CHEMISTRY LETTERS, pp. 1483-1486, 1979. © The Chemical Society of Japan 1979

# THE REACTION OF π-ALLYLNICKEL HALIDES WITH 2-PYRIDYL CARBOXYLATES
# A NEW SYNTHESIS OF β,γ-UNSATURATED KETONES

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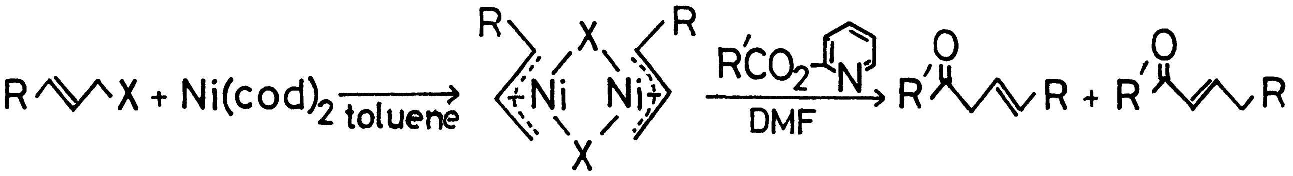
Various π-allylnickel halides were found to react with 2-pyridyl carboxylates to give β,γ-unsaturated ketones chemospecifically in good yields.

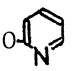
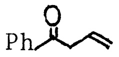
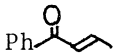
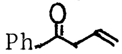
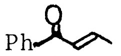
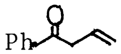
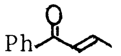
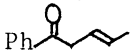
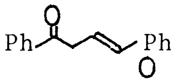
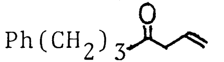
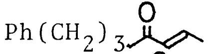
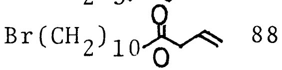
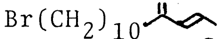
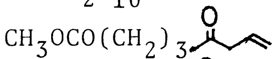
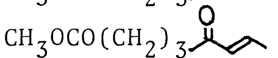
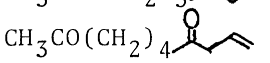
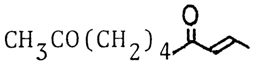
π-allylnickel halides are, in general, rather stable complexes, and have widely been used in organic synthesis. The complexes are easily prepared in high yields by the reaction of a variety of allylic halides with nickel carbonyl or bis-(cyclooctadiene)nickel in toluene.1) They react with aryl, vinyl, and alkyl halides, aldehydes, ketones, and quinones. However, the reactions of π-allylnickel halide complexes with carboxylic acid derivatives such as acyl chlorides or carboxylic acid methyl esters have not been carried out successfully so far.1),2)

In this communication, we wish to report new syntheses of β,γ-unsaturated ketones by the reaction between π-allylnickel halides and 2-pyridyl carboxylates as depicted in the following equation.



Under argon atmosphere, an N,N-dimethylformamide (DMF) solution (1 ml) of 2-pyridyl benzoate (0.5 mmol)3) was added to a DMF solution (1 ml) of π-allylnickel bromide complex (0.5 mmol), prepared from allyl bromide (1.0 mmol) and bis-(cyclooctadiene)nickel (Ni(cod)$_2$, 1.0 mmol) at room temperature. The reaction mixture was stirred at room temperature for 15h and worked up with phosphate buffer solution (ph 7) (20 ml), extracted with $CH_2Cl_2$, and the extract was dried over

Table 1. Reaction of π-allylnickel complexes with 2-pyridyl carboxylates

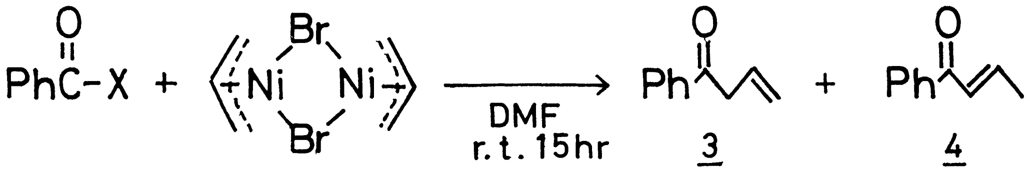
| R in RCOO | Allyl halide | Ratio[a] | Conditions | | Ketones | | Yield (%)[c],[d] |
|---|---|---|---|---|---|---|---|
| | | | temp.(°C), | time(h) | | (isomer ratio)[b] | |
| Ph |  | 0.5 | r.t. | 15 |  | 69 | 29 |
| | | | | |  | 31 | |
| Ph |  | 1 | r.t. | 15 |  | 75 | 73 |
| | | | | |  | 25 | |
| Ph |  | 2 | r.t. | 15 |  | 74 | 92 |
| | | | | |  | 26 | |
| Ph |  | 2 | r.t. | 15 |  | | 79 |
| Ph |  | 2 | r.t. | 15 |  | | 50 |
| $Ph(CH_2)_3$ |  | 2 | 45 | 10 |  | 85 | 72 |
| | | | | |  | 15 | |
| $Br(CH_2)_{10}$ |  | 2 | 45 | 8 |  | 88 | 61 |
| | | | | |  | 12 | |
| $CH_3OCO(CH_2)_3$ |  | 2 | 45 | 14 |  | 87 | 71 |
| | | | | |  | 13 | |
| $CH_3CO(CH_2)_4$ |  | 2 | 45 | 4 |  | 84 | 51 |
| | | | | |  | 16 | |

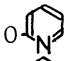
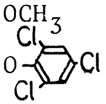
a) Molar ratio of π-allylnickel complex to 2-pyridyl carboxylate.
b) The ratio of ketone isomers was determined by NMR spectrum.
c) All the products gave satisfactory NMR and IR spectra.
d) Yield was based on 2-pyridyl carboxylate.

$Na_2SO_4$. After removal of the solvent, purification of the residue by means of silica gel thin layer chromatography gave a mixture of 1-phenyl-3-buten-1-one (1) and 1-phenyl-2-buten-1-one (2) in 73% yield, whose ratio of 1 to 2 was 75:25. When 1.0 mmol of π-allylnickel bromide was used in the same reaction, the combined yield increased up to 92%. Table 1 shows the results of the reactions between various nickel complexes and 2-pyridyl carboxylates.

The use of excess amounts of π-allylnickel complexes was necessary to obtain ketones in good yields because the decomposition of these complexes took place

Table 2. Reaction between π-allylnickel bromide with various benzoic acid derivatives



| X | Ratio a) | Ketone b)<br>3 : 4 | Yield (%) c) |
|---|---|---|---|
|  | 2 | 74 : 26 | 92 |
|  | 2 | 66 : 34 | 55 |
| Cl | 2 | 84 : 16 | 11 |
| $OCH_3$ | 2 | — | 0 |
|  | 2 | — | 0 |

a) Molar ratio of π-allylnickel complex to benzoic acid derivative.

b) The ratio of ketone isomers was determined by NMR spectrum.

c) Yield was based on bezoic acid derivative.

during the reaction. Fortunately, the excess nickel complexes did not further react with the produced unsaturated ketones and therefore undesirable formation of homoallyl alcohols was avoided.

The reaction of π-allylnickel complexes with 2-pyridyl carboxylates having the other functional group, such as bromide, ketone, or methyl ester, afforded ketones without damage of the functional group.

It was also found that the treatment of π-crotylnickel bromide or π-cinnamylnickel bromide with 2-pyridyl benzoate only produced β,γ-unsaturated ketones.

Table 2 shows that the results of the reactions between π-allylnickel bromide and various benzoic acid derivatives. The use of 2-pyridyl benzoate gave the best result, while no satisfactory yields of ketones were given by the other benzoic acid derivatives or in some cases no detectable amount of ketone was found. These results indicate that 2-pyridyl benzoate is more susceptible to reduction by π-allyl complexes to produce radical anion than the other benzoyl derivatives. The produced radical anion couples with the allyl moiety of π-allyl complexes to form β,γ-unsaturated ketones.4)

It is noted that various π-allylnickel complexes react with 2-pyridyl carboxylates chemospecifically to give β,γ-unsaturated ketones in good yields under mild conditions.

## References and Notes

1) M. F. Semmelhack, Org. React., Vol. 19, 115 (1972).

2) L. S. Hegedus, S. D. Wagner, E. L. Waterman, and K. Sürala-Hansen, J. Org. Chem., 40, 593 (1975).

3) All 2-pyridyl carboxylates were prepared from acyl chlorides and 2-hydroxypyridine, or carboxylic acids and 2-hydroxypyridine in the presence of 2-chloro-1-ethylpyridinium p-toluenesulfonate in 80-90% yields: M. Araki, S. Sakata, H. Takei, and T. Mukaiyama, Bull. Chem. Soc. Jpn., 47, 1777 (1974); K. Saigo, M. Usui, K. Kikuchi, E. Shimada, and T. Mukaiyama, ibid., 50, 1863 (1977).

4) The reactions of π-allylnickel complexes are, in general, thought to involve electron transfer processes: L. S. Hegedus and L. L. Miller, J. Am. Chem. Soc., 97, 459 (1975); L. S. Hegedus, B. R. Evans, D. E. Korte, E. L. Waterman, and K. Sjöberg, ibid., 98, 3901 (1976).

(Received October 8, 1979)