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On the Reaction of *p*-Toluenesulfinyl Chloride with Anisole

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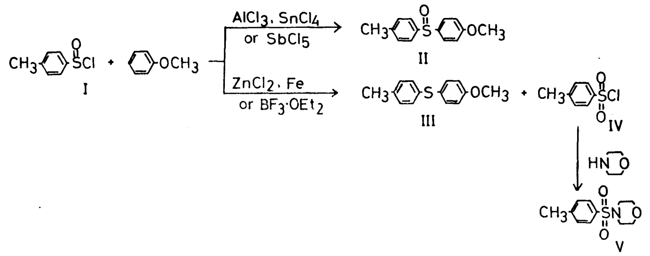
Concerning the Friedel-Crafts-type reaction, sulfonyl chloride and sulfenyl chloride have been well known to give aromatic sulfone[1] and sulfide[2] respectively; however, with one exception,[3] the reaction of sulfinyl chloride with aromatics has not been reported. In this experiment, the reaction of *p*-toluenesulfinyl chloride (I) with anisole was studied with various catalysts as a series of electrophilic aromatic substitutions with the chlorides of organic sulfur acids.[2]



Scheme 1.

When the reaction of anisole with I in the presence of aluminum chloride was conducted in carbon disulfide or excess anisole at −15—20 °C, *p*-anisyl *p*-tolyl sulfoxide (II) was obtained in a good yield after the hydrolysis of the reaction product. The use of antimony pentachloride or stannic chloride in place of aluminum chloride led also to the formation of II. On the other hand, when a 10% excess molar amount of zinc chloride or boron trifluoride etherate, or a catalytic amount of iron powder, was used as the catalyst, the sulfoxide II was not obtained; instead, *p*-anisyl *p*-tolyl sulfide (III) and *p*-toluenesulfonyl chloride (IV) were formed. Compound IV was identified as *N*-(*p*-toluenesulfonyl) morpholine (V). The seresults are summarized in Table 1.

The sulfoxide formation may be explained by a mechanism similar to that of the Friedel-Crafts acylation.[1] This assumption was supported by the IR spectra of mixtures of I and the catalysts (*vide infra*) and by the isolation of a 1: 1 complex of II with antimony pentachloride. The sulfide formation is ascribed to the reduction of the initially-formed II with I. In fact, control experiments revealed that II and the complexes of II with the catalysts for sulfide formation were reduced by I at room temperature in accord with the following equation.[4]

Scheme 2.

This is the first example of the reduction of sulfoxide by sulfinyl chloride, although there is one precedent for sulfinyl chloride functioning as a reducing agent; it is the reduction of pyridine *N*-oxide with *p*-nitrobenzene-

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[1] G. A. Olah, Ed., "Friedel-Crafts and Related Reactions," Vol. III, part 2, Interscience Pub., N. Y. (1964), p. 1003.

[2] T. Fujisawa, T. Kobori, N. Ohtsuka, and G. Tsuchihashi, *Tetrahedron Lett.*, **1968**, 4533 and 5071; T. Fujisawa and N. Kobayashi, *J. Org. Chem.*, **36**, 3546 (1971) and references cited therein.

[3] C. Courtot and J. Frenkiel, *C.R. Acad. Sci. Paris*, **199**, 557 (1934).

[4] The complexes of II with the catalysts for sulfoxide formation were not reduced to III on treatment of them with I at room temperature.

TABLE 1. REACTION OF *p*-TOLUENESULFINYL CHLORIDE WITH ANISOLE IN THE PRESENCE OF VARIOUS CATALYSTS

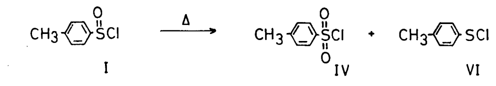
Catalyst	Molar ratio Cat/I	Medium	Temp. (°C)	Time (hr)	Yield (%)		
					II[a]	III[b]	V[a]
$AlCl_3$	1.1	CS_2	−15	5	75	0	0
$AlCl_3$	1.1	Anisole	R.T.	24	81	0	0
$SnCl_4$	1.1	CS_2	R.T.	24	40	0	0
$SbCl_5$	1.1	CS_2	R.T.	24	22	0	0
$ZnCl_2$	1.1	CS_2	R.T.	24	0	47	16
$BF_3 \cdot OEt_2$	1.1	CS_2	R.T.	24	0	46	11
Fe	0.01	Anisole	R.T.	24	0	64	5
None	—	Anisole	Reflux	3	0	70	23

a) Isolated yields.
b) Determined by glpc.

sulfinyl chloride at 180 °C.[5]

The catalyst dependence of the products may be due to the difference in the interaction between the catalysts and I. The IR spectra of mixtures of I and aluminum chloride, stannic chloride, or antimony pentachloride in carbon disulfide showed shifts of absorption due to the sulfinyl group to wave numbers lower by 129—179 cm^{-1}, but no such shifts were observed in the case of zinc chloride, boron trifluoride etherate, or iron powder. These findings suggest that the sulfinyl group of I interacts with the catalysts for the sulfoxide formation,[6] and that free sulfinyl chloride effects the reduction of sulfoxides.

The sulfide formation was observed also in the absence of a catalyst. Although the reaction of anisole with I did not occur at room temperature, the reaction in boiling anisole gave III in a 70% yield. This reaction path is different from that of the catalyzed reaction; *i.e.*, the formation of III is to be ascribed to the electrophilic aromatic substitution of *p*-toluenesulfenyl chloride (VI),[7] which may itself be formed by the disproportionation of I. Concerning the disproportionation of a sulfinyl chloride, it has been described that methanesulfinyl chloride decomposes to the corresponding sulfenyl and sulfonyl chlorides on standing for several months.[8] *p*-Toluenesulfinyl chloride (I) did not undergo the disproportionation at room temperature, not even in the presence of a catalyst, but it gave the corresponding sulfonyl chloride, IV, on heating at 140 °C.[9]



Scheme 3.

We are grateful to the Kawakami Memorial Foundation for its partial support of this research.

Experimental

The melting points are uncorrected. The infrared spectra were run on a Perkin-Elmer 337 spectrophotometer. All the NMR spectra were recorded on a Varian HA-100 spectrometer. The chemical shifts of the NMR spectra are reported in parts per million downfield from the internal TMS (δ). The glpc analyses were conducted using a Hitachi K-53 chromatograph with a 3% SE-30 column. *p*-Toluenesulfinyl chloride (I) was prepared by treating sodium *p*-toluenesulfinic acid with thionyl chloride according to the method of Kurzer.[10]

Reaction of I with Anisole in Carbon Disulfide in the Presence of Aluminum Chloride. Aluminum chloride (3.70 g, 28 mmol) was added to a solution of I (4.36 g, 25 mmol) and anisole (2.70 g, 25 mmol) in carbon disulfide (20 ml) cooled to −30 °C. The mixture was stirred for 5.5 hr at 0—−15 °C and then heated under reflux for 30 min to complete the reaction. The reaction mixture was poured into a mixture of ice and water. The carbon disulfide layer was separated and dried with calcium chloride. The removal of the carbon disulfide afforded *p*-anisyl *p*-tolyl sulfoxide[11] (4.6 g, 75%), which was subsequently recrystallized from *n*-hexane; mp 68—70 °C; IR (KBr) 1030 cm^{-1}; NMR ($CDCl_3$) δ 2.33 (s, 3H), 3.77 (s, 3H), 6.90 (d, 2H), 7.19 (d, 2H), 7.47 (d, 2H), 7.52 (d, 2H).

Found: C, 68.26; H, 5.73; S, 13.02%. Calcd for $C_{14}H_{14}O_2S$: C, 68.35; H, 5.87; 13.09%.

When antimony pentachloride was used as a catalyst in this reaction, a 1 : 1 complex of *p*-anisyl *p*-tolyl sulfoxide with antimony pentachloride (14 g, 86%) was obtained. The complex was recrystallized from chloroform–*n*-hexane; mp 178—179 °C; IR (KBr) 850 cm^{-1} (sulfoxide); NMR ($CDCl_3$) δ 2.47 (s, 3H), 3.91 (s, 3H), 7.07 (d, 2H), 7.40 (d, 2H), 7.65 (d, 2H), 7.72 (d, 2H). Found: C, 30.90; H, 2.62; S, 6.06; Cl, 32.75%. Calcd for $C_{14}H_{14}O_2SSbCl_5$; C, 30.83; H, 2.59; S, 5.88; Cl, 32.51%. When the complex was subjected to column chromatography (silica gel–chloroform), *p*-anisyl *p*-tolyl sulfoxide (22%) was obtained.

In a similar way, when stannic chloride was used as the catalyst in the reaction, the sulfoxide was also obtained (see Table 1).

Reaction of I with Anisole in Carbon Disulfide in the Presence of Boron Trifluoride Etherate. To a solution of I (4.36 g, 25 mmol) and anisole (2.70 g, 25 mmol) in carbon disulfide (20 ml) was added boron trifluoride etherate (3.9 g, 28 mmol)

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[5] S. Oae and K. Ikura, This Bulletin, **39**, 1306 (1966).

[6] Some Lewis acids were reported to coordinate to oxygen atom of sulfoxide; D. W. Meek and R. S. Drago, *J. Amer. Chem. Soc.*, **82**, 6013 (1960).

[7] A similar aromatic substitution with sulfenyl chloride in the presence of catalyst has been reported; *cf.* Ref. 2.

[8] I. B. Douglass and D. A. Koop, *J. Org. Chem.*, **29**, 951 (1964).

[9] *p*-Toluenesulfenyl chloride could not be isolated because of instability at the temperature.

[10] K. Kurzer, "Organic Syntheses," Coll. Vol. IV, p. 937 (1964).

[11] The preparation of the corresponding optically active sulfoxide has been reported, K. K. Andersen, W. Gaffield, N. E. Papanikolaou, J. W. Foley, and R. I. Perkins, *J. Amer. Chem. Soc.*, **86**, 5637 (1964).

at room temperature. The solution was stirred for 24 hr at room temperature and then heated under reflux for 1 hr. After the removal of the carbon disulfide by distillation, morpholine (5 ml) was added, and then the reaction mixture was poured into water. The mixture was extracted with chloroform. After the removal of the chloroform and excess morpholine under reduced pressure, the oily residue was recrystallized from ether to give *N*-(*p*-toluenesulfonyl)morpholine (0.35 g, 11%). A glpc of the remaining residue after the removal of the ether indicated the presence of *p*-anisyl *p*-tolyl sulfide (46%).

In a similar way, when equimolar amounts of zinc chloride and a catalytic amount of iron powder were used as catalyst in the reaction, the sulfide was also obtained (see Table 1).

Reaction of I with Anisole in the Absence of a Catalyst. A solution of anisole (27 g, 250 mmol) and I (4.36 g, 25 mmol) was heated under reflux for 3 hr. Morpholine (5 ml) was added to the reaction mixture, and then it was poured into water. The mixture was treated in the same manner described above. The results were recorded in Table 1.

Reduction of II with I. The general procedures were as follows: equimolar amounts of Lewis acid and *p*-anisyl *p*-tolyl sulfoxide were added to carbon disulfide, and the mixture was stirred for 2 hr at room temperature. Then equimolar amounts of I were added, and the mixture was stirred for 24 hr at room temperature, followed by refluxing for 1 hr. Morpholine was then added to the mixture. After the hydrolysis of the mixture with ice-water, the organic layer was analyzed by glpc. The results are summarized in Table 2.

TABLE 2. REDUCTION OF *p*-ANISYL *p*-TOLYL SULFOXIDE WITH *p*-TOLUENESULFINYL CHLORIDE

Catalyst	Molar ratio Cat/I	Yield (%)	
		III	V
None	—	62	69
Fe	0.01	76	50
$AlCl_3$	1.1	0	
$BF_3 \cdot OEt_2$	1.1	63	
$ZnCl_2$	1.1	59	