

Corrigendum

**Corrigendum to “Large scale synthesis of
acetylene dicarboxaldehyde mono and diacetal”**
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Abstract—In order to succeed in the acidolysis step of the synthesis (1,1,4,4-tetramethoxybut-2-yne **3b** yielding 4-dimethoxybut-2-ynal **2b**) it is necessary to use undried commercial 95–97% formic acid.
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We were questioned by several chemists who could not reproduce our last step of synthesis (**3b** yielding **2b**).

An investigation concerning this problem reveals that:

- Formic acid (99%) from Acros Organics (Cat. No. 14793), that was used in the previous experiments, was from an old bottle. A new bottle of formic acid from the same origin gives bad results.
- Formic acid 98% (Cat. No. 8841) from Lancaster, and formic acid 97% from Avocado (Cat. No. 13285) also gives bad results.
- Formic acid 95–97% from Aldrich (Cat. No. 10,652-16) gives results rather comparable to our older results. A few modifications of the experimental procedure are reported below:

4,4-Dimethoxybut-2-ynal (2b). A 1-L round-bottomed flask, charged with dichloromethane (150 mL) and crude 1,1,4,4-tetramethoxybut-2-yne (**3b**) (50 g, 287 mmol) is cooled at 0 °C. Another flask charged with formic acid (280 g, 6 mol) and dichloromethane (150 mL) is also cooled at 0 °C. During this time, a water bath is regulated at 20 °C. The cooled solution of formic acid is then rapidly added to the diacetal solution. The neck is sealed with a rubber septum equipped

with a stainless steel syringe needle (to allow carbon dioxide evolution from reaction of formic acid with acetal **3b**). The flask is rapidly covered by a large opaque towel, and the reaction is stirred, in the 20 °C regulated water bath, in the dark, for 20 h. The yellow to reddish yellow solution is partitioned three times with ice cooled water (150 mL), the aqueous phase is extracted three times with dichloromethane (100 mL), the new organic phase is washed with ice cooled water (100 mL), and then the organic phase is dried (mixture of Na₂SO₄ and NaHCO₃). The solution is concentrated on a rotary evaporator while keeping the bath temperature below 25 °C, to give 31.5 g, 85% of 4,4-dimethoxybut-2-ynal (**2b**).

Because of the influence of formic acid quality on the yields, it is recommended to follow the reaction by NMR: a 0.5 mL sample of the reaction mixture is evaporated under high vacuum (0.2 mm); to ensure that all the dichloromethane has been removed, ethyl alcohol is added and the solution is again evaporated under vacuum. NMR spectrum is performed in CDCl₃. Area of the peak at 5.22 ppm (CH(OMe)₂ of dialdehyde) has to be compared with the areas of peaks at 5.32 ppm (CH(OMe)₂ and 9.28 ppm (CHO) of the monoaldehyde).