

Palladium-catalyzed synthesis of sulfinic acids from aryldiazonium tetrafluoroborates, sulfur dioxide and hydrogen

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Abstract

ArN_2BF_4 (Ar = Ph, *p*-Tol, *p*-ClC₆H₄) are converted into the corresponding sulfinic acids (ArSO₂H) in the presence of SO₂, H₂ and catalytic amounts of Pd/C at room temperature. The isolated yields are: PhSO₂H: 84% (4 h); *p*-TolSO₂H: 84% (2 h) and *p*-ClC₆H₄SO₂H: 93% (4 h). © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Throughout the last two decades, diazonium salts have gained attraction in various palladium-catalyzed syntheses. Selected examples are Heck-type reactions [1], Suzuki-type reactions [2] and carbonylations [3]. Homogenous (e.g., Pd(OAc)₂) or heterogenous catalysts (e.g., Pd on activated charcoal) can be employed.

Our interest in the synthesis of sulfinic acids [4–6] prompted us to investigate the conversion of diazonium salts with SO₂. Here, we were guided by similarities between SO₂ and CO.

In principle, the synthesis of sulfinic acids from diazonium salts has already been described in the late 1890s [7,8]. Aniline derivatives are

diazotized in an aqueous sulfuric acid solution and converted with SO₂ in the presence of overstoichiometric amounts of copper powder [7] or copper(I) salts [8]. The reaction is believed to proceed via a radical pathway [9]. The high amount of copper required is a substantial disadvantage.

2. Experimental

2.1. Reagents and solvents

Diazonium salts are prepared by adaption of the method by Dunker [10] and stored under argon at –28°C.

Solvents are purified and degassed by standard methods. A total of 10% Pd on activated charcoal is purchased from Merck KGaA, Germany.

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2.2. General procedure

The diazonium salt and the heterogeneous Pd catalyst are transferred into a glass beaker inside a 150 ml hastelloy[®] autoclave equipped with a stirring bar. The autoclave is rapidly closed, three times evacuated and refilled with dry argon. A total of 40-ml Et₂O and 1-ml MeOH are introduced in a stream of argon by means of a stainless steel syringe. The autoclave is successively pressurized with SO₂ (2 bar) and H₂ ($p_{\text{total}} = 30$ bar). The reaction mixture is then stirred at room temperature. After reaction, the pressure is released carefully and the solid catalyst residue is separated by centrifugation or filtration. The volume of the resulting solution is reduced to approximately 10 ml in vacuum, followed by an extraction with three portions of 10% aqueous Na₂CO₃ solution. The aqueous layer is then acidified with 4 ml concentrated sulfuric acid p.a. (*Cave*: hydrochloric acid will accelerate the disproportionation of the sulfinic acids [11].)

The resulting acidic solution is extracted three times with 30-ml diethyl ether. After drying the organic layer over anhydrous MgSO₄, the solvent is evaporated yielding the pure sulfinic acid, which is sensitive towards disproportionation.

The amount of diazonium salt left after the reaction was weighed to determine the conversion.

2.3. NMR data

Benzene sulfinic acid. ¹H NMR (300 MHz, CDCl₃): δ = 7.39–7.45 (m, 2 H), 7.60–7.64 (m, 2 H), 10.4 (br s, 1 H).

¹³C NMR (75 MHz, CDCl₃): δ = 125.0, 129.0, 132.0, 145.8.

4-Toluene sulfinic acid. ¹H NMR (300 MHz, CDCl₃): δ = 2.33 (s, 3 H), 7.18–7.24 (m, 2 H), 7.50–7.52 (m, 2 H), 9.30 (br s).

¹³C NMR (75 MHz, CDCl₃): δ = 21.5, 125.0, 129.7, 142.6, 143.0.

4-Chlorobenzene sulfinic acid. ¹H NMR (300 MHz, CD₃CN): δ = 7.24–7.50 (m, 2 H), 7.58–7.74 (m, 2 H), 8.30 (br s, 1 H).

¹³C NMR (75 MHz, CD₃CN): δ = 127.3, 130.1, 138.3, 147.6.

3. Results and discussion

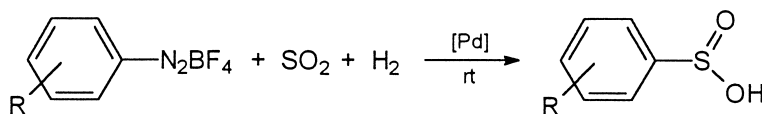
3.1. Influence of substituents and of reaction time

We now report the first synthesis of aromatic sulfinic acids from diazonium tetrafluoroborates, sulfur dioxide and hydrogen in the presence of a palladium catalyst (Scheme 1).

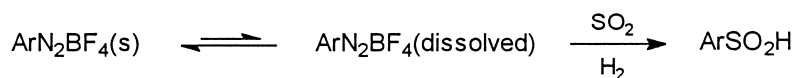
Palladium on activated charcoal serves as catalyst and diethyl ether is employed as solvent. A small amount of methanol is added, thus suppressing the disproportionation of the sulfinic acids to a certain extent [5]. As the diazonium tetrafluoroborates are only slightly soluble in the solvent applied, we propose a rapid equilibrium between the solid and the dissolved salt according to Scheme 2. The low solubility might reduce the conversion when compared to a completely homogeneous system, but it might also reduce side reactions.

Table 1 contains the results obtained.

The reaction was carried out at different pressures ranging from 10 to 90 bar. Since no effect



Scheme 1. Catalytic synthesis of aromatic sulfinic acids from diazonium salts.



Scheme 2. Possible equilibrium and product formation.

was observed, the pressure was maintained at 30 bar.

We have focused our attention on the influence of substrates bearing different electronic properties.

As can be derived from Table 1, the use of benzene diazonium tetrafluoroborate leads to a high activity. After 2 h 80% of the substrate is converted. Doubling of the reaction time only leads to a marginal increase in conversion. Selectivities are excellent, reaching up to 100%. The only by-products identified are the disproportionation products of the sulfinic acids (i.e., thiosulfonates, sulfonic acids and water).

A significant increase in activity is observed introducing a methyl substituent into the aromatic ring in the *para* position. After half an hour a yield of 54% at 63% conversion is achieved. After 1 h the conversion is nearly quantitative, but a prolongation of the reaction time results in a decrease in selectivity. This accounts for the fact that electron releasing substituents in aromatic sulfinic acids lead to an increase in the disproportionation rate ($R = \text{Ph}$: $k_{\text{rel}} = 1.0$, $R = p\text{-Tol}$: $k_{\text{rel}} = 2.4$, $R = p\text{-ClC}_6\text{H}_4$: $k_{\text{rel}} = 0.54$) [12]. This means that toluene sulfinic acid is decomposed to a higher degree than benzene sulfinic acid under the same reaction conditions.

For the chlorine containing compound *p*-ClC₆H₄N₂BF₄ the yield after 2 h reaction time is also significantly higher than for the unsubstituted diazonium salt. Yet, the activity is lower in comparison to the tolyl compound *p*-TolN₂BF₄.

It can be summarized that the different activities of the three compounds examined are not attributable to electronic effects alone. Electron withdrawing effects increase in the series CH₃ < H < Cl, whereas the activity follows the order *p*-TolN₂BF₄ > *p*-ClC₆H₄BF₄ > PhN₂BF₄. This corresponds to Kikukawa's observations in the carbonylation of aryldiazonium salts [3]. In his case the yields are not dependent on electronic effects either (e.g., $R = p\text{-MeO}$: c.y. = 73%, $R = p\text{-Tol}$: c.y. = 60%, $R = p\text{-ClC}_6\text{H}_4$: c.y. = 93%).

3.2. Influence of the catalyst concentration

In order to obtain some information concerning the influence of the catalyst concentration, experiments with substrate:catalyst ratios ranging between 110:1 and 1100:1 have been carried out. The results are presented in Table 2.

With the highest sub.:cat. ratio (entry 1) a conversion of 29% after 4 h is achieved. Dou-

Table 1
Sulfinic acids from diazonium salts: influence of substituents and of reaction time

<i>t</i> (h)	R = H			R = <i>p</i> -CH ₃			R = <i>p</i> -Cl		
	Yield ^a (%)	Conversion (%)	Selectivity (%)	Yield ^a (%)	Conversion (%)	Selectivity (%)	Yield ^a (%)	Conversion (%)	Selectivity (%)
0.5	–	–	–	54	63	86	–	–	–
1	19	22	86	83	98	85	41	49	84
2	81	81	100	84	96	88	89	97	92
4	84	86	98	76	100	76	93	100	93

Conditions: 2.6 mmol RC₆H₄N₂BF₄, cat.: 10% Pd on activated charcoal, sub.:cat. = 55:1, solvent: 40 ml Et₂O + 1 ml MeOH, room temperature, $p(\text{SO}_2) = 2$ bar, $p(\text{H}_2) = 30$ bar.

^aIsolated yield.

Table 2
Sulfinic acids from diazonium salts: influence of the catalyst concentration

No.	$n(\text{sub.}):$ $n(\text{cat.})$	Yield ^b (%)	Conversion (%)	TON
1	1100:1	29	29	322
2	550:1	57	62	316
3	275:1	67	82	186
4	110:1	82	92	91
5 ^a	110:1	85	98	94

Conditions: 5.2 mmol PhN_2BF_4 , cat.: 10% Pd on activated charcoal, solvent: 40 ml Et_2O + 1 ml MeOH, room temperature, $p(\text{SO}_2) = 2$ bar, $p(\text{H}_2) = 30$ bar, $t = 4$ h.

^a $t = 6$ h.

^b Isolated yield.

bling the amount of catalyst (entry 2) leads to a doubling of the conversion. As expected, these two experiments provide the highest turnover number (TON). Any further addition of catalyst will decrease the TON.

As in Kikukawa's carbonylation experiments [3], we also employed Et_3SiH and polymethylhydrosiloxane as hydrogen source. In these cases

the yield was never higher than 27%. The use of hydrogen instead of silanes leads to much higher yields as presented in Tables 1 and 2.

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