

Reaction of α -Substituted β -Bromostyrenes with Dicarboxydicyanonickelate(0) Anion in Alkaline Medium under Carbon Monoxide

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The reactions of (*E*)- and (*Z*)- β -bromostyrene (**1a**) with dicarboxydicyanonickelate(0) anion generated *in situ* in the presence of sodium or calcium hydroxide under carbon monoxide gave a carbonylated product mixture of (*E*)-cinnamic acid [(*E*)-(**2a**)], 3,4-diphenylhexanedioic acid (**4**), and 3-phenylpropionic acid (**5**). In contrast, in the reactions of α -methyl- and phenyl- β -bromostyrenes (**1b** and **c**) the corresponding nitriles (**3b** and **c**) were formed, together with the carboxylic acids (**2b** and **c**).

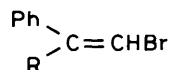
The carbonylcyanonickelate(0) anions $[\text{Ni}(\text{CN})_n(\text{CO})_{4-n}]^{n-}$ ($n = 1$ or 2) are the only transition metal complexes containing cyanide as ligand known to mediate carbonylation of organic halides.¹⁻³ The reactions of halides with the nickelate may also give a mixture of carbonylation and cyanation products.² However, little is known about factors affecting the course of the reaction.

As part of our study of transition metal-catalysed carbonylation of organic halides in alkaline medium,⁴ we have studied the reactions of α -substituted β -bromostyrenes (**1a–c**) with dicarboxydicyanonickelate(0) generated *in situ* in the presence of sodium or calcium hydroxide under a normal pressure of carbon monoxide in either aqueous methanol or 1,4-dioxane.

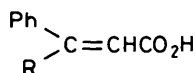
Results and Discussion

When the reaction of (*E*)- β -bromostyrene [(*E*)-(**1a**)] (1 equiv.) with dicarboxydicyanonickelate(0) prepared from potassium tetracyanonickelate(II) (1 equiv.), tin powder (1 equiv.), and

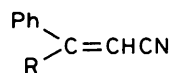
sodium hydroxide (12.5 equiv.) was carried out in aqueous methanol at 60 °C under carbon monoxide for 10 h, 3,4-diphenylhexanedioic acid (**4**) (41%) was obtained as the major product, together with 3-phenylpropionic acid (**5**) (28%), and (*E*)-cinnamic acid [(*E*)-(**2a**)] (12%) (Table). In contrast, the reaction of (*E*)-(**1a**) in dioxane–water selectively afforded the acid (**5**) (66%) along with *trans*-3,4-diphenylcyclopentanone (**6**) (20%). A similar solvent-dependent product distribution was observed in reactions using zinc in place of tin for the nickelate preparation. The acid (**2a**) obtained from each reaction of (*Z*)-(**1a**) was exclusively the *E*-isomer, suggesting that the configuration of the bromide is not retained to give the more stable stereoisomeric acid. It was confirmed that cinnamitrile (**3a**) was hydrolysed under the reaction conditions used for (**1a**) to give an almost equimolar mixture of (**2a**) and cinnamide, no other products being detected. However no evidence for the formation of cinnamamide was obtained in the reactions of (**1a**). These results indicate that the reaction of (**1a**) with the nickelate is predominantly a carbonylation.



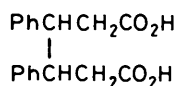
- (1) **a**; R = H
b; R = Me
c; R = Ph



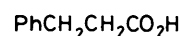
- (2) **a**; R = H
b; R = Me
c; R = Ph



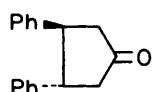
- (3) **a**; R = H
b; R = Me
c; R = Ph



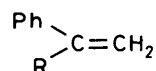
(4)



(5)



(6)

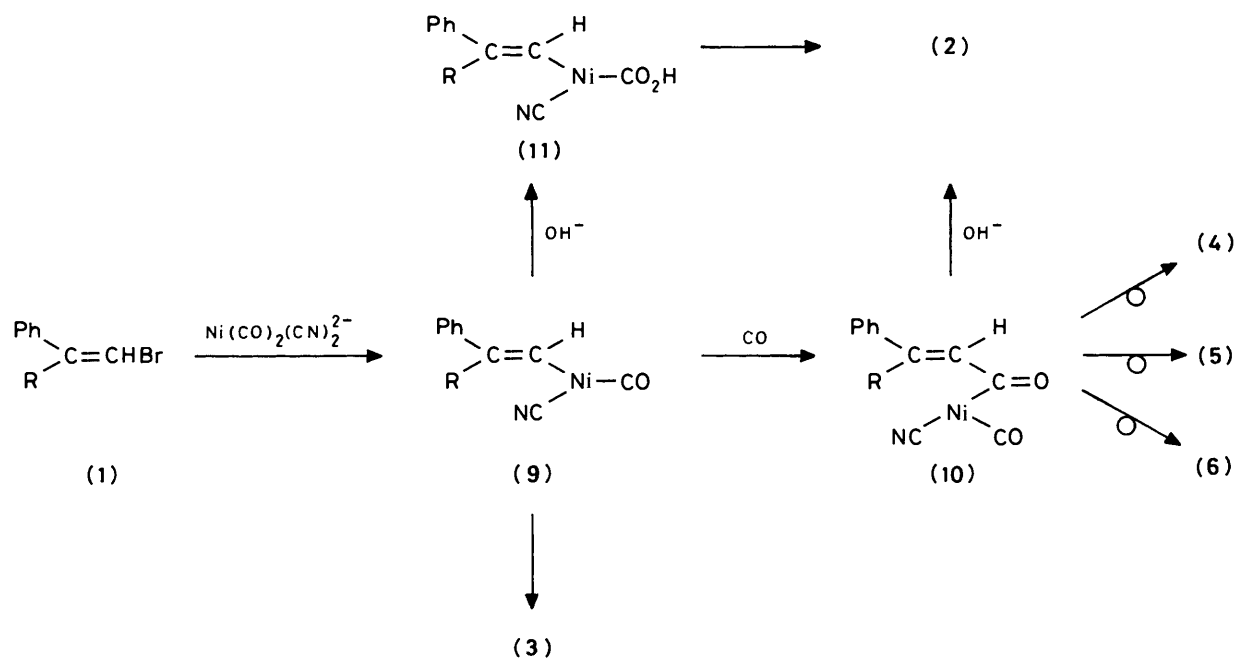


- (7) R = Me
(8) R = Ph

Table. Carbonylation of β -bromostyrenes (**1a–c**)^a

Bromide	Reductant	Base	Solvent	Products (% yield) ^{b,c}
(<i>E</i>)-(1a)	Sn	NaOH	MeOH	(2a) (12), (4) (41), (5) (28)
(<i>E</i>)-(1a)	Sn	NaOH	Dioxane	(5) (66), (6) (20)
(<i>E</i>)-(1a)	Zn	NaOH	MeOH	(2a) (43), (4) (30), (5) (5)
(<i>E</i>)-(1a)	Zn	NaOH	Dioxane	(2a) (39), (5) (36), (6) (15)
(<i>E</i>)-(1a)	Zn	NaOH ^d	MeOH	(2a) (60), (4) (13), (5) (3)
(<i>E</i>)-(1a)	Zn	NaOH ^d	Dioxane	(2a) (45), (5) (7), (6) (20)
(<i>E</i>)-(1a)	Sn	Ca(OH) ₂	MeOH	(2a) (71), (4) (3), (5) (2)
(<i>E</i>)-(1a)	Sn	Ca(OH) ₂	Dioxane	(2a) (66), (6) (4)
(<i>E</i>)-(1a)	Zn	Ca(OH) ₂	MeOH	(2a) (75), (4) (3), (5) (2)
(<i>E</i>)-(1a)	Zn	Ca(OH) ₂	Dioxane	(2a) (68), (5) (2), (6) (10)
(<i>Z</i>)-(1a)	Zn	NaOH	MeOH	(2a) (43), (4) (28), (5) (6)
(<i>Z</i>)-(1a)	Zn	NaOH	Dioxane	(2a) (28), (5) (35), (6) (13)
(<i>Z</i>)-(1a)	Zn	Ca(OH) ₂	MeOH	(2a) (64), (5) (4)
(<i>E</i>)-(1b)	Zn	NaOH	MeOH	(2b) (52; <i>E</i> : <i>Z</i> 7.4:1), (3b) (23; <i>E</i> : <i>Z</i> 7.9:1), (7) (11)
(<i>E</i>)-(1b)	Zn	NaOH	Dioxane	(2b) (30; <i>E</i> : <i>Z</i> 7.4:1)
(<i>E</i>)-(1b)	Zn	Ca(OH) ₂	MeOH	(2b) (12; <i>E</i> : <i>Z</i> 8.0:1), (7) (5)
(<i>E</i>)-(1b)	Zn	Ca(OH) ₂	MeOH	(2b) (30; <i>E</i> : <i>Z</i> 12:1), (3b) (49; <i>E</i> : <i>Z</i> 14:1), (7) (5)
(1c)	Zn	NaOH	MeOH	(2c) (67), (3c) (24), (8) (6)
(1c)	Zn	NaOH	Dioxane	(2c) (12), (3c) (10), (1c) (75)
(1c)	Zn	Ca(OH) ₂	MeOH	(2c) (19), (3c) (40), (1c) (35)

^a At 60 °C for 10 h under carbon monoxide; [bromide]:[K₂Ni(CN)₄]:[reductant]:[OH⁻] 1:1:1:12.5. ^b Yield determined by g.l.c. analysis. ^c The acid (**2a**) was exclusively the *E*-isomer (determined by g.l.c. and ¹H n.m.r.) in each case. ^d 3 Equiv. of OH⁻.

**Scheme.**

Base concentration in the reaction medium was found to affect the product composition. On decreasing the amount of sodium hydroxide used from 12.5 to 3 equiv., the relative yield of the normal carbonylation product (**2a**) increased and that of (**4**) and (**5**) decreased. When the less soluble calcium hydroxide was used as base in place of sodium hydroxide, (**2a**) was the predominant product in each case. These results suggest that an excess of hydroxide ion in the medium enhances formation of the reductively carbonylated products (**4**) and (**5**).

The reaction of (*E*)-1-bromo-2-phenylpropene [(*E*)-(1b)], using zinc and sodium hydroxide in methanol–water, gave a mixture of 3-phenylbut-2-enoic acid (**2b**) (52%; *E*:*Z* 7.4:1), 3-

phenylbut-2-enitrile (**3b**) (23%; *E*:*Z* 7.9:1), and α -methylstyrene (**7**) (11%). A similar product mixture was obtained from the reaction of (*E*)-(1b) in dioxane–water. When calcium hydroxide was used as base in methanol–water, the nitrile (**3b**) (49%; *E*:*Z* 14:1) was the major product. This is in marked contrast to the fact that in the reaction of (**1a**) under the same conditions the acid (**2a**) was the predominant product. The trend of product distribution in the reaction of 1-bromo-2,2-diphenylethene (**1c**) in each case was similar with that observed with (**1b**). The nitriles (**3b** and **c**) are fairly stable under these reaction conditions and were recovered in 78–97% yield. These results indicate that an α -substituent on β -bromostyrene

enhances the cyanation reaction and depresses the formation of reductively carbonylated products.

The intermediate leading to the normal carbonylation product (**2**) may be a cinnamoylnickel complex (**10**); nucleophilic attack by hydroxide on (**10**) gives (**2**) (Scheme).^{5,6,†‡} Reductive elimination from a styrylnickel complex (**9**) is also the most probable process for the formation of the nitrile (**3**). The fact that the reaction of (**1a**) using calcium hydroxide as base predominantly gives the acid (**2a**), whereas the nitriles (**3b** and **c**) are produced from (**1b** and **c**) as the major products, implies that the rate of the migratory insertion of the ligand carbon monoxide from the intermediate (**9**) to give (**10**), relative to the reductive elimination of (**3**), is a function of the α -substituent on β -bromostyrene; in the reaction of (**1a**) the migratory insertion is extremely fast, whereas with (**2b** and **c**) the reductive elimination is fast enough to compete with the migratory insertion.

The following results are suggestive of the paths leading to the reductively carbonylated products (**4**) and (**5**). (a) The acid (**2a**) is stable and did not change into either (**4**) or (**5**) under the conditions employed for the reaction of (**1a**). (b) The reaction of an equimolar mixture of (**1a**) and 4-chlorocinnamic acid (**12**) gave only the products from (**1a**), the acid (**12**) being recovered quantitatively. These facts suggest that both the reductive coupling leading to (**4**) by one-electron reduction and the two-electron reduction to give (**5**) might occur in the intermediate (**10**). The active species for the reductions would be a nickel hydride and/or its equivalent formed from the reaction of the carbonylnickelate with an excess of hydroxide ion in the medium.^{5,6} The details of the mechanism and the solvent-dependent composition of (**4**) and (**5**) are, however, unclear.

Experimental

¹H N.m.r. spectra were obtained with a JMN-PS-100 spectrometer for CDCl₃ solutions. G.l.c.-mass spectra were obtained with a Hitachi RMU-6M spectrometer and Fourier transform i.r. spectra with a Nippon Bunko FT/IR-3 spectrometer using a calcium fluoride cell. G.l.c. analysis was carried out with a Shimadzu GC-8A gas chromatograph.

Vinyl bromides (*E*)-(**1a**),⁷ (*Z*)-(**1a**),⁸ (*E*)-(**1b**),⁹ and (**1c**)¹⁰ were prepared by reported methods. Other starting materials were commercially available. The experimental details given here may be regarded as typical in methodology and scale.

Reaction of the Bromostyrene (E)-(1a) with Dicarboxydicarbonylnickelate(0) in Methanol-Water in the Presence of Tin and Sodium Hydroxide.—Dicarbonyldicyanonickelate(0) anion was generated by mixing potassium tetracyanonickelate(II) (2 mmol), tin powder (2 mmol), and sodium hydroxide (25 mmol) in water (10 ml) under a normal pressure of carbon monoxide, and stirring for 5 h at room temperature.¹¹§ Then, a solution of the olefin (*E*)-(**1a**) (2 mmol) in methanol (10 ml) was added and

† The possibility that the acid (**2**) is also produced by reductive elimination from the intermediate (**11**) (Scheme) formed by the reaction of (**9**) with hydroxide, however, cannot be excluded.

‡ The following result suggests that participation of a path via phenylacetylene formed by dehydrobromination of (**1a**) to give (**2a**) is negligible. The reaction of phenylacetylene under the conditions used for (**1a**) gave a complex mixture of neutral products: the major product was 2,4-diphenylcyclopent-2-enone, the yield of acidic products being less than 10%.

§ The Fourier transform i.r. spectrum of the nickelate solution showed four characteristic peaks for [Ni(CN)₂(CO)₂]²⁻ at ν_{CO} 1 981 and 1 919 cm⁻¹ and ν_{CN} 2 077 and 2 058 cm⁻¹ (Figure).¹² A peak at 2 124 cm⁻¹ for [Ni(CN)₄]²⁻ was observed as a very weak shoulder, indicating that only a small amount of the starting nickelate remains. A similar spectrum was obtained when zinc powder was used instead of tin.

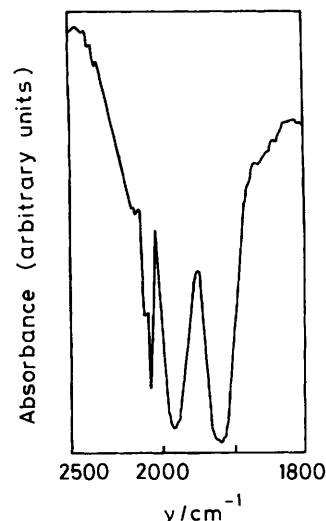


Figure. Fourier transform i.r. spectrum of aqueous dicarbonyldicyanonickelate prepared using tin

the resulting mixture was stirred at 60 °C for a further 10 h. The mixture was poured into dilute hydrochloric acid and extracted with ether. The acidic products were extracted with aqueous sodium carbonate. After acidification and re-extraction with ether the products were methylated with diazomethane in ether. Analysis by g.l.c.-mass spectrometry confirmed the formation of (*E*)-(**2a**) (12%), (**4**) (41%), and (**5**) (28%). The methyl esters of (**2a**), (**4**), and (**5**) were also isolated by column chromatography on silica gel (hexane-ethyl acetate as eluant). The methyl ester of (**4**) had m.p. 180 °C (from ethanol) (lit.,¹³ 178 °C); δ_{H} 2.36—2.52 (m, 4 H), 3.24—3.52 (m, 2 H), 3.40 (s, 6 H), and 7.16—7.50 (m, 10 H).

Products.—The following products are known and were identified by comparison with authentic specimens: (*E*)-(**2b**),¹⁴ (*Z*)-(**2b**),¹⁵ (**2c**),¹⁰ (*E*)-(**3b**),¹⁶ (*Z*)-(**3b**),¹⁶ (**3c**),¹⁶ and (**6**).¹⁷

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