CONCLUSIONS

The action of light in the Cu(II) d-d transition region on systems containing polyvinyl alcohol and cupric ions leads to a decrease in the cupric ion concentration and the appearance of a new band. The system returns to the initial state in the dark.

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THE SELECTIVE COUPLING OF ARYL AND STYRYL HALIDES WITH BUTYLZINC CHLORIDE IN THE PRESENCE OF A HOMOGENEOUS NICKEL CATALYST

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Negishi et al. [1, 2] have shown that the <u>in situ</u> conversion of organomagnesium compounds to organozinc compounds R^1ZnC1 permits an improvement in the yield of cross-coupling reactions with aryl and vinyl halides RX catalyzed by palladium complexes. However, in addition to the cross-coupling products RR^1 , the use of aliphatic organozinc compounds also gives the products of homocoupling R_2 and reduction of the halide RH [2].

In order to clarify the possibility of selective cross coupling through alkylzinc halides, we studied the catalytic action of palladium and nickel complexes in the reaction of butylzinc chloride obtained from BuLi and $ZnCl_2$ in 1:1.1 ratio with aryl and styryl halides at about 20°C in ether-THF.

$$BuZnCl + RX \xrightarrow{Cat} BuR + R_2 + RH$$
(1)

Table 1 indicates that the reaction of PhI with BuZnCl catalyzed by palladium complexes is not selective (Nos. 1-4) and change in the composition of the catalytic system does not have a significant effect on the ratio of the cross-coupling and homocoupling products, PhBu and Ph₂ (Nos. 1-4). The reduction product (benzene) in the presence of palladium catalysts is virtually not formed. In going from PhI to PhBr, the rates of formation of PhBu and Ph₂ are reduced to the same extent (No. 5). Biphenyl is probably formed from PhZnCl, which, in turn, arises as a result of radical exchange [3]

$$PhI + BuZnCl \rightarrow PhZnCl + BuI$$
(2)

All these reactions are apparently equally sensitive to the nature of the palladium catalyst.

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Niimher		Catalvet	Time h	Reactio	n product y	ield, '	h (by gas-lic	quid (chromatograph	y)
1001111N	ΥY			RB(7		R		RH	
£	PhI	(Ph ₃ P) ₂ PhPdI	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	PhBu		53	h ₂	47	PhH	tr _c c
2	Iud	(Ph ₃ P) ₂ PdCl ₂	5	PhBu		45]]	h_2	55	PhH	tr
ŝ	PhI	(CH ₃ CN) ₂ PdCl ₂	7	PhBu		52	h_2	34	PhH	tr
4	PhI	(Ph ₃ P) ₂ PdCl ₂ +Ph ₃ P d	20	PhBu		61	h_2	25		
5	PhBr	(Ph ₃ P) ₂ PdCl ₂	20	PhBu		28	h_2	21		
9	PhI	(Ph ₃ P) ₂ NiCl ₂	₩	PhBu		77 1	h_2	80	PhH	tr
7	PhBr	Same	4	PhBu		74]]	h_2	6	PhH	tr
8	PhCl	*	-	PhBu		84]]	h_2	12	PhH	tr
6	4-MePhBr	*	20	4-MePhBu		65	(4-MePh) ₂	ц	MePh	6
10	4-MeOPhBr	*	20	4-MeOPhBu		48	(4-MeOPh) ₃	н	MeOPh	ø
11	2-MePhBr	*	20	2-MePhBu		32			MePh	25
12	PhCH=CHBr e (16/84)	$(Ph_3P)_2PdCl_2$	4	PhCH=CHBu	(16/84) f	84			PhCH=CH2	tr
13	PhCH=CHBr (16/84)	$(Ph_3P)_2NiCl_2$	4	PhCH=CHBu	(21/79)	90			PhCH=CH ₂	6
14	PhCH=CHBr (>98Z)	Same	4	PhCH-CHBu	(92/8)	71			PhCH=CH2	8
15	PhCH=CHCl (16/84)	*	4	PhCH=CHBu	(16/84)	84			PhCH=CH ₂	8
al mmole	RX in 1 ml THF, B	buZnCl (1 ml M solut	ion, 1.	1 mmole), (.01 mmo]	e Pó	complex	or	0.05 mmole	Ni com-

TABLE 1. Reaction of Aryl and Styryl Halides with BuZnCl^{a, b}

1 f or al mmole RX in 1 ml THF, BuZnCl (1 ml M solut plex at about 20°C. ^bThe reaction conditions were not optimized. cTraces. d0.04 mmole. eReaction performed at 0°C. fZ/E ratio.

The selectivity of the cross-coupling reaction increases sharply using a nickel complex as the catalyst (Nos. 6-8). This implies that the nickel complex catalyzes reaction (2) to a lesser extent. We should note that the yield and selectivity when using $(Ph_3P)_2NiCl_2$ as the catalyst are independent of the nature of the halide in PhX. The amount of Ph₂ formed in the reactions of PhX is only 8-12% while benzene is virtually absent.

Aryl bromides substituted with electron-withdrawing groups react with organozinc compounds to form cross-coupling products in high yield [1], and thus, these compounds were not studied in the present work.

The introduction of para electron-donor substituents in PhBr leads to a decrease in the yield of the cross-coupling product and production of 6-8% reduction product (Nos. 9 and 10). Blocking the reaction site with an ortho-methyl group leads to a further decrease in the yield of the cross-coupling product and an increase in the reduction product yield to 25% (No. 11). Virtually no homocoupling products are formed in the case of electron-donor substituents.

The greater activity of vinyl halides in cross-coupling reactions relative to aryl halides is also evident in their reaction with BuZnCl. β -Bromostyrenes, in contrast to PhBr, react with BuZnCl upon catalysis by both palladium and nickel complexes to form β -butylstyrenes (Nos. 12-14). These reactions proceed with steric selectivity. The reduction product, styrene, is not formed from E- β -bromostyrene on the palladium catalyst, as in the case of PhI, but 8-9% styrene is formed on the nickel catalyst.

The cross-coupling with β -chlorostyrene proceeds with the same facility and steric selectivity (No. 15).

EXPERIMENTAL

All the experiments were carried out in an argon atmosphere. A sample of BuZnCl was obtained by the reaction of BuLi in ether with a solution of anhydrous $ZnCl_2$ (10% excess in THF). PhBu and E- β -butylstyrene [4] were identified using standards. The PMR spectra were taken on a Tesla BS-497 spectrometer. The gas-liquid chromatographic analysis was carried out on a Tsvet-110 chromatograph using a 3 m × 3 mm column packed with 3% SE-30 on Chromatone N-Super with helium as the gas carrier. Thin-layer chromatography was carried out on Silpearle.

<u>Preparation of Z- β -Butylstyrene.</u> A sample of 1 ml 1.1 M solution of BuZnCl (1.1 mmole) in ether-THF and 0.033 g (0.05 mmole) (Ph₃P)₂NiCl₂ were added to a solution of 0.18 g (1 mmole) Z- β -bromostyrene in 1 ml THF and stirred for 4 h at about 20°C. The mixture was treated with 4% hydrochloric acid and the aqueous layer was extracted with ether. The combined ethereal extracts were washed with water and dried over CaCl₂. Ether was distilled off and thin-layer chromatography with hexane as the eluent was used to isolate 0.091 g (57%) Z- β -butylstyrene. PMR spectrum (CCl₄, δ , ppm): 0.7-1.6 m (7H, C₃H₇), 2.10-2.50 m (2H, CH₂), 5.57 d.t (1H, CH_{β}, J_{β , γ} = 7.3, J_{α , β} = 12 Hz), 6.35 d (1H, =CH_{α}, J_{α , β} = 12 Hz), 7.18 m (5H, C₆H₅) [5].

CONCLUSIONS

The use of $(Ph_3P)_2NiCl_2$ as catalyst permits the cross-coupling of unsubstituted aryl and styryl halides, including bromides and chlorides, with aliphatic compounds such as BuZnCl with high selectivity.

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