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# SYNTHESIS OF VINYL IODIDES FROM VINYL BROMIDES AND POTASSIUM IODIDE BY MEANS OF NICKEL CATALYST(1)

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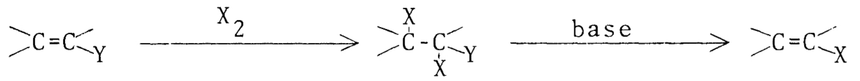
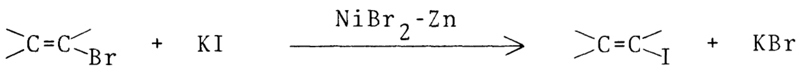
Vinyl bromides such as (*E*)-β-methoxycarbonyl-, (*E*) or (*Z*)-β-phenyl-, (*Z*)-β-ethoxy-, or β,β-dimethylvinyl bromide smoothly reacted with an iodide ion in the presence of nickel catalyst to give the corresponding vinyl iodides with complete retention of configurations.

Vinyl halides are important substrates in organic chemistry and numerous approaches to their synthesis have been advanced.2) The application of the usual method for the preparation of vinyl chlorides or bromides as shown in the following sequence to the preparation of vinyl iodides is far from being satisfactory.3) Therefore, the displacement of X (Br or Cl) in vinyl halides with an iodide ion might provide a useful method for the preparation of vinyl iodides.



X = Br or Cl
Y = H or $CO_2H$

We have found that the conversion of vinyl bromides into vinyl iodides is achieved by the assistance of nickel catalyst under very mild conditions. The catalyst system is composed of nickel(II) bromide and zinc powder as a reducing agent.4) The results summarized in Table 1 indicate that the procedure has generality and high degree of stereoselectivity: the vinyl bromides having not only an electron-withdrawing group (Run 1-3) but also an electron-donating group (Run 4, 5) afford sufficient yields of the corresponding vinyl iodides and the configuration is completely retained throughout the displacement reaction. Dimerization of vinyl groups occurs as a side reaction: for example, in Run 4, ca. 1% of 2,5-dimethyl-2,4-hexadiene is obtained. The active species in the catalytic displacement reaction is probably decomposed during the dimerization reaction. Thus, in the case of methyl (*Z*)-β-bromoacrylate, where the displacement and the dimerization proceed in the comparable rates, a large amount of the starting bromide is recovered (Run 6). In the presence of a stoichiometric amount of zinc powder, methyl (*Z*)-β-bromoacrylate is completely consumed to yield dimethyl (*Z*,*Z*)-muconate (79%).5)



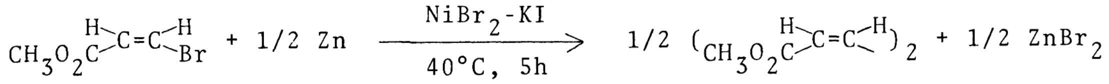
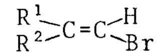
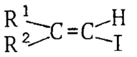
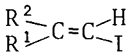


Table 1. Synthesis of Vinyl Iodides

| Run |  $^{R^1}_{R^2}{>}C{=}C{<}^{H}_{Br}$ | | Temp. | Time | Yield a)  $^{R^1}_{R^2}{>}C{=}C{<}^{H}_{I}$ |  $^{R^2}_{R^1}{>}C{=}C{<}^{H}_{I}$ |
|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | (°C) | (h) | (%) | (%) |
| 1 | $CH_3O_2C$ | H | 35 | 1 | 98 | 0 |
| 2 | $C_6H_5$ | H | 40 | 3 | 95 | <0.5 |
| 3 | H | $C_6H_5$ | 40 | 3 | 88 | 2 |
| 4 | $CH_3$ | $CH_3$ | 60 | 3 | 93 | - |
| 5 | H | $C_2H_5O$ | 60 | 3 | 95 | <1 |
| 6 b) | H | $CH_3O_2C$ | 40 | 1.5 | 25 | 0 |

Reaction conditions: vinyl bromide, 0.5 mmol; KI, 1.25 mmol; $NiBr_2$, 0.01 mmol (0.059 ml of 0.17M-DMF solution); Zn, 0.03-0.06 mmol; HMPA, 0.44 ml; under $N_2$.

a) Yield was determined by GLC, being based on vinyl bromide used.

b) (*Z*)-$CH_3O_2CCH{=}CHBr$ (recovered) 50%, (*Z*,*Z*)-$CH_3O_2CCH{=}CHCH{=}CHCO_2CH_3$ 16%.

The following procedure for the preparation of (*Z*)-β-iodostyrene is representative: a mixture of 1.8 g (10 mmol) of (*Z*)-β-bromostyrene, 4.2 g (25 mmol) of KI, 1.2 ml of 0.17 M-DMF solution of Ni(II)$Br_2$ (0.20 mmol), 50.8 mg (0.78 mmol) of Zn powder, and 8.8 ml of HMPA was flushed with nitrogen at -15°C and then kept at 40°C for 3 h with stirring. The reaction mixture was then shaken with ether-dilute HCl. The organic layer was separated, washed with an aqueous solution of $Na_2S_2O_7$ and water, and dried over $Na_2SO_4$. After removal of ether, the residue was distilled under reduced pressure to give 1.66 g (74%) of (*Z*)-β-iodostyrene. Bp 60.5°C at 0.5 mmHg.6)

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1) Part V of Nucleophilic Displacement Catalyzed by Transition Metal. Part IV: K. Takagi, N. Hayama, and T. Okamoto, Chem. Lett., 1978, 191.

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3) H. Dorn, "Preparative Organic Chemistry," ed by G. Hilgetag and A. Martini, John Wiley & Sons, New York (1972), p. 107.

4) This catalyst system is also effective for the conversion of aryl bromides into aryl iodides.1)

5) The reaction conditions are the same as those of Run 6 except that zinc powder of 0.5 mole equivalent to vinyl bromide was used. After the usual workup, the residual solid was recrystalized from hexane-MeOH. Mp 70.5-72°C (lit,7) 73°C).

6) Only one paper described hitherto the preparation of (*Z*)-β-iodostyrene from (*Z*)-β-styrylbis(dimethylglyoximato)pyridinecobalt(III): D. Dodd, M. D. Johnson, B. S. Meeks, D. M. Titchmarsh, K. N. Van Duong, and A. Gaudemer, J. Chem. Soc., Perkin Trans. 2, 1976, 1261.

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