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# IMPROVED PREPARATION OF ALIPHATIC PROPYNOIC ESTERS

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**Summary.** An improved procedure of esterification of propynoic acid, based on the N, N'-dicyclohexylcarbodiimide 4-dimethylaminopyridine condensation, is presented, which gives good results with primary, secondary, allylic and homoallylic alcohols. Reactions conditions are mild. Some limitations are given.

Propynoic esters are compounds of interest, bearing a very reactive triple bond and being involved in various transformations such as coupling reactions, cycloadditions, ionic or radical additions, and important synthetic schemes (see for examples (1-9)). Although many methods of preparation have been described up to now, esterification of propynoic acid remains still difficult. Satisfactory yields could be obtained by treating propynoic acid with a large excess of the required alcohol in the presence of a stoechiometric amount of sulfuric acid or an excess of boron trifluoride (8,11). These methods could only be applied in the case of costless or acid insentive alcohols. The use of propynoic acid chloride (2) seemed limited because of its instability (it must be stored at -78°C to prevent its decomposition) ant its somewhat hazardous preparation (12). Another route involving diethyl azodicarboxylate and triphenylphosphine has been recently described (10). It gave a moderate yield of allyl propinoate. We report here a very convenient preparation of aliphatic propynoic esters, based on the well known N, N'-dicyclohexylcarbodiimide (DCC) 4-dimethylaminopyridine (DMAP) condensation (13-15). It only required a stoechiometric amount of alcohol, left unchanged acid-sensitive materials and gave esters in good yield, without any isomerisation of unsaturated substrates.

$$HC{\equiv}C{-}CO_2H \quad + \quad ROH \xrightarrow{\text{DCC - DMAP}} HC{\equiv}C{-}CO_2R$$

With tertiary alcohols, like in other DCC - based methods (16), yields were very low, whereas with aliphatic, benzylic, secondary, allylic, homoallylic alcohols or diols, satisfactory results were obtained. In order to get good yields, we found that DMAP and DCC had to be added to the mixture of propynoic acid and alcohol because some polymerisation occured when the acid and DMAP were directly mixed together and that a low addition temperature had to be used to minimize polymerization risks of the unstable anhydride intermediate (10).

## Esterification of propynoic acid

To a solution of propynoic acid (3.52g, 44 mmol) and alcohol (40 mmol) (20 mmol for a diol) in dry diethylether (20 ml) at -20°C under nitrogen was added dropwise a solution of DCC (9.27g, 45 mmol), DMAP (0.36g, 3 mmol) in 100 ml of dry diethylether. The cooling bath was then removed and the mixture stirred for 10h at room temperature. The mixture was filtered, washed with a cooled solution of N HCl (2 x 50 ml) and a saturated solution of sodium chloride (2 x 50 ml). Evaporation of the dried solution gave a residue which was chromatographed on a silica gel column using a petroleum ether/diethylether (93 / 7) solution as eluent. When 2-propen-1-ol was used, the ester was purified by distillation ($Eb_{25}$ 56°C. Lit (10) ;$Eb_{760}$ 133-134°C)

**Table : Propynoic esters**

| Alcohol | Yield (%)(a) | $^1$H-NMR ($CCl_4$, (ppm)) |
|---|---|---|
| 1-Octanol | 68 | 0.80-1.8 (m,15H) ; 2.85 (s,1H) ; 4.12 (t,2H) |
| 1.4-Butanediol | 66 | 1.65-1.9 (m,4H) ; 2.82 (s,2H) ; 4.15 (m,4H) |
| Benzyl alcohol | 52 | 2.85 (s,1H) ; 5.0 (s,2H) ; 7.15 (s,5H) (19) |
| α–Methylbenzyl alcohol | 76 | 1.50 (d,2H) ; 2.80 (s,1H) ; 5.85 (q,1H) ; 7.20 (s,5H) |
| 3,5-Hexadien-1-ol | 72 | 2.30 (q,2H) ; 2.75 (s,1H) ; 4.05 (t,2H) ; 4.80-6.45 (m,4H) |
| 2-Propen-1-ol | 75 | 2.90 (s,1H) ; 4.60 (d,2H) ; 5.10-6.30 (m,3H) (10) |
| 3-Phenyl-2-propen-1-ol | 71 | 2.90 (s,1H) ; 4.65 (d,2H) ; 5.80-6.70 (m, 2H) ; 7.20 (s,5H) (20) |
| t-Butanol | 0 (18) | |
| 1-Methyl-1-phenyl ethanol | 0 | |

(a) Satisfactory microanalyses obtained : C ± 0.40, H ± 0.31

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