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STEREOSPECIFIC NICKEL AND PHASE TRANSFER CATALYZED CARBONYLATION OF VINYL BROMIDES AND CHLORIDES

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Summary: Nickel cyanide catalyzes the carbonylation of vinyl bromides and chlorides to α,β-unsaturated acids.

Phase transfer catalysis is a valuable method for effecting a variety of metal catalyzed carbonylation reactions[1]. Recently, it has been found that nickel cyanide is an active catalyst for the carbonylation of allyl halides[2], aryl iodides[3], and benzyl chlorides , the latter reaction being promoted by lanthanide reagents.[4] We now wish to report that the nickel salt can function as a catalyst precursor for the stereospecific carbonylation of vinyl bromides and even certain unsaturated chlorides to α,β-unsaturated acids.

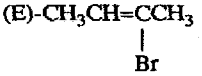
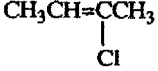
Treatment of trans-β-bromostyrene with 6N sodium hydroxide, toluene, catalytic quantities of cetyltrimethylammonium bromide (CTAB) and nickel cyanide (10:1 ratio of unsaturated halide/$Ni(CN)_2{\cdot}4H_2O$), for 2.5 hours at 95°C and one atmosphere of carbon monoxide, afforded pure trans-cinnamic acid in 75% yield. Reaction is slower in the absence of CTAB, with the acid isolated in 54% yield after a reaction time of six hours. One can use a higher substrate/nickel ratio but the reaction is less efficient (50:1 ratio of trans-PhCH=CHBr/$Ni(CN)_2{\cdot}4H_2O$ gave the acid in 57% yield after 2.5 hours, in the presence of CTAB). The carbonylation reaction is also applicable to other β- and α-bromostyrenes, and to β-chlorostyrene (Table 1), occurring with retention of stereochemistry. Non-aromatic vinyl bromides (e.g., 1-bromo-2-methylpropene, 2-bromo-2-butene) can also be carbonylated to the corresponding acids, while 2-chloro-2-butene is inert. However, cyclic chloroolefins are reactive, as witnessed by the formation of cyclopentene 1-carboxylic acid or the cyclohexene analog in good yields.

The key catalytic species in these reactions is probably the cyanotricarbonylnickelate anion.[2] This method is clearly superior to the recently described use of in situ generated dicarbonyldicyanonickelate dianion for the carbonylation reaction. The latter process is stoichiometric in nature and only proceeds for β-bromostyrenes. In addition, it is not highly stereoselective and by-products such as reductively coupled diacids can be formed in appreciable yields.[5]

The following general procedure was used: to degassed toluene (20 ml.) and NaOH (20 ml. of 6 - 7.25N) was added $Ni(CN)_2{\cdot}4H_2O$ [1.0 mmol] and 0.063 g (0.17 mmol) of CTAB (CO atmosphere). The reaction mixture was stirred and heated for40-50 minutes at 95-100° C. A toluene (3 - 5 ml.) solution of the vinyl halide (10 mmol) was added, in small portions, over a period of two hours, and then stirring was

Table 1

$Ni(CN)_2 \cdot 4H_2O$ and CTAB Catalyzed Carbonylation of Vinyl Halides

Halide	Reaction Time hr	Yield of Corresponding Acid [a] %
(E)-PhCH=CHBr	2.5	75[b]
	6.0	54[c]
(E)-3,4-$(CH_3O)_2C_6H_3CH$=CHBr	1.5	97
PhC(Br)=CH_2	3.0	65
$(CH_3)_2C$=CHBr	8.0	45
 (E)-$CH_3CH{=}C(Br)CH_3$	6.0	89
(E)-PhCH=CHCl	18.0	39
 $CH_3CH{=}C(Cl)CH_3$	18.0	--
1-chlorocyclopentene	3.0	55
1-chlorocyclohexene	12.0	82

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[a] Isolated yields. Products were characterized by comparison of spectral data [ir,nmr (H-1, C-13), ms] and gc retention times with those for authentic materials. [b] 5% of PhCH=CHCN was also isolated. [c] No CTAB.

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continued at 95 - 10°C until reaction was complete (see Table for reaction times). After cooling, the phases were separated, the aqueous phase was neutralized with 10% HCl, and then extracted with ether. Concentration of the dried (Na_2SO_4) ether extract afforded the acid. Further purification, if required, was effected by distillation or recrystalization.

In conclusion, nickel cyanide is of genuine use for the carbonylation of vinyl bromides and chlorides under phase transfer conditions. This method is simple both in execution and work-up, and exhibits excellent stereochemical control.

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References

1. des Abbayes, H., New J. Chem., 1987, 11,535.
2. Joo, F.; Alper, H., Organometallics, 1985, 4, 1775.
3. Amer., I.; Alper, H., J. Org. Chem., 1988, 53, 5147.
4. Amer., I.; Alper, H., J. Am. Chem. Soc., 1989, 111, 927.
5. Miura, M.; Shimoura, N.; Nomura, M.; J. Chem. Soc., Perkin Trans. I. 1988, 1993.

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