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SOLID-LIQUID PHASE TRANSFER AND COBALT CATALYZED SYNTHESIS OF BUT-2-ENOLIDE

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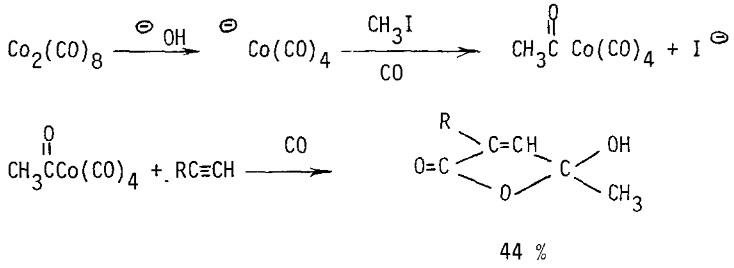
Summary : Tris dioxa-3,6-heptylamine (TDA) is an effective solid-liquid phase transfer catalyst for the synthesis of hydroxybut-2-enolide from alkyne and benzyl bromide under CO atmosphere.

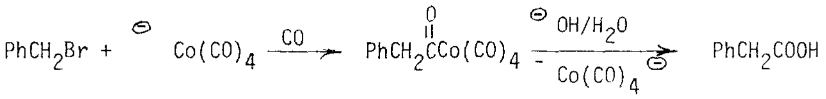
Phase transfer catalysis has been shown to be useful for effecting a variety of metal catalyzed reactions[1]. Most of these have been performed using liquid-liquid systems involving anionic species transferred from aqueous to organic phase by onium salts. A solid-liquid two-phase combination has also been extensively used in organic synthesis[2]. Its application to transition metal catalyzed reactions using macrocyclic polyethers as complexing agents for alkali cations has also been reported[3]. This last technique is particularly useful when the presence of water is incompatible with the reaction conditions.

This was encountered when the carbonylation of alkynes catalyzed by $Co_2(CO)_8$ in the presence of methyl iodide[4,5] was extended to other alkyl halides. In the reported reaction, alkynes react smoothly with CO and CH_3I in a liquid-liquid two-phase system to yield the corresponding but-2-enolide, most probably via the intermediate formation of the acylcobalt complex.



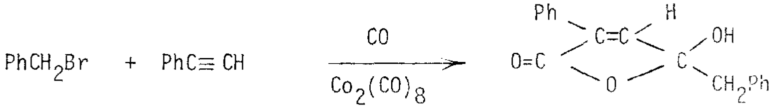
Conditions : 5N NaOH/benzene, CTAB, RT, 1 atm.
CTAB = Cetyltrimethylammonium bromide

When benzylbromide was used, no but-2-enolide was formed, due to the fast hydrolysis of the acylcobalt[6] intermediate prior to the alkyne complexation. Thus phenylacetic acid was the only product obtained.



$$PhCH_2Br + \overset{\ominus}{Co}(CO)_4 \xrightarrow{CO} PhCH_2\overset{O}{\overset{\|}{C}}Co(CO)_4 \xrightarrow[-\ \overset{\ominus}{Co}(CO)_4]{\ominus OH/H_2O} PhCH_2COOH$$

This inconvenience was circumvented by performing the reaction in the absence of water in a solid-liquid system using a new kind of chelating agent[7], $N\left[(CH_2)_2O-(CH_2)_2-OCH_3\right]_3$ (TDA), which has the same properties as a crown ether but without the toxicity[8] and the work-up difficulties encountered with the macrocyclic catalysts.



40 %

In a typical experiment, the tetracarbonyl anion was generated under CO (1 atm) from $Co_2(CO)_8$ (0.102 g, 0.3 mmole) and NaOH (4.4 g, 11.2 mmol) in the presence of TDA (0.194 g, 0.6 mmole) in toluene (20 ml). A mixture of benzyl bromide (1.2 ml, 10 mmoles) and phenylacetylene (1.1 ml, 10 mmoles) was then added dropwise and the suspension was heated to 60° C while stirring for 12 hrs. The lactone was then isolated from the organic phase in 40 % yield after purification by chromatography[9].

Acknowledgement

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9) The structure of the product was determined on the basis of spectral data (i.r., n.m.r., m.s.) ; the yield was of isolated product but not optimized.

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