

The vinylation of aryl iodides using homogeneous platinum complex catalyst

Ashutosh A. Kelkar, Chemical Engineering Division,
National Chemical Laboratory, Pune 411 008, India

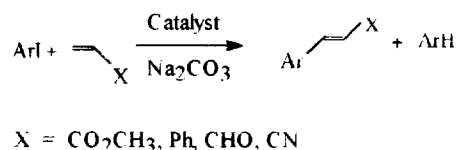
Abstract : Vinylation of aryl iodides using $\text{Pt}(\text{COD})\text{Cl}_2/\text{PPh}_3$ as a catalyst system was studied. High selectivity to vinylation products was observed with inorganic bases. Copyright © 1996 Published by Elsevier Science Ltd

Vinylation is a versatile process for the functionalization of a variety of organic halides. The palladium catalysed vinylation of aryl halides has been extensively studied by Heck and others because of its wide application in organic synthesis¹. Recently there are reports on the vinylation using other catalysts comprising complexes of nickel, cobalt, rhodium and iridium²⁻⁵. Although oxidative addition reactions of organic halides are known with platinum complexes, there is no report on the platinum catalyzed vinylation of organic halides. In this paper we report vinylation of organic halides with platinum catalyst.

$\text{Pt}(\text{COD})\text{Cl}_2$ [COD = 1, 5-cyclooctadiene] was prepared according to the literature procedure⁶. In a typical experiment iodobenzene (5 mmol), methyl acrylate (10 mmol), Na_2CO_3 (10 mmol) and $\text{Pt}(\text{COD})\text{Cl}_2$ (0.1 mmol) were placed in a round bottomed flask. 1-methylpyrrolidinone (5, ml) was used as solvent and the reaction mixture was heated to 130°C for 24 h. After the usual workup the reaction product was isolated by passing through a column of silica gel.

From the preliminary experiments it was observed that reaction did not proceed at 100°C indicating that certain minimum temperature is required for catalytic activity (Table I, sr. no. 4). Therefore all the work in the present study was carried out at 130°C. Depending on the reaction conditions vinylation product or dehalogenation

product was formed (Scheme 1)



(Scheme 1)

Vinylation was carried out using various bases at 130°C and the results are presented in Table 1. With Na_2CO_3 as inorganic base ethyl cinnamate was formed with very high selectivity due to reduction in the formation of benzene by dehalogenation. With organic bases such as triethylamine and tri-n-butylamine, only benzene was formed as a product with traces of ethyl cinnamate. Organic bases have ability to act as a source of hydride and with ethyl acrylate being poor electron donor, there is competition between the vinylation and dehalogenation reaction⁷. With palladium⁸ and nickel⁹ catalysts both dehalogenation and vinylation products are obtained. However with Pt catalyst only dehalogenation product was observed.

Various aryl iodides and olefins were examined to test the applicability of platinum catalyst. Results are presented in Table 2. Various aryl iodides reacted with methyl acrylate to provide corresponding vinylation product in good yield. In the presence of electron donating group such as $-\text{OCH}_3$, conversion was higher while in the presence of electron withdrawing groups such as Cl a lower conversion was observed. Various olefins were studied using iodobenzene and highest conversion was obtained with methyl acrylate. With other olefins poor conversion was observed. With acrylonitrile and methacrolein conversion as well as selectivity was poor mainly due to the polymerization. Thus Pt is found to be active for a variety of aryl iodides as well as olefins.

The mechanism of platinum catalyzed vinylation is probably similar to the generally accepted mechanism with palladium catalysts¹. Reduction of catalyst precursor to zero valent complex is supposed to be the necessary step for the formation of catalytically active species. The reduction of platinum complex in the present system can occur via hydrogen transfer from 1-methylpyrrolidinone used as a solvent. The high selectivity for the vinylation using inorganic base in the present work is due to the absence of reducing agent. In the presence of an organic base with easily releasable hydrogen, such as triethylamine, reduction of aryl halide is promoted as in the case of palladium catalysts⁷. These catalyst systems are not suitable for vinylation reaction. Catalyst system with inorganic base gives high selectivity to vinylation reaction with moderate activity.

The present work has shown that platinum is a potential catalyst for vinylation of aromatic halides with high selectivity. Further work is necessary to improve the activity of the catalyst and also study the catalytically active species.

Table 1 : Vinylation of iodobenzene: effect of bases

| Sr. No. | Base | Temperature (°C) | Conversion (%) | Yield (%) |
|---------|---------------------------------|------------------|----------------|-----------|
| 1 | Triethylamine* | 130 | 85 | trace |
| 2 | Tri-n-butylamine* | 130 | 80 | trace |
| 3 | Na ₂ CO ₃ | 130 | 75 | 85 |
| 4 | Na ₂ CO ₃ | 100 | nil | nil |

Reaction Conditions:

Iodobenzene : 5, mmol; Methyl Acrylate : 10, mmol; Base : 10, mmol

Pt(COD)Cl₂ : 0.1, mmol; PPh₃ : 0.2, mmol, 1- methylpyrrolidinone : 5, ml ; Reaction time : 24, h

* In these reactions benzene was formed as the dehalogenation product

Table 2 : Results on the screening of various aryl iodides and olefins in the platinum complex catalyzed vinylation reaction

| Sr. No. | Aryl iodides | Olefin | Conversion (%) | Selectivity (%) |
|---------|--------------------------------------|---------------------|----------------|-----------------|
| 1 | C ₆ H ₅ I | Methyl acrylate | 75 | 85 |
| 2 | 4-ClC ₆ H ₄ I | Methyl acrylate | 32 | 90 |
| 3 | 4-MeOC ₆ H ₄ I | Methyl acrylate | 90 | 88 |
| 4 | 4-MeC ₆ H ₄ I | Methyl acrylate | 59 | 95 |
| 5 | 2-ClC ₆ H ₄ I | Methyl acrylate | 49 | 95 |
| 6 | C ₆ H ₅ I | Methyl methacrylate | 41 | 88 |
| 7 | C ₆ H ₅ I | Styrene | 34 | 80 |
| 8 | C ₆ H ₅ I | Acrylonitrile | 26 | 40 |
| 9 | C ₆ H ₅ I | Methacrolein | 32 | 50 |

Reaction Conditions:

Aryl iodide : 5, mmol; Olefin : 10, mmol; Na₂CO₃ : 10, mmol Pt(COD)Cl₂ : 0.1, mmol;

PPh₃ : 0.2, mmol, 1- methylpyrrolidinone : 5, ml Reaction time : 24, h

References

1. Heck R.F. in Trost B.M. and Fleming I. (Eds.), "Comprehensive Organic Synthesis" Pergamon, Oxford, 1991, **4**, 833
2. Heck R.F. in "Organic Reactions", Dauben W.G., Ed. Wiley, New York, 1982, **27**, 345
3. Boldrini G.P., Savoia D., Taglivanchi E. and Umani A.,
J. Organomet. Chem. 1986, **301**, C62
4. Kelkar A.A., Hanaoka T., Kubota Y. and Sugi Y., Cat. Let., 1994, **29**, 69
5. Iyer S., J.Organomet.Chem., 1995, **490**, C27
6. Drew D. and Doyle J.R., in "Inorg. Syntheses" Cotton F.A. Ed.,
Mcgraw Hill, New York, 1972, **13**, 47
7. Cabri W., Candiani I., DeBernardinis S., Francalanci F. and Penco S.,
J.Org.Chem., 1991, **56**, 5797
8. Kelkar A.A., Hanaoka T., Kubota Y. and Sugi Y., J.Mol.Cat., 1994, **88**, L113

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