CHEMISTRY LETTERS, pp. 1371-1372, 1987.

# Palladium Catalyzed Reaction of Acyltins with Organic Halides

Masanori KOSUGI,* Hiroyuki NAKA, Saburo HARADA, Hiroshi SANO,
and Toshihiko MIGITA*
Department of Chemistry, Faculty of Technology, Gunma University,
Kiryu, Gunma 376

Palladium catalyzed reaction of acyltins with organic halides were investigated. Among the halides, acyl halides and allylic halides were good substrates, and the latter gave allylic ketones in good yields.

Acyltin compounds were virtually unknown and believed to be very labile compounds.[1,2] Quite interestingly, the Pd-catalyzed reaction of acyltins with acyl chlorides were reported to give the corresponding α-diketones in moderate yields.[3]

$$Bu_3SnCOR^1 + R^2COCl \xrightarrow{[Pd]} R^1COCOR^2 + R^1COR^2 + R^1COBu$$

In our series of Pd-catalyzed cross-coupling reactions of organotin reagents with organic halides, we and Soderquist reported that (α-ethoxyvinyl)tributyltin was a good reagent as a masked acyl anion equivalent.[4,5]

$$Bu_3SnC(OEt)=CH_2 + RX \xrightarrow{[Pd]} [RC(OEt)=CH_2] \xrightarrow{H^+} RCOCH_3$$

In view of ketone synthesis using organotin reagents, our interest was focussed on the Pd-catalyzed reaction of acyltins with various organic halides. In this letter, we report the possible utility of acyltins for Pd-catalyzed reaction, revealing that not only acyl chlorides, but also allylic halides were effective substrates.

$$Bu_3SnCOR^1 + R^2X \xrightarrow{[Pd]} R^2COR^1 + Bu_3SnX$$

Table 1 shows the results of the Pd-catalyzed reaction of acyltins with various organic halides. It was found that the reaction of propanoyltributyltin with methyl iodide, bromobenzene, and benzyl chloride gave no or low yield (0, 19, and 30%, respectively) of the corresponding ketone. In these reaction mixture, methyl, phenyl, and benzyltributyltin were detected in 26, 15, and 35% yields, respectively. Using less amounts of the catalyst, the product yields were lowered.

On the other hand, the reaction of benzoyl chloride with propanoyltin in the presence of only 1 mol% of the catalyst gave the corresponding α-diketone in 43% yields being comparable to those reported.[3] The reaction of methallyl chloride also in the presence of 1 mol% of the catalyst gave 5-methyl-5-hexen-3-one and 5-methyl-4-hexen-3-one in 40 and 37% yields, respectively. The latter seems to form via isomerization of the former under the reaction conditions. However, the following conditions gave only the former product; a solution of propanoyltri-

Table 1. Pd-Catalyzed Reaction of Propanoyltributyltin with Organic Halides[a)]

| R-X | Catalyst (mol%) | Product (GLC yield/%) | |
|---|---|---|---|
| MeI | $Pd(PPh_3)_4$ (10) | MeCOEt (0) | $MeSnBu_3$ (26) |
| PhBr | | PhCOEt (19) | $PhSnBu_3$ (15) |
| $PhCH_2Cl$ | | $PhCH_2COEt$ (30) | $PhCH_2SnBu_3$ (35) |
| PhCOCl | $PdCl_2(PPh_3)_2$ (1) | PhCOCOEt (43) | |
| $CH_2=CMeCH_2Cl$ | $Pd(PPh_3)_4$ (1) | $CH_2=CMeCH_2COEt$ (40) | $Me_2C=CHCOEt$ (37) |

a) Reactions were carried out at 100 °C for 20 h.

butyltin (1.3 mmol), allylic halide (1.0 mmol), $Pd_2(dba)_3CHCl_3$ (0.5 mol%), and triphenylphosphine (2 mol%) in benzene (1 $cm^3$) was heated at 60 °C for 20 h. Addition of an excess amount of the triphenylphosphine retarded the rate of the reaction. Table 2 shows the results of the reaction of propanoyltributyltin with various allylic halides. As expected from the intermediacy of π-allylic palladium complex, crotyl chloride and α-methylallyl chloride gave the same products (5-hepten -3-one and 4-methyl-5-hexen -3-one) in similar ratios.

Thus, acyltins showed rather restricted reactivities toward the Pd-catalyzed reaction with halides, but may be usable reagents for preparation of some allylic ketones.

Table 2. Pd-Catalyzed Reaction of Propanoyltributyltin with Allylic Halides

| Allylic halide | GLC yield/% | Product (distribution) | |
|---|---|---|---|
| $CH_2=CHCH_2Br$ | 44 | $CH_2=CHCH_2COEt$ | |
| $CH_2=CMeCH_2Cl$ | 84 | $CH_2=CMeCH_2COEt$ | |
| $MeCH=CHCH_2Cl$ | 86 | $MeCH=CHCH_2COEt$ (75) | $CH_2=CHCHMeCOEt$ (25) |
| $CH_2=CHCHMeCl$ | 72 | (75) | (25) |
| $Me_2C=CHCH_2Br$ | 54 | $Me_2C=CHCH_2COEt$ | |
| $PhCH=CHCH_2Cl$ | 62 | $PhCH=CHCH_2COEt$ (58) | $CH_2=CHCHPhCOEt$ (42) |
| $n\text{-}PrCH=CHCH_2Br$ | 97 | $n\text{-}PrCH=CHCH_2COEt$ (77) | $CH_2=CHCHPr^nCOEt$ (23) |

The gift of tributyltin oxide by Hokkoh Kagaku Kogyo Co. Ltd. is acknowledged. The present work was partially supported by a Grant-in-Aid for Special Project Research No. 61225002 from the Ministry of Education, Science and Culture.

References

1) J. A. Soderquist and A. Hassner, J. Am. Chem. Soc., 102, 1577 (1980); J. A. Soderquist and G. J. Hsu, Organometallics, 1, 830 (1982).
2) K. J. H. Kruithof, R. F. Schmitz, and G. W. Klumpp, J. Chem. Soc., Chem. Commun., 1983, 239
3) J-B. Verhac, E. Chanson, B. Jousseaume, and J-P. Quintard, Tetrahedron Lett., 26, 6075 (1985).
4) M. Kosugi, T. Sumiya, Y. Obara, M. Suzuki, H. Sano, and T. Migita, Bull. Chem. Soc. Jpn., 60, 767 (1987).
5) J. A. Soderquist and W. W. H. Leong, Tetrahedron Lett., 24, 2361 (1983).

( Received April 23, 1987 )