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Palladium-Catalyzed Carbonylation of (Arylsulfonyliminoiodo)-benzenes to Arylsulfonyl Isocyanates

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Abstract: In the presence of palladium complexes as catalysts, carbonylation of (arylsulfonyliminoiodo)benzenes to arylsulfonyl isocyanates can be accomplished with 50-80% yield.

The catalytic carbonylation of aromatic nitroso- and nitro-compounds with CO to aromatic isocyanates and their derivatives in the presence of transition metal catalysts has attracted widespread attention as an alternative to synthetic methods based on phosgene[1]. Mechanistically, nitrenes were implicated as active intermediates in these reactions, but their involvement still awaits conclusive evidence.

In our search for N-carbonylation *via* nitrene addition to carbon monoxide, we have found that arylsulfonamidate salts can be carbonylated to arylsulfonyl isocyanates with CO in the presence of Pd-catalysts[2], as shown in eq. (1). Prompted by this novel reaction, we have examined the behavior of the known nitrene source (tosyliminoiodo)benzene, $4\text{-}CH_3C_6H_4SO_2N{=}IC_6H_5$ (**1e**), under catalytic carbonylation conditions. We now report that the Pd-catalyzed carbonylation of **1e** can be accomplished and it constitutes a new, convenient route for the synthesis of arylsulfonyl isocyanates.

$$[ArSO_2NCl]K + CO \xrightarrow{Pd(II)} ArSO_2NCO + KCl \qquad (1)$$

(Tosyliminoiodo)benzene is considered to be the nitrogen analogue of iodosylbenzene. During the past decade, many attempts have been made to effect the transfer of the tosylimino moiety of **1e** to hydrocarbons, which would be the equivalent of hydroxylation and epoxidation with iodosylbenzene. Using Fe(III) and Mn(III) porphyrins as catalysts, Breslow *et al.* were successful in inserting the tosylimino group into a carbon-hydrogen bond of cyclohexane[3]. A much better yield was reported when intramolecular insertion could be achieved[4]. Catalytic reactions of 1e with olefins resulted in allylic amination and formation of aziridines[5]. The chemoselectivity of this latter interaction was strongly dependent on the catalyst used.

If an arylsulfonylnitrene is actually the primary product of the interaction of 1e with the catalyst, (arylsulfonyliminoiodo)benzenes can be suitable starting materials for catalytic carbonylation into arylsulfonyl isocyanates.

We have found that the catalytic transformation of (arylsulfonyliminoiodo)benzenes 1 to arylsulfonyl isocyanates 2 can indeed be accomplished.

$$\underset{(1)}{ArSO_2N{=}IPh} + CO \xrightarrow[\text{solvent}]{\text{Pd-catalyst}} \underset{(2)}{ArSO_2NCO} + PhI \tag{2}$$

The experimental conditions are essentially the same as those used for the carbonylation of N-chlorosulfonamidates[2] (solvent: dichloromethane, 1,2-dichloroethane; $t = 20\text{-}60\ ^{\circ}C$; $p^{\circ}_{CO} = 20\text{-}50$ bar). Suitable catalysts for the transformation depicted by eq. (2) are chloro-complexes of palladium(II), such as $PdCl_2(PhCN)_2$, $PdCl_2(CH_3CN)_2$, or $PdCl_2$ with CH_3CN or PhCN additive.

The starting compounds 1a - 1g are listed in Table 1 together with the yields of the product isocyanates, 2a - 2g. The latter were identified by their strong ν_{as}NCO stretching band between 2220 and 2245 cm^{-1}. For qualitative and quantitative analysis the isocyanates were converted to N-arylsulfonyl-N'-(2-chlorophenyl)ureas, 3, by adding an equimolar amount of 2-chloroaniline. Physical data of adducts 3 are also presented in Table 1.

It is noteworthy that carbonylation of 1c and 1f is restricted to the formation of sulfonyl isocyanates the nitro groups remaining untouched, as has been proved by FAB-MS and IR analyses.

The fact that carbonylation of both N-chloroarylsulfonamidates and (arylsulfonyliminoiodo)benzenes take place under identical reaction conditions and afford arylsulfonyl isocyanates, makes it plausible that these reactions occur via CO insertion into the palladium-nitrogen bond of coordinated arylsulfonylnitrenes. This is in line with the behavior of an imidocarbonylruthenium cluster[6].

Table 1.Yields of arylsulfonyl isocyanates 2 in the catalytic carbonylation of (arylsulfonyliminoiodo)benzenes

1	Ar	Yield of 2[†] (%)	Reaction time (min)	$(M+H)^+$ of 3 (monoisotopic)[††]	Selected IR bands of 3[‡]
a	Phenyl	64	30	311	1696 (νCO), 1599, 1546, 1446, 1354 ($\nu_{as}SO_2$), 1161 (ν_sSO_2)
b	2-Bromophenyl	53	20	389	1703 (νCO), 1540, 1445, 1349 ($\nu_{as}SO_2$), 1163 (ν_sSO_2)
c	2-Nitrophenyl	80	40	356	1679 (ν_{CO}), 1537(br), 1358 ($\nu_{as}SO_2$), 1167 (ν_sSO_2)
d	4-Chloro phenyl	67	30	345	1697 (νCO), 1599, 1547, 1359 ($\nu_{as}SO_2$), 1163 (ν_sSO_2)
e	4-Methylphenyl	60	40	325	1698 (νCO), 1599, 1547, 1444, 1353 ($\nu_{as}SO_2$), 1160 (ν_sSO_2)
f	4-Nitrophenyl	70	20	356	1699 (νCO), 1602, 1550, 1537, 1442, 1359(br), 1164 (ν_sSO_2)
g	3,5-Dichlorophenyl	52	35	379	1703 (νCO), 1600, 1547, 1365 ($\nu_{as}SO_2$), 1167 (ν_sSO_2)

[†] Determined by HPLC analysis of the isolated sulfonylurea 3.

[††] From Fast Atom Bombardment Mass Spetroscopy.

[‡] KBr (cm^{-1}); every spectrum shows several strong νNH vibrations in the 3380-2820 cm^{-1} region.

Further studies of this new reaction involving its extension to sulfonylimines of other main group elements are in progress in this Laboratory.

Experimental: A 45 cm^3 stainless steel reactor (Parr Model 4712) was charged with 2.7 g (0.0069 mol) of (2-nitrophenylsulfonyliminoiodo)-benzene ($2-NO_2C_6H_4SO_2N=IPh$), 67 mg of $PdCl_2(PhCN)_2$, 10 cm^3 of dry CH_2Cl_2 and 0.1 cm^3 of CH_3CN. The reactor was pressurized to 38 bar with carbon monoxide and stirred for 40 min at ambient temperature. The slightly opaque, tea-brown liquid was transferred into a Schlenk-tube under N_2. A 0.1 cm^3 sample was diluted with 5 cm^3 of CH_2Cl_2 and analyzed in a KBr cell. The intense band at $\tilde{\nu} = 2240$ (ν_{as}NCO) indicated the presence of 2-nitrobenzenesulfonyl isocyanate. The rest of the reaction mixture was treated with 0.88 g (0.0069 mol) of 2-chloroaniline. Vigorous reaction took place, which was followed by the immediate formation of pale-yellow crystals. The latter was removed by filtration, washed with diethyl ether, yielding 1.96 g (80.0 %) N-(2-nitrophenylsulfonyl)-N'-(2-chlorophenyl)urea, 3c. The same procedure was followed in the synthesis of 1a, b, d - g.

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REFERENCES

1. (a) Cenini, S.; Pizzotti, M.; Crotti, C. in Ugo, R. (Ed.), *Aspects of Homogeneous Catalysis*; Reidel: Dordrecht, 1988; Vol. 6, pp.97-198.
   (b) Cenini, S; Crotti, C; in Noels, A.F.; Graziani, M; Hubert, A.J. (Eds), *Metal Promoted Selectivity in Organic Synthesis;* Kluwer: Dordrecht, 1991, pp. 311-328.
2. Besenyei, G.; Németh, S.; Simándi, L. I. *Angew. Chem. Int. Ed.* 1990, *29*, 1147-8.
3. Breslow, R.; Gellman, S. H. *J. Chem. Soc. Chem. Commun.* 1982, 1400-1.
4. Breslow, R.; Gellman, S. H.*J. Am. Chem. Soc.* 1983, *105*, 6728-9.
5. (a) Mansuy, D.; Mahy, J-P.; Dureault, A.; Bedi, G.; Battioni, P. *J. Chem. Soc. Chem. Commun.* 1984, 1161-3.
   (b) Mahy, J-P.; Bedi, G.; Battioni, P.; Mansuy, D. *Tetrahedron Lett.* 1988, *29*, 1927-30.
   (c) Evans, D. A.; Faul, M. M.; Bilodeau, M. T. *J. Org. Chem.* 1991, *56*, 6744-6.
   (d) O'Connor, K.J.; Wey, S-J.; Burrows, C. J. *Tetrahedron Lett.* 1992, *33*, 1001-4.
6. Han, S.; Macklin, D.; Nguyen, S.T.; Geoffroy, G.L. *Organometallics*, 1992, *11*, 1242-1255.

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