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PALLADIUM-CATALYZED TRANSFORMATION OF ARENEDIAZONIUM SALTS TO ACYL ARENES BY ORGANOTIN COMPOUNDS AND CARBON MONOXIDE[1)]

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Arenediazonium salts (ArN_2X; Ar=2-Me-C_6H_4, 3-Me-C_6H_4, 4-Me-C_6H_4, 2-Cl-C_6H_4, 4-Cl-C_6H_4, 4-Br-C_6H_4, 4-I-C_6H_4, 3-NO_2-C_6H_4, 4-NO_2-C_6H_4, and C_6H_5; X=BF_4 and PF_6) were effectively transformed to acyl arenes (ArCOR; R=Me, Et and Ph) in good yields (55-90%) by R_4Sn and CO under palladium catalysis.

Although arenediazonium salts (ArN_2X) have been used to introduce various functional groups into aromatic ring, acyl groups have rarely been introduced. Copper catalyzed reaction of ArN_2X with aldoximes was known to give arylated oximes which are hydrolyzed to aldehydes or ketones.[2)] However, the yields were generally low. Reactions of ArN_2X with $Ni(CO)_4$[3)] or $Fe(CO)_5$[4)] gave a mixture of ArCOOH and Ar_2CO in low yields. Recent palladium-catalyzed reaction of ArN_2X with CO and RCOONa, in which aroyl palladium species are assumed to be an intermediate, affords excellent methods for transformation of ArN_2X to ArCOOH[5)] or ArCOOCOR.[6)] Now we wish to report a direct transformation of ArN_2X to acyl arenes utilizing metathesis between the *in situ* formed aroyl palladium species and R_4Sn in the presence of CO (eq. 1).

$$ArN_2X + CO + R_4Sn \xrightarrow{Pd(OAc)_2\ (2\ mol\%)} ArCOR\ (R=Me,\ Et,\ Ph) \qquad (1)$$

A mixture of Me_4Sn (11 mmol), $Pd(OAc)_2$ (0.2 mmol) and CH_3CN (60 ml) was placed in a 300 ml of glass autoclave. An ArN_2X (X=BF_4 or PF_6) (10 mmol) wrapped in Saran film was held on loosely to stirring rod and was added to the reaction mixture by rotating the stirring rod after introduction of CO (9 kg/cm^2). Fine black powders formed by the introduction of CO disappeared on mixing the ArN_2X with the solution. The mixture was then stirred for 0.5 h. The completion of reaction was easily discerned by reappearance of black dispersion. Carbon monoxide was purged and the reaction mixture was refluxed for 1 h. When this procedure was omitted, unknown impurities remained in the products even after distillation. After removal of CH_3CN, the residue was diluted by ether and was neutralized by *aq*. Na_2CO_3. Pure acetophenone derivatives were obtained by vacuum distillation. The isolated yields of pure ArCOMe based on ArN_2X are summarized in Table I. The presence of Cl^- (by the use of ArN_2Cl or an addition of LiCl) in the reaction decreased the yields drastically, less than 10%, and increased untractable tarry materials. Furthermore, the presence of Cl^- in the isolation procedure, *e.g.*,

Table I. Acylation of ArN$_2$X by CO and Me$_4$Sn

ArCOMe(Ar)	Yield(%)[a]	ArCOMe(Ar)	Yield(%)[a]
Ph	55	4-Cl	90
2-Me	63	4-Br	84
3-Me	(70)[b]	4-I	79
4-Me	86	3-NO$_2$	70
2-Cl	76	4-NO$_2$	85

a) Isolated and purified yields based on ArN$_2$BF$_4$. ArN$_2$PF$_6$ was used for Ph and 4-NO$_2$-C$_6$H$_4$.
b) Small amounts of impurities were contaminated.

washing by brine or hydrochloric acid, must be avoided, because it caused a difficulty to remove Me$_3$SnCl. Fairly good yields were obtained irrespective of the nature of a substituent on aromatic ring. The excellent yields of nitroacetophenones are noticeable because nitro group on aromatic ring interferes in the Friedel-Crafts acylation. Haloarenes are frequently used in palladium-catalyzed reactions of aromatics,7) e.g., aryl ketones have been synthesized by a reaction of haloarenes with organotin compounds under CO.8) In the present method, however, halogen substituents do not enter into the reaction because of high reactivity of diazonium group. Thus, ArN$_2$X are excellent precursors for the arylpalladium species containing halogen substituents.

Et$_4$Sn and Ph$_4$Sn were also utilized in this reaction as shown in Table II. When Ph$_4$Sn was used, a mixture of ArN$_2$BF$_4$ and Pd(OAc)$_2$ should be added to a solution of Ph$_4$Sn in CH$_3$CN after introduction of CO to obtain the crossed diaryl ketone selectively.

Table II. Acylation of ArN$_2$BF$_4$ by eq. 1

ArN$_2$BF$_4$	R$_4$Sn	Method[a]	Reaction	Products, Yields(%)[b]		
Ar	R		time, h	ArCOR,	RCOR,	R-R
Ph	Et	A	6	40	-	-
4-Me	Ph	A	7	74	$\sim$10	$\sim$8
"	Ph	B	7	63	$<$0.5	$\sim$2
4-Br	Ph	B	6	59	$<$0.5	$\sim$2

a) Method A; ArN$_2$BF$_4$ was added finally. Method B; A mixture of ArN$_2$BF$_4$ and Pd(OAc)$_2$ was added finally.
b) Isolated yields based on ArN$_2$BF$_4$. The composition was determined by GLC and NMR.

References

1) Part VII in the series "Reaction of Diazonium Salts with Transition Metals". Part VI; K. Kikukawa, K. Kono, K. Nagira, F. Wada, and T. Matsuda, *J. Org. Chem.*, in press. 2) C. S. Rondestvest, *Org. React.*, 11, 189 (1960). 3) J. C. Clark and R. C. Cookson, *J. Chem. Soc.*, 687 (1962). 4) G. N. Schrauzer, *Chem. Ber.*, 94, 1891 (1961). 5) K. Nagira, K. Kikukawa, F. Wada, and T. Matsuda, *J. Org. Chem.*, 45, 2365 (1980). 6) K. Kikukawa, K. Kono, K. Nagira, F. Wada, and T. Matsuda, *Tetrahedron Lett.*, 21, 2877 (1980). 7) R. F. Heck, *Acc. Chem. Res*,. 12, 146 (1979). 8) M. Tanaka, *Tetrahedron Lett.*, 2601 (1979).

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