# A New Efficient Catalytic System for the Meyer–Schuster Rearrangement

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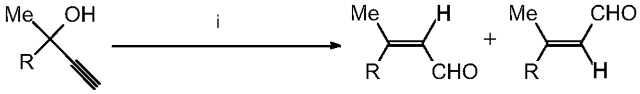
The Meyer–Schuster rearrangement is efficiently catalysed by a system comprising ammonium metavanadate, diphenyl silanediol and dicarboxylic acid.

The Meyer-Schuster rearrangement of tertiary propargyl alcohols **1** into the corresponding α, β-unsaturated aldehydes **2** is a reaction of great practical importance, especially as concerns the synthesis of fragrances, vitamins and some other natural substances. To effect the rearrangement, various vanadic esters are commonly employed as catalysts: *e.g.* alkyl[1] and silyl[2] vanadates and polymeric silyl vanadates.[3,4]

We now report a new, high-efficiency catalytic system based on commercially available ammonium metavanadate. Almost inactive as such, this inorganic salt proved to be a very good catalyst when used in the presence of diphenyl silanediol and ($C_4$–$C_7$) dicarboxylic acids, the sequence in which the reagents are mixed being also significant. In a typical procedure, propargyl alcohol **1a–e** (0.4–0.7 mol) was added to a stirred, boiling mixture of $Ph_2Si(OH)_2$ (32 mmol), dicarboxylic acid (2–7 mmol) and $NH_4VO_3$ (3–7 mmol) in xylene (600 ml). The resulting solution was refluxed until the reaction was complete (1.5–2.5 h, monitored by GLC) and then distilled *in vacuo* to afford unsaturated aldehydes **2a–e** as mixtures of *Z*- and *E*-isomers in isolable yields of 80% (**2a**), 82% (**2b**), 77% (**2c**), 80% (**2d**) and 82% (**2e**) (Scheme 1).



**1a–e** *Z*–**2a–e** *E*–**2a–e**

**a** R = $CH_2CH_2CH{=}CMe_2$
**b** R = $CH_2CH_2CMe{=}CMe_2$
**c** R = $CH_2CH_2CH_2CMe{=}CH_2$
**d** R = $CH_2CH_2CH_2CMe_2(OMe)$
**e** R = $CH_2CH_2CH_2CMe_2(OEt)$

**Scheme 1** *Reagents:* i, $NH_4VO_3 + Ph_2Si(OH)_2$, $(CH_2)_n(COOH)_2$; $n = 2$–5.

Such a dramatic activation of ammonium metavanadate by diphenyl silanediol is obviously due to condensation of these two compounds resulting, under the above conditions, in the formation of catalytically active silyl and polysilyl vanadate groups. This hypothesis is supported by a noticeable evolution of ammonia, and also by the stereochemical results of the rearrangement which resemble those described earlier for polysilyl vanadates;[4] in all cases the thermodynamically unfavoured *Z*-isomers of aldehydes **2** are formed somewhat preferably (ratio *Z*-**2**:*E*-**2** 1.1–1.3, GLC).

Thus, the present method is distinct from the known ones[1–4] by the *in situ* formation of polysilyl vanadates. The function of dicarboxylic acid is both to activate this process and to inhibit the self-condensation of the target aldehydes induced by the basicity of polysilyl vanadates.[5]

The method is also applicable, however, with lower yields, to the synthesis of unsaturated ketones from propargyl alcohols having a non-terminal triple bond, including those containing additional functional groups (alkoxy, acetoxy, *etc.*) and double bonds.

## References

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