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NICKEL-CATALYZED ULLMANN-TYPE COUPLING OF ALKENYL HALIDES WITH ZINC POWDER

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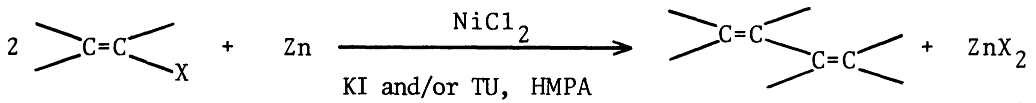
Convenient procedure for an Ullmann-type coupling of alkenyl halides using zinc powder, nickel(II) chloride, and potassium iodide and/or thiourea is presented. One double bond in the produced diene retained the configuration of a starting material, while partial cis-trans isomerization was observed in the second one.

An Ullmann-type coupling of alkenyl halides provides a straightforward route to symmetrical conjugated dienes. It has been shown recently that transition metal complexes such as bis(cycloocta-1,5-diene)nickel,1) tris(triphenylphosphine)-nickel,2) and so on3) can efficiently couple these otherwise inert halides under mild conditions. However, the fact that the complexes are air-sensitive,1-3a) or effective only for activated alkenyl halides3b) has limited their synthetic usefulness. We now wish to report a far more convenient procedure of general applicability using a simple nickel(II) salt as a catalyst.

The reduction of a nickel(II) salt like nickel(II) bromide or chloride with zinc powder takes place in the presence of potassium iodide4) and/or thiourea (TU) in hexamethylphosphoric triamide (HMPA) yielding a dispersed metallic nickel. We found that this in situ generated species is a reactive catalyst for a homo coupling of alkenyl halides with zinc powder (eq. 1).5) The results with various alkenyl halides are summarized in Table 1. A variety of alkenyl bromides and iodides including terminal, internal, or alicyclic ones gave the corresponding dienes in fair to good yields, whereas alkenyl chlorides were unreactive under the examined conditions. Although readily available alkenyl bromides were used as substrates of most experiments, they might not directly afford homo-coupling products. That is, under the present conditions, alkenyl bromides are known to rapidly react with potassium iodide to yield corresponding alkenyl iodides6) which are possibly predominant sources of homo-coupling products. Supporting evidence for this series of transformations of alkenyl bromides to dienes is given by runs 7-9 in Table 1 where one can see a decrease in a reactivity of alkenyl bromide upon the exclusion of potassium iodide.



(1)

X=Br or I

The stereochemistry of this coupling reaction should be noted. At first sight, every reaction appears to proceed with partial isomerization of double bond.

Table 1. Ni-catalyzed homo coupling of alkenyl halides with Zn powder[a)]

Run	Alkenyl halide	(Z/E)	KI	TU	Temp °C	Time h	Yield %	(E,E):(E,Z):(Z,Z)
1	$(CH_3)_2C{=}CHBr$		+	-	40	2	80	
2	$H_2C{=}C(CH_3)Br$		+	+	50	1.5	38	
3	$c\text{-}C_8H_{13}Br^{b)}$		+	+	50	2	$80^{c)}$	
4	$CH_3CH{=}CHBr$	(>99/1)	+	+	50	0.5	64	(0 : 6 : 94)
5	$PhCH{=}CHBr$	(<1/99)	+	-	40	1	78	(90 : 10 : 0)
6	$PhCH{=}CHBr$	(98/2)	+	-	40	2	76	(4 : 30 : 66)
7	$CH_3O_2CCH{=}CHBr$	(>99/1)	+	-	25	1.5	90	(12 : 19 : 69)
8	$CH_3O_2CCH{=}CHBr$	(>99/1)	-	+	40	1.5	11	(0 : 45 : 55)
9	$CH_3O_2CCH{=}CHI$	(>99/1)	-	+	25	2	78	(14 : 10 : 76)
10	$CH_3O_2CCH{=}CHBr$	(>99/1)	-	-	40	1.5	0	

a) In the presence of 0.25 mmol of alkenyl halide, 0.25 mmol of Zn, 0.1 mmol of $NiCl_2$, 0.5 mmol of KI (when used), and 0.005-0.02 mmol of TU (when used) in 0.5 ml of HMPA under nitrogen. Yields were determined by GLC using internal standards. b) 5 mmol of 1-bromocyclooctene was used. c) Isolated yield.

However, one of the two double bonds in a produced diene invariably retained the configuration of alkenyl halide except for methyl β-haloacrylates. For example, (E)-β-bromostyrene afforded (E,E)-diene mainly and (E,Z)-diene as minor product but no (Z,Z)-isomer. The extent of isomerization of the second double bond was affected by electronic properties of substituents bonded to β-carbon in an interesting manner: alkenyl halides containing electron-donating groups gave lesser amount of isomerized dienes than those containing electron-withdrawing groups did. This tendency is marked contrast with the previously reported ones using bis(cycloocta-1,5-diene)nickel as a coupling agent.[7)] Thus, the present reaction not only affords a convenient procedure for homo coupling of alkenyl halides under mild conditions but also might complement the previous ones.

References

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7) Methyl (Z)-β-bromoacrylate affords (Z,Z)-diene as a sole product, whereas (Z)-1-bromopropene affords a mixture of (Z,Z) and (Z,E)-isomers (50 : 50). See ref. 1 and also R. S. Smith and J. K. Kochi, J. Org. Chem., 41, 502 (1976).

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