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THE REACTION OF trans-β-BROMOSTYRENE WITH POTASSIUM HEXACYANODINICKELATE(I) IN THE PRESENCE OF OLEFINS

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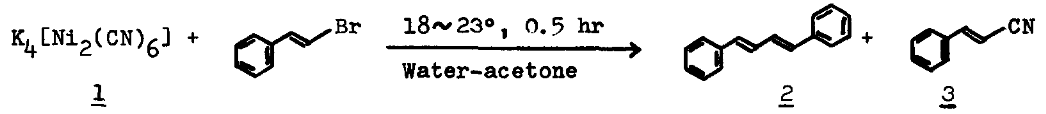
It is well known that a variety of organic halides react with low-valent transition metal complexes with concomitant metal-carbon bond formation$^{1)}$. Previously we have reported the reaction of potassium hexacyanodinickelate(I) (1) with various organic halides in aqueous solution and proposed the formation of unstable organonickel(II) complexes as intermediates in these reactions$^{2)}$. Therein, the high reactivity of *trans*-β-bromostyrene toward the cyanonickel(I) reagent is interesting; *i.e.*, the bromide reacted exothermically with 1 to give the coupling product, *trans*, *trans*-1,4-diphenyl-1,3-butadiene, (2) (72.9%) and the cyanation product, *trans*-β-cyanostyrene, (3) (6.6%) (eq 1). But the hydrogenolysis product, styrene, was not obtained in detectable amount.



(1)

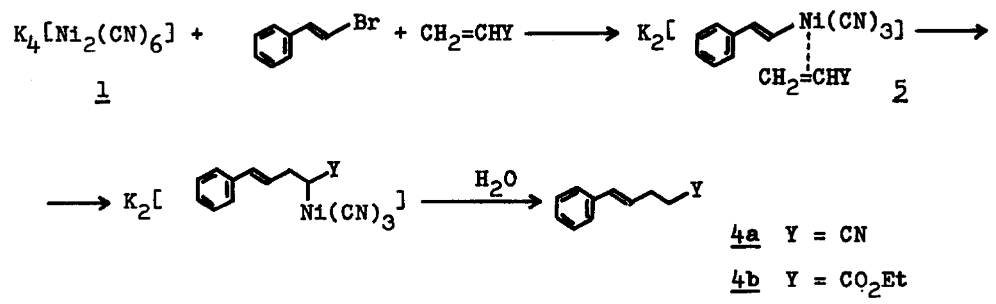
In this communication we describe the result of the reaction of 1 or nickel carbonyl with *trans*-β-bromostyrene in the presence of olefins which would lead to a new synthetic reaction such as styrylation or cinnamoylation of olefins. The reaction of 1 with *trans*-β-bromostyrene was carried out in aqueous acetone or N,N'-dimethylformamide(DMF) solution in the presence of acrylonitrile or ethyl acrylate under nitrogen. The results are summarized in Table 1. One of the successful experimental variations is as follows. To a solution containing 0.035 mol of 1 in 40 ml of water and 140 ml of DMF was added 20 g (0.377 mol) of acrylonitrile at -20° with stirring. The initially blood-red solution turned transparent yellow immediately. *trans*-β-Bromostyrene (6.4 g, 0.035 mol) in 30 ml of DMF was added dropwise at the temperature. The reaction mixture was gradually warmed to 10° during 15 hr with efficient stirring and, finally, a yellowish green suspension was obtained. After filtration of inorganic materials, the filtrate was poured into 400 ml of water and extracted with n-hexane. The organic layer was fractionally distilled under reduced pressure to give 1.39 g (30.7%) of 3 and 3.10 g of colorless liquid (bp 166~167°/19 mm). This compound was characterized as *trans*-5-phenyl-4-pentenonitrile (4a) (yield, 56.5%) from the following data: ir 2270 (C≡N) and 965 cm^{-1} (*trans*-disubstituted double bond); nmr (CCl_4) τ 2.80 (5H, m, C_6H_5-) τ 3.45~4.20 (2H, m, *trans* -CH=CH-) and τ 7.57~7.80 (4H, m, $-CH_2-CH_2-$); mass spectrum, molecular ion $^m/e$ 157. The nitrile 4 was converted to the amide by the action of H_2O_2 in aqueous ethanol: mp 133~133.5° (benzene); ir (KBr) 1650 cm^{-1} (C=O). *Anal*. Calcd for $C_{11}H_{13}ON$: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.45; H, 7.51; N, 8.02. Recrystallization of the residual solid from ethanol gave 0.19 g (5.2%) of 2. When ethyl acrylate was used instead of acrylonitrile, ethyl *trans*-5-phenyl-4-pentenoate (4b) was obtained in a lower yield.

Table 1. Reaction of Potassium Hexacyanodinickelate(I) (1) with *trans*-β-Bromostyrene in the Presence of Olefins[a]

Olefin	Solvent	Temp, °C	Time, hr	Conversion, %	Product, %[b] 2	3	4
Acrylonitrile	Water-DMF	-20 to 10	15	*ca*. 100	5.2	30.7	56.5
Acrylonitrile	Water-acetone	25 to 29	8	80	16.5	36.3	18.2
Acrylonitrile	Water-acetone	0	13	80	18.4	20.3	30.7
Acrylonitrile	Water-acetone	-20 to -3	18	50	1.7	6.2	40.5
Ethyl acrylate	Water-acetone	-18 to 10	16	40	8.5	4.2	17.4
None	Water-DMF	-20 to 10	15	85	61.6	6.5	....

[a] Molar ratio 1 : bromide : olefin = 1 : 1 : 8~11 [b] Yields are calculated based on the used bromide.

A postulated mechanism for the reaction involves initial formation of organonickel(II) σ complexes 5 (eq 2).

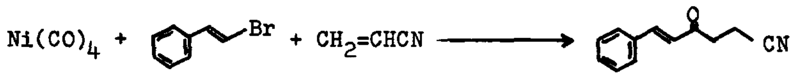


(2)

As may be seen in the Table, the ratio of these three products changed markedly depending on the reaction conditions especially on temperature; i.e., when the reaction was carried out in aqueous acetone, the yields of by-products (2 and 3) increased with increasing temperature at the expense of the desired product 4. It should also be noted that the formation of 3 in significant yields was observed in these reactions compared to the results in the absence of olefins. It seems likely that a strong coordination of acrylonitrile or ethyl acrylate facilitated the conversion of the intermediate 5 to the nitrile 3$^{3)}$. Indeed, the reaction of 1 with trans-β-bromostyrene in aqueous DMF in the presence of olefins with weaker coordinating ability such as α-methacrylonitrile or cyclohexene gave the nitrile 3 in lower yield (6∼9%) in addition to the coupling product 2 (62∼69%), and in these cases any products corresponding to 4 were not detected.

Organic halides containing β,γ-unsaturated bonds are known to react with metal carbonyls via the formation of unstable organotransition metal σ complexes, some of which exhibit high reactivity toward compounds such as olefin, diene, and/or acetylene in synthetically useful reactions$^{4)}$. However, the corresponding reactions of vinyl halides remain almost unexplored. According to the best of our knowledge the only example is the base-catalyzed carboxylation of vinyl halides by nickel carbonyl in protic media$^{5)}$.

Therefore, in connection with the above styrylation of olefins, the reaction of nickel carbonyl with trans-β-bromostyrene was carried out in the presence of acrylonitrile. A mixture of nickel carbonyl (3.4 g, 0.020 mol), trans-β-bromostyrene (3.7 g, 0.020 mol), and acrylonitrile (5.3 g, 0.10 mol) in 50 ml of wet (98%) DMF was stirred at 50∼55° for 20 hr under nitrogen. Upon work-up, 1.25 g of colorless liquid was obtained by distillation under reduced pressure (bp 125~150°/ 0.3 mm), which crystallized on standing. Recrystallization from ethanol gave 1.02 g of colorless needles which were found to be 3-(*trans*-cinnamoyl)-propionitrile (6) (yield, 28%): mp 91~91.5°; ir (KBr) 2260 (C≡N), 1690 (C=O), and 1615 cm^{-1} (C=C); nmr ($CDCl_3$) τ 2.40 (1H, d, J= 16.5 cps, C_6H_5-C$\underline{H}$=CH-), τ 2.55 (5H, m, $C_6\underline{H}_5$-), τ 3.27 (1H, d, J= 16.5 cps, C_6H_5-CH=C$\underline{H}$-), and τ 6.93 and 7.32 (4H, A_2B_2 type, -C(=O)-C$\underline{H}_2$C$\underline{H}_2$-CN); mass spectrum, molecular ion $^m/e$ 185. *Anal*. Calcd for $C_{12}H_{11}ON$: C, 77.81; H, 5,99; N, 7.56. Found: C, 77.70; H, 5.69; N, 7.61. The presence of 4a in the reaction products was not detected by gas chromatographic analysis.



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(3)

Thus a new type of styrylation and cinnamoylation of olefins were achieved, although the yields were not satisfactory as yet, opening a possibility for preparation of vinyl or vinyloyl compounds.

Our studies on these new reactions are continuing and will be reported in due course.

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