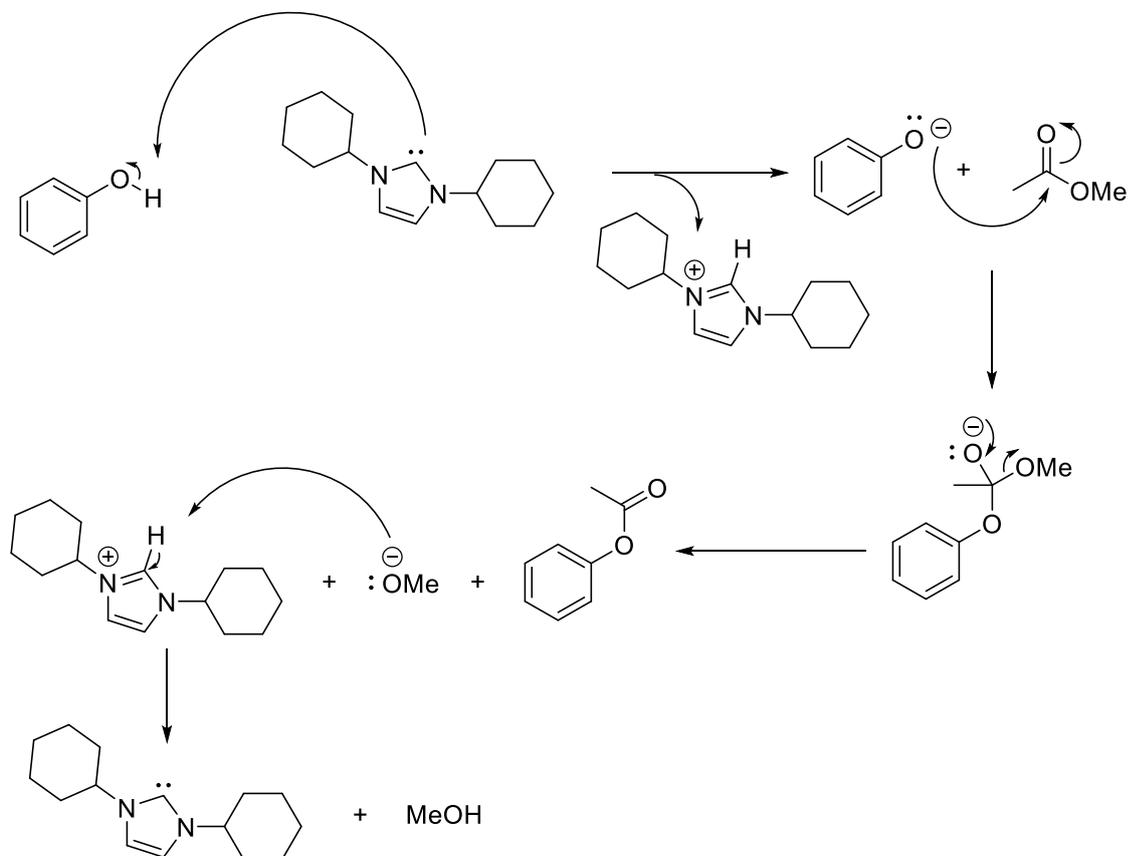
According to literature ^[2], transesterification is preferable compared to the conventional esterification from carboxylic acid and alcohol since some carboxylic acids are less soluble in organic solvents and will thus seldom undergo a homogeneous esterification.

Due to them often being commercially available, mostly methyl- and ethyl esters are used in transesterification reactions. Transesterification is widely applied not for laboratory synthetic purposes only but in various industrial processes, for example:

1. Polymerisation (e.g. polyester production).
2. Biodiesel production from oil seeds, vegetable oils, animal fats, waste cooking oil and microbial lipids.
3. In food processing.

The transesterification reaction encourages sustainability, since the process principles atom economy and waste reduction at source.^[3]

III. Mechanism: [2] [4]



Scheme 2: Proposed reaction mechanism for the transesterification.

In this reaction, first a phenoxide ion is formed by the abstraction of the phenol proton by the free electron pair of the carbene (NHC). Following, a nucleophilic addition occurs whereby the electron on the phenoxide attacks the electrophilic carbonyl centre on the methyl acetate. This action causes an electron shift onto the oxygen of previous carbonyl. To equalize the negative charge, elimination of a methoxide group occurs forming the new ester product. Lastly, the eliminated methoxide anion will attack the proton on the imidazole complex, which leads to the formation of methanol and carbene catalyst regeneration. Molecular sieve is used to remove Methanol from the reaction mixture, shifting the reaction equilibrium to the product side.

IV. Procedure: ^[1]

This procedure is carried out under argon atmosphere.

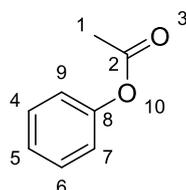
Into a screw cap vial, 2.5 mol % of NHC catalyst and 0.5 g of molecular sieve (4 Å) are poured. Then, 1 mL of THF, 0.074 g (1.0 mmol) of acetic acid methyl ester and 0.188 g of benzyl alcohol (2.0 Eq., 2.0 mmol) are added sequentially into the vial. The resulting mixture is stirred at room temperature for an hour. After this reaction time, the solvent is removed under reduced pressure. The residue is further purified by flash chromatography, using a 10% ethyl acetate/hexanes solution as eluent.

V. Results and Analysis:

Mass of Product = *Actual yield* = 127.2 mg

Theoretical yield = 136.2 mg

Percentage yield = 94 %



¹H-NMR (400 MHz, CDCl₃): δ=7.45 (t, 1H, 5-H), 7.37 (q, 2H, 4-H, 6-H), 7.08 (t, 2H, 9-H, 7-H), 2.31 (s, 3H, 1-H) ppm. (Note: If you can state the multiplicity of the NMR signal, you are also obligated to determine the coupling constant $J_{H,H}$)

¹³C-NMR (100 MHz, CDCl₃): δ= 169.0 (o, 1 C, C-2), 151.3 (+, 1 C, C-8), 129.1 (+, 2 C, C-4, C-6), 125.5 (+, 1 C, C-5), 121.6 (+, 2 C, C-7, C-9), 20.3 (+, 1 C, C-1) ppm.

MP: 1XX ° C

The spectroscopic data are in accordance to literature ^[1].

VI. References:

- [1] Grasa, G.A., Güveli, T., Singh, R., Nolan, S. P., *J. Org. Chem.* **2003**, 68, 7, 2812-2819.
- [2] Otera, J., *Chem. Rev.* **1993**, 93, 1449-1470.
- [3] Aresta M., Dibenedetto, A., Pastore, C., *Stud. Surf. Sci. Catal.* **2004**, 153, 221-226.
- [4] Smith, M.B., March, J., *March's Advanced Organic Chemistry*, 6th Edition, John Wiley & Sons, Inc., New York, **2007**.