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Direct Synthesis of Alkyl 2-Alkynoates from Alk-1-ynes, CO_2, and Bromoalkanes Catalysed by Copper(I) or Silver(I) Salt

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Alkyl alkynoates are synthesized directly from alk-1-ynes, CO_2, and bromoalkanes in the presence of a catalytic amount of copper(I) or silver(I) salt.

Alk-2-ynoates are versatile intermediates in organic synthesis, especially in cycloaddition reactions and have been prepared by transformation of other functional groups. Mostly, however, the carboxyl functions is introduced directly. Reaction of a metallated alkyne $RC\equiv CM$ (M=Li, Na, K and MgX) with CO_2 and chloroformic ester gives alkynoic acid and alkyl alkynoate, respectively.[1] Of course these reactions are stoichiometric since the metallated alkynes are not regenerated *in situ*. During the course of our studies directed toward the effective utilization of CO_2, we were able to bring about a catalytic reaction for the synthesis of alk-2-ynoates directly from alk-1-yne, CO_2, and bromoalkane mediated by copper(I) or silver(I) salt in the presence of K_2CO_3, eqn. (1).

$$R^1C\equiv CH + CO_2 + R^2Br \xrightarrow[\text{Cat : Cu}^{\text{I}}\text{ or Ag}^{\text{I}}]{K_2CO_3} R^1C\equiv CCO_2R^2 \tag{1}$$

A mixture of alk-1-yne (5 mmol), 1-bromohexane (10 mmol), and K_2CO_3 (30 mmol) was allowed to react under an atmosphere of CO_2 (balloon) in the presence of CuI (0.2 mmol) at 100 °C for 4 h in *N,N*-dimethylacetamide (DMAc; 15 ml). After aqueous work-up, the product was isolated by silica gel chromatography (hexane–ethyl acetate).

CuBr, AgI, and $AgNO_3$ can be utilized successfully as the catalyst. $CuBr_2$ gave somewhat a lower yield of the product. The choice of solvent and base is particularly important. Polar aprotic solvents such as DMF, DMAc, *N*-methylpyrrolidone, and 1,3-dimethyl-2-imidazolidinone are suitable for this reaction. The reaction did not occur at all in THF and MeCN. Employment of a stronger base such as triethylamine or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) suffers from alkylation of the base with bromoalkane. K_3PO_4 can be used as the base instead of K_2CO_3 at the expense of the product yield.

Ethynylbenzene, *p*-ethynyltoluene, and oct-1-yne reacted well with CO_2 and 1-bromohexane to afford the corresponding hexyl alkynoates in 89, 79 and 78% yield, respectively. Prop-2-yn-1-ol which bears a hydroxy group was exclusively converted to a different type of product, hexyl prop-2-ynyl carbonate, on the reaction with CO_2 and 1-bromohexane. The formation of unsymmetrical carbonate from alcohol, CO_2, and haloalkane has been reported elsewhere.[2] But-3-yn-1-ol behaved similarly. The protection of prop-2-yn-1-ol and but-3-yn-1-ol by forming tetrahydropyranyl ether gave rise to the expected alkynoate in 50–55% yield. The reactions with functionalized alk-1-ynes like ethyl prop-2-ynoate, prop-2-ynyl ethanoate, butyl prop-2-ynyl carbonate, and trimethylsilylethyne were either complicated or sluggish. The reaction of ethynylbenzene with fairly reactive α-bromotoluene afforded the expected alkynoate in 55% yield together with 43% yield of dibenzyl carbonate, which arose from the reaction of α-bromotoluene and K_2CO_3. Formation of the symmetrical carbonate predominated with ethyl bromoacetate. 1-Iodohexane can be employed instead of 1-bromohexane although the yield slightly declines.

The probable reaction pathway involves (*i*) copper acetylide formation,[1] (*ii*) CO_2 insertion into the copper–carbon bond[3] and (*iii*) ester formation with bromoalkane with regeneration of the copper salt.[3–5] The insertion reacton of CO_2 into a copper–carbon bond has been the subject of several investigations.[3,6–8]

$$\begin{aligned} &R^1C\equiv CH \xrightarrow[\text{Step } i]{CuX,\ K_2CO_3} R^1C\equiv CCu \xrightarrow[\text{Step } ii]{CO_2} \\ &R^1C\equiv CCO_2Cu \xrightarrow[\text{Step } iii]{R^2Br} R^1C\equiv CCO_2R^2 + CuBr \end{aligned} \tag{2}$$

The key of the reaction is the use of a polar aprotic solvent such as DMAc or DMF. Since copper phenylpropynoate ($PhC\equiv CCO_2Cu$) is fairly unstable at 35 °C in DMF to decarboxylation, the crucial effect of the solvent would be ascribed to the third step.

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