Selective Cyanation of Bromostyrenes by Pentacyanocobaltate(II) and Nuclear Magnetic Resonance Evidence for the Formation of Intermediate σ-Styryl–Cobalt(III) and η-Cinnamonitrile–Cobalt(I) Cyano-complexes

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Summary. Cis- and *trans-β-* and α-bromostyrenes were converted catalytically and stereoselectively into unsaturated nitriles under mild conditions; n.m.r. evidence for the formation of the title intermediates suggests a catalytic cycle involving the pentacyanocobalt (I) ion as the active species.

PREVIOUSLY,[1] we described the hydrocyanation of acetylenes to unsaturated nitriles by pentacyanocobaltate(II) *via* σ-alkenylcyanocobaltate(III) complexes. This suggested that σ-alkenylcyano-complexes, prepared by other methods, would be converted into unsaturated nitriles. It has been reported that σ-alkenylcyano-complexes, obtained by the reaction of vinyl halides with alkaline $[Co(CN)_5H]^{3-}$, were converted into unsaturated nitriles on treatment with acid and base, but this has not been studied in detail.[2] We now report the catalytic and stereoselective cyanation of bromostyrenes in the absence of acid and base, and the intermediate formation of new η-olefin–cobalt complexes, as well as σ-alkenyl complexes. Compared with the cyanation of β-bromostyrenes by CuCN,[3] $K_4[Ni_2(CN)_6]$ + KCN,[4] or $Pd(PPh_3)_4$ + KCN,[5] the present method is more convenient and gives excellent yields and selectivity under milder conditions.

Reactions were performed by addition of the bromostyrenes to an aqueous solution of the cyanocobaltate under H_2 or N_2. The results are shown in Table 1. *Cis-* and *trans-β*-bromostyrenes gave *cis* and *trans*-cinnamonitriles, respectively, together with small amounts of hydrogenolysis and hydrogenation products. The *cis*-isomer was more reactive than the *trans*. Greater reactivity

Table 1. Cyanation of *cis*- and *trans*-β-bromostyrenes[a]

PhCH=CHBr/mmol		CN:Co	Time/h[b]	Total yield %[c]	Product (PhCH=CHCN) (%)[d]	
					cis	*trans*
cis[e]	5	4·95	2	55	96	3
	10	,,	4	166	90	5
	5	,,	3	67	84	11[f]
	10[g]	,,	5	167	86	6
	15[g]	,,	8	256	82	15[h]
	5	6·0	2·5	52	81	12
	15	,,	5	259	86	7
trans[i]	5	4·95	8	53	0	92
	10	,,	18	138	0	92
	10	,,	9	150	0	92
	5[g]	,,	24	64	0	95[j]
	5	6·0	24	81	0	82

[a] $CoCl_2$, 5 mmol; KOH, 10 mmol, in 25 cm^3 H_2O, at 45 °C; under H_2 (except where indicated). [b] Reaction time for >99% conversion. [c] Based on [Co]. [d] Other products are: $PhCH{=}CH_2$, $PhCH_2Me$, $PhCH_2CH_2CN$, and $PhCH{=}CHCONH_2$. [e] *cis-trans* = 92:8. [f] Without KOH. [g] Under N_2. [h] KCN (5 mmol) was added after 5 h. [i] *cis*:*trans* = 1:99. [j] At 55 °C.

was observed with the *trans*-isomer, for CN:Co<5:1 than for CN:Co>5:1.[1] The reaction was promoted by the presence of hydrogen and KOH. Without KOH, the reaction was deactivated by deposition of a yellow precipitate. At CN:Co = 4·95:1, with a ratio of bromostyrene to cobalt complex of 2:1 reaction was complete, but addition of KCN was necessary to complete the reaction for a 3:1 ratio of bromostyrene:cobalt complex. This suggests that addition of KCN to maintain CN:Co<*ca.* 5:1 in an aqueous phase is effective for the catalytic cyanation of bromostyrenes in large excess, but prolonged reaction lowers the selectivity owing to the slow hydration of nitriles to amides. Slow isomerisation of *cis*-cinnamonitrile to the *trans*-isomer was observed after disappearance of *cis*-β-bromostyrene. α-Bromostyrene gave α-cyanostyrene as the main product, together with α-cyanoethylbenzene. The reaction was slow; addition of 5 cm^3 of benzene prevented the polymerisation of α-cyanostyrene. The total yield, from 5 mmol of α-bromostyrene, was 46% after 12 h at 55 °C and CN:Co = 4·95:1 in H_2; α-cyanostyrene: α-cyanoethylbenzene = 80:20.

The rather low yield, even after the complete conversion of bromostyrenes, suggested that the products were trapped as stable intermediates. ^1H and ^{13}C N.m.r. spectra of the reaction solutions in D_2O indicated clearly that two kinds of intermediates were formed: η-olefin- and σ-alkenyl-complexes. We observed two pairs of doublets at higher and lower fields, and the coupling constants (J_H and J_{CH}) showed that they were olefinic. Details of the olefinic proton and carbon resonances are given in Table 2. The large upfield shifts of the olefinic doublets, which are characteristic of η-olefin-complexes,[6,7] and observation of the nitrile and phenyl carbons indicated the presence of η-cinnamonitrile–Co complexes. This was supported by the observation of identical spectra from reactions using cinnamonitriles in place of bromostyrenes. These are the first examples of η-olefin–cyanocobalt complexes. The complexes which show olefinic doublets at lower fields are less stable than the η-olefin-complexes, and ^{13}C n.m.r. spectra were observed by cooling the samples. The downfield shifts of the olefinic doublets suggested that the complexes were σ-β-styryl–Co complexes.[6] The broadening of the carbon peak at lowest field seems to reflect the formation of a C–Co bond.† Transformation of the σ-complex into the η-complex was indicated by the dependence of the relative concentration of these complexes on the reaction time. In the case of α-bromostyrene, only the σ-complex was detected: for the $=CH_2$ group,

Table 2. ^1H and ^{13}C N.m.r. chemical shifts and coupling constants for the –CH=CH– groups of intermediate complexes and products[a]

Reactant		Intermediate complexes				Products (PhCH=CHCN)			
		δ_C p.p.m.	J_{CH}[b]/Hz	δ_H	J_H[b]/Hz	δ_C/p.p.m.	J_{CH}[b]/Hz	δ_H	J_H[b]/Hz
cis-PhCH=CHBr	η	11·4[c]	164	2·43	8·8	94·9[e]	175	5·43	12·2
		44·8	154	3·85		148·6	162	7·12	
	σ	130·4	154	7·68	7·5				
		140·0	145	7·90					
trans-PhCH=CHBr	η	10·9[d]	162	2·74	10·0	96·2[f]	171	5·86	16·6
		47·7	156	3·98		150·4	158	7·38	
	σ	140·5	154	6·84	16·5				
		147·4	142	7·80					

[a] Measured on a JEOL FX-100 spectrometer. Dioxan (δ_C 67·4 p.p.m.) and Me_4Si were used as references in D_2O and $CDCl_3$, respectively. [b] Sharp doublet. δ_C(CN) [c]133·1. [d] 132·5. [e] 117·4. [f] 118·1 p.p.m.

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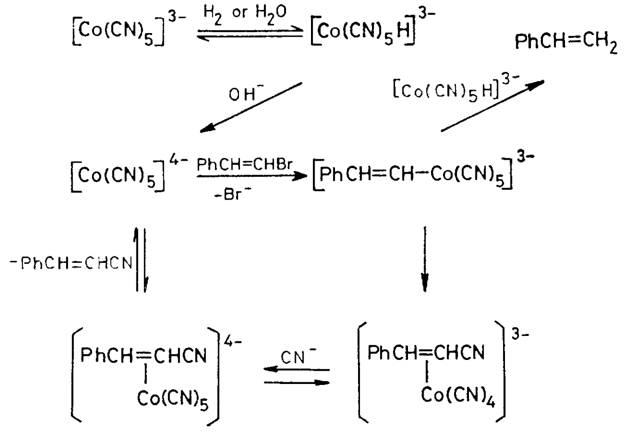
† We observed similar broadening with some other σ-alkenyl and σ-alkyl cyanocobaltates (unpublished results), but the evidence is not conclusive at present, as to whether the carbon peak is necessarily broadened by C–Co bond formation.

δ_H 5·15 and 5·54, J_H 2·7 Hz; δ_C 124 p.p.m., J_{CH} 149 and 159 Hz.



SCHEME

Since it is reasonable to assume the formation of σ-Co^{III} and η-Co^{I} complexes, we propose the mechanism in the Scheme for this reaction, in which the pentacyanocobalt(I) ion is the active species. The formation of pentacyanocobalt(I) ion in alkaline solution of $[Co(CN)_5H]^{3-}$ has been reported.[8] The retention of stereochemistry and lack of deuterium incorporation into the olefinic group, which was shown by the sharp doublets in the n.m.r. spectra, can be explained in terms of nucleophilic substitution of the bromides by the Co^{I} species as observed for cobaloxime (I),[9] followed, probably, by the migration of the vinyl group to the CN ligand. The formation of stable η-complexes suggests that η-β-bromostyrene–Co complexes may participate in the initial substitution.

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