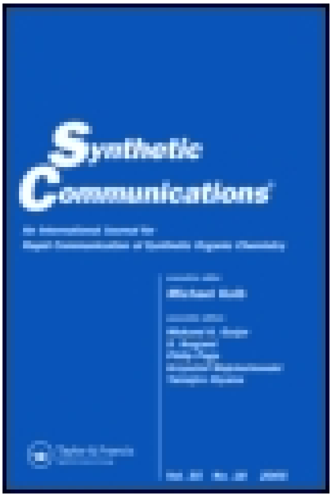

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PROCEDURES FOR THE NICKEL-CATALYZED CONVERSION OF OLEFINIC AND CYCLOOLEFINIC CHLORIDES INTO IODIDES

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Abstract

A number of olefinic and cycloolefinic chlorides have been converted into the corresponding iodides by treatment with an excess of sodium iodide in dimethylformamide in the presence of bis(1,5-cyclooctadienyl)nickel or a mixture of nickel bromide and zinc powder.

Olefinic iodides have been prepared from the corresponding bromides by nickel-catalyzed displacement by iodide in dimethylformamide[1]. In this communication we describe similar procedures with olefinic and cycloolefinic chlorides, which in a number of cases are more readily available than the bromides.

As pre-catalyst bis(1,5-cyclooctadienyl)nickel can be used, but the actual catalyst can also be generated (more conveniently) from $NiBr_2.3H_2O$ and zinc powder.

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$$RCH{=}CHCl \xrightarrow[NaI,\ DMF,\ 150^{\circ}C]{NiBr_2.3H_2O,\ Zn\ or\ Ni(COD)_2,} RCH{=}CHI$$

$R = Ph, n\text{-}C_8H_{17}, C_3H_7C{\equiv}C$

The reactions did not fully proceed to completion, but the starting compound and product could be easily separated by distillation. The reaction seems to proceed with retention of configuration around the double bound. The method is subject to some limitations. Chlorides with a low thermal stability, e.g. Aryl-C(Cl)=CHCl and $C_4H_9C{\equiv}CC(Cl){=}CH_2$ gave only intracable material. Attemps to convert the volatile *E*-ClCH=CHCl failed. Aromatic chlorides reacted relatively slowly and dehydrohalogenation was an important side reaction.

Product	b.p. °C/mm Hg	Isolated Yield (%)	Method A or B¤	*Z/E* ratio chloride	*Z/E* ratio iodide
PhCH=CHI	75/2	61	A	19/81	20/80
$C_8H_{17}CH{=}CHI$	84/2	60	A	12/88	13/87
		54	B	12/88	13/87
$C_3H_7C{\equiv}C\text{-}CH{=}CHI$	110/43	49	A	10/90	8/92
1-Iodocyclohexene		61	A	-	-
		58	B	-	-
1-Iodocycloheptene	115/42	49	A	-	-

¤ A = $Ni(COD)_2$
B = Zn, $NiBr_2.3H_2O$

Procedure A: Pre-catalyst bis(1,5-cyclooctadienyl)nickel

A 500-ml three-necked round-bottomed flask equipped with a thermometer-gas inlet combination, a reflux condenser with a gas outlet and a magnetic stirring bar, was charged with 0.30 mol of dry sodium iodide, 80 ml of dry dimethylformamide and 0.10 mol of the chloro compound[2-4]. After evacuation and admitting nitrogen (twice) 5 mmol of $Ni(COD)_2$ [5] was added. The resulting yellow-green mixture was heated under reflux (during heating the colour changed to dark-red). The residue was followed with GLC. Sometimes the reaction stopped due to inactivation of the catalyst. This problem was overcome by adding the catalyst in three portions with 1-hour intervals. As a rule the reactions proceeded to 90 - 95 % completion. When no further conversion was observed (after 3 - 5 hours), the reaction mixture was cooled to room temperature and a solution of 30 g of ammonium chloride in 300 ml of water and 100 ml of pentane was added with stirring. The mixture was filtered through Celite and the aqueous layer extracted three times with pentane. The combined organic layer was washed with water, dried over anhydrous $MgSO_4$ and then concentrated under reduced pressure. Careful fractionation through a 25 cm Vigreux column gave the iodides (purity ≥ 97 % according NMR and GLC).

Procedure: $NiBr_2.3H_2O$, powdered zinc

The apparatus was the same as used in method A. After charging the flask with sodium iodide (0.30 mol), DMF (80 ml), the chloro compound (0.10 mol), $NiBr_2.3H_2O$ (2 mmol) and zinc powder (8 mmol), the air was replaced by nitrogen and the mixture heated under reflux. When the ratio of iodide and chloride (GLC) had become copnstant (after 3 - 5 hours, ~ 90 % conversion) the mixture was cooled to room temperature and the product isolated as described above.

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