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### REACTIONS OF ORGANOCADMIUM REAGENTS WITH SULFONYL HALIDES II. ACTION OF ARENESULFONYL CHLORIDES ON SELECTED DIARYLCADMIUM COMPOUNDS

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## REACTIONS OF ORGANOCADMIUM REAGENTS WITH SULFONYL HALIDES II. ACTION OF ARENESULFONYL CHLORIDES ON SELECTED DIARYLCADMIUM COMPOUNDS†

by

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### ABSTRACT

The reaction of diarylcadmium compounds with arenesulfonyl chlorides was explored. Five different diarylcadmium reagents, diphenylcadmium, di-*p*-tolylcadmium, di- $\alpha$ -naphthylcadmium, dibenzylcadmium and di-*p*-anisylcadmium, were selected to interact with benzene- or *p*-toluenesulfonyl chlorides. Unlike acid chlorides which react with these reagents to form ketones in high yields, the sulfonyl chlorides gave sulfones in moderate to poor yields. Beside the sulfones, sulfinic acids, biaryls, and haloarenes were obtained in moderate to good yields. Only di-*p*-anisylcadmium gave poor yield of *p,p'*-dianisyl.

Possible pathways are suggested and discussed.

Although the reaction of organometallic compounds with acid chlorides have been extensively investigated, the corresponding reaction with sulfonyl halides received but little attention. As early as 1921, Hepworth and Clapham<sup>1</sup> studied the reaction of some sulfonyl chlorides with organomagnesium reagents. These studies were later extended by Wedekind *et al.*<sup>2</sup> and by Gilman and coworkers.<sup>3</sup> While the reaction of phenyllithium with some benzylsulfonyl halides was studied recently by Shirota *et al.*,<sup>4</sup> apparently the reaction of organocadmium reagents with sulfonyl halides have not been investigated. In a previous communication,<sup>5</sup> we reported preliminary results obtained in our laboratory concerning the reaction of diphenylcadmium with some sulfonyl chlorides. In extension of this work, we have investigated the course of the reaction of some representative diarylcadmium compounds with benzene- and toluenesulfonyl chlorides.

### Results and Discussion

The conditions employed in this study are those under which good yields of ketones were obtained from the reaction of organocadmium reagents with

acid chlorides. Under these conditions, diphenylcadmium in ether or benzene was found to react with benzenesulfonyl chloride to give diphenylsulfone, biphenyl, chlorobenzene and benzenesulfinic acid. Similar reaction using di-*p*-tolylcadmium instead of diphenylcadmium, afforded phenyl *p*-tolyl sulfone, *p,p'*-bitolyl, *p*-chlorotoluene and benzenesulfinic acid. The yields of the comparable products of these two experiments were almost the same (*cf.* Table I, runs 1 and 2).

Under the same conditions, di- $\alpha$ -naphthylcadmium reacted with benzenesulfonyl chloride to give  $\alpha$ -naphthyl phenyl sulfone,  $\alpha,\alpha'$ -binaphthyl,  $\alpha$ -chloronaphthalene and benzenesulfinic acid. Similar reaction with dibenzylcadmium yielded small amounts of benzyl phenyl sulfone. However, benzyl chloride and dibenzyl were obtained in high yields. Finally, the reaction of benzenesulfonyl chloride with di-*p*-anisylcadmium gave *p*-anisyl phenyl sulfone and *p,p'*-dianisyl in poor yields, but the yield of the halogen exchange product, *p*-chloroanisole, was double that obtained in the preceding experiments. These results are shown in Table I.

It seems that this reaction is of general nature and other arenesulfonyl chlorides may be used. For example, when the reaction of these five organocadmium reagents were repeated using *p*-toluenesulfonyl chloride

† For Part I see reference 5.

TABLE I

## Reaction Products of Diarylcadmium with Benzenesulfonyl Chloride

Run	Cadmium reagent	Sulfone [ArSO <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ]		Biaryl	Haloarene	Benzene-sulfinic acid, %	Benzene-sulfonic acid, % <sup>b</sup>
		Ar	Yield <sup>a</sup> %				
1	Diphenyl-cadmium	Phenyl	23	Biphenyl	Chlorobenzene	25.5	32
2	Di- <i>p</i> -tolyl-cadmium	<i>p</i> -Tolyl	23	<i>p,p'</i> -Bitolyl	<i>p</i> -Chlorotoluene	28	33
3	Dibenzyl-cadmium	Benzyl	2.0	Bibenzyl	Benzyl chloride	45	45
4	Di- $\alpha$ -naphthyl-cadmium	$\alpha$ -Naphthyl	20	$\alpha,\alpha'$ -Bi-naphthyl	$\alpha$ -Chloro-naphthalene	29.5	35
5	Di- <i>p</i> -anisyl-cadmium	<i>p</i> -Anisyl	4.6	<i>p,p'</i> -Bi-anisyl	<i>p</i> -Chloroanisole	33.5	35

<sup>a</sup> Isolated yield.<sup>b</sup> Formed by hydrolysis of unreacted benzenesulfonyl chloride during steam distillation.

TABLE II

Reaction Products of Diarylcadmium with *p*-Toluenesulfonyl Chloride

Run	Cadmium reagent	Sulfone [ArSO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> ]		Biaryl	Haloarene	<i>p</i> -Toluene-sulfinic acid, %	<i>p</i> -Toluene-sulfonic acid, % <sup>b</sup>
		Ar	Yield <sup>a</sup> %				
1	Diphenyl-cadmium	Phenyl	30.5	Biphenyl	Chlorobenzene	23	26
2	Di- <i>p</i> -tolyl-cadmium	<i>p</i> -Tolyl	19.5	<i>p,p'</i> -Bitolyl	<i>p</i> -Chlorotoluene	38	22.5
3	Dibenzyl-cadmium	Benzyl	0.3	Bibenzyl	Benzyl chloride	35	32
4	Di- $\alpha$ -naphthyl-cadmium	$\alpha$ -Naphthyl	30	$\alpha,\alpha'$ -Bi-naphthyl	$\alpha$ -Chloro-naphthalene	14.5	24.5
5	Di- <i>p</i> -anisyl-cadmium	<i>p</i> -Anisyl	4.5	<i>p,p'</i> -Bi-anisyl	<i>p</i> -Chloroanisole	30.5	36.5

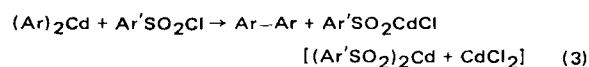
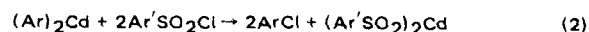
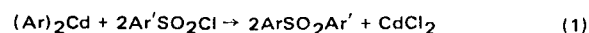
<sup>a</sup> Isolated yield.<sup>b</sup> Formed by hydrolysis of unreacted *p*-toluenesulfonyl chloride during steam distillation.

instead of benzenesulfonyl chloride, similar results were obtained as shown in Table II.

The products reported above were identified by physical methods and/or by direct comparison with authentic samples. They were separated from the reaction mixture by extraction with ether followed by separation of the sulfinic acid with 5% sodium hydroxide solution.<sup>†</sup> The residue after evaporation of ether was subjected to steam distillation, and both the steam distillable and non-distillable products were fractionated according to the procedure described in

the experimental section. The yields shown in Tables I and II are those of the isolated pure materials and based on the bromoarenes from which the cadmium reagents were prepared.

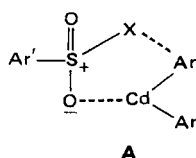
From the results presented above, it is reasonable to assume that the following competing reactions are involved:



<sup>†</sup> Because sulfinic acids are unstable, they were converted immediately to the corresponding benzyl sulfones.

Reaction (1) may proceed by an  $S_N2$ -like substitution on sulfur. Similar interpretation was offered earlier<sup>3,4</sup> for formation of sulfones from lithium reagents or Grignard reagents and sulfonyl chlorides. Alternatively, it may involve addition of the cadmium reagent on oxygen and sulfur followed by elimination of organocadmium chlorides. The data at hand cannot differentiate between these two possibilities.

Reaction (2) is a halogen-metal exchange between the sulfonyl chlorides and the organocadmium reagents, possibly *via* a transition similar to that proposed previously by Shirota *et al.*<sup>4</sup> for the formation of halobenzene from the reaction of phenyllithium with benzenesulfonyl halides:



Sulfinic acids are formed by hydrolysis of the cadmium salts produced by eqs (2) and (3). On the other hand, sulfonic acids (*cf.* Tables I and II) are not true products of the reaction and are formed by hydrolysis of the unreacted sulfonyl chlorides during the steam distillation step.

The formation of biaryls is of particular interest since these compounds were not found among the reaction products of diaryl cadmium with acid chlorides, in spite of the special efforts made to detect them. That the biaryls are primary products of the reactions under investigation and not due to thermal cleavage of the organocadmium reagents was confirmed by carrying out the reaction at  $0^\circ$ . Under these conditions, biphenyl was obtained in 15% yield from the reaction of diphenylcadmium with benzenesulfonyl chloride. Of course at low temperatures, the reaction is expected to be slower, and this could be responsible for the lower yield. However, while this shows that biaryls are indeed original products of this reaction, it does not exclude the possibility that at least some of the biaryls may be formed *via* thermal decomposition of the organometallic compounds. However, other evidence suggests that no free radical intermediate was involved in this reaction. The evidence includes:

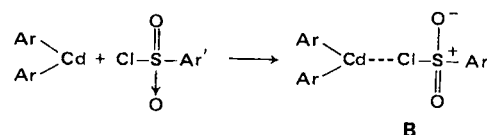
- The yield of biaryls did not change when the reaction was carried out in benzene instead of ether as a solvent. Had a free aryl radical been involved, this yield should increase due to phenylation of the solvent.<sup>6</sup>
- In benzene solution, no *p*-methylbiphenyl could be detected in the reaction products of di-*p*-tolyl

cadmium and benzenesulfonyl chloride, indicating that no free tolyl radical was formed.

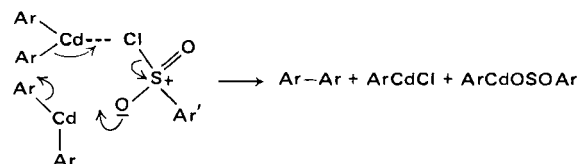
- In presence of a hydrogen-donating solvents such as hexane no hydrogen abstraction took place.

- Exclusion of oxygen by carrying out the reaction under nitrogen atmosphere did not change the results.

It is clear, therefore, that the results presented above are in agreement with our previous suggestion<sup>5</sup> that this reaction may involve as a first-step coordination between the cadmium reagent and the sulfonyl chloride as follows:



It is possible that the charge-transfer complex **B** may collapse to give biaryl or react with another molecule of diaryl cadmium as follows:



Evidence in favor of the latter possibility will be reported in the near future.

## Experimental Section

### General Procedure

The cadmium reagents were prepared from bromoarenes (0.055 mole) according to the published procedure.<sup>7</sup> To a solution of these reagents in benzene or ether, there was added in one portion a solution of 0.0435 mole of benzenesulfonyl chloride (or toluenesulfonyl chloride) in 20 ml of dry ether and the reaction mixture was heated under reflux for one hour. The flask was then cooled in an ice bath and the product was decomposed with ice-cold sulfuric acid. The organic layer was separated and the aqueous layer was extracted twice with ether.

The combined organic solution was extracted twice with 20 ml portions of cold 5% sodium hydroxide solution. From the aqueous extracts, benzenesulfinic acid (or toluenesulfinic)\* was liberated by neutralization and converted immediately to the corresponding benzyl sulfone by the published procedure.<sup>8</sup>

The ether solution, after separation of sulfinic acids, was fractionated by steam distillation. The steam distillable fraction was fractionally distilled through a 2-ft column to give the products described under the individual runs. The steam non-distillable fraction was either purified by crystallization or chromatographed as described under the individual runs.

When the water left in the steam distillation flask was evaporated to dryness, the sulfonic acids† remained.

#### Action of Benzenesulfonyl Chloride on Diphenylcadmium

Distillation of the steam distillable products gave 0.7 g (16.5%) benzene, 1.4 g (23%) chlorobenzene and 1.1 g (29%) biphenyl. Recrystallization of the residue from steam distillation gave 2.2 g (23%) of diphenyl sulfone, mp 129°. All these products were identical in all respects with authentic samples.

#### Action of Toluenesulfonyl Chloride on Diphenylcadmium

In this run, benzene (0.7 g, 16.5%), chlorobenzene (1.3 g, 21%) and diphenyl (1.15 g, 30%) were separated from the steam distillable fraction. Recrystallization of the steam non-distillable fraction gave 3.1 g (30.5%) of phenyl *p*-tolyl sulfone identical with authentic sample.

#### Action of Benzenesulfonyl Chloride on *p*-Ditolylcadmium

*p*-Ditolylcadmium (prepared from 9.4 g *p*-bromotoluene) reacted with benzene sulfonyl chloride according to the general procedure described above. Fractional distillation of the steam distillable products gave 0.8 g (15.6%) of toluene, 1.7 g (25%) of *p*-chlorotoluene and 1.3 g (27.5%) of *p,p'*-bitolyl, mp 125°; *M*<sup>+</sup>, *m/e* 232.

#### Action of *p*-Toluenesulfonyl Chloride on *p*-Ditolylcadmium

The steam distillable products from this reaction were: toluene (0.8 g, 15.6%), *p*-chlorotoluene (1.9 g, 28%) and *p,p'*-bitolyl (1.15 g, 23.5%). Ditolyl sulfone (2 g, 19.5%) was obtained from the residue left after steam distillation.

#### Action of Benzenesulfonyl Chloride on Dibenzylcadmium

The steam distillable products from this reaction were: toluene (0.9 g, 17.6%), benzyl chloride (2.4 g, 35.5%) and dibenzyl (1.8 g, 36%). The residue that remained after steam distillation was recrystallized to give 0.2 g (2%) benzyl phenyl sulfone, mp 148°; lit.<sup>8</sup> mp 148°.

#### Action of *p*-Toluenesulfonyl Chloride on Dibenzylcadmium

The following compounds were separated from the steam distillable products of this reaction: toluene (0.9 g, 17.5%), benzyl chloride (2.3 g, 34%) and dibenzyl (2.4 g, 48%). The residue from steam distillation gave, after recrystallization, 0.03 g (0.3%) benzyl *p*-tolyl sulfone.

#### Action of Benzenesulfonyl Chloride on di- $\alpha$ -naphthylcadmium

Di- $\alpha$ -naphthylcadmium (prepared from 11.4 g, 0.055 mole,  $\alpha$ -bromonaphthalene) was treated with benzenesulfonyl chloride according to our general procedure. After separation

of benzenesulfinic acid (1.95 g, 29.5%), the following compounds were separated from the steam distillable portion of the products: naphthalene (1.2 g, 22.5%) and  $\alpha$ -chloronaphthalene (2.2 g, 25.5%).

The non-steam distillable fraction was chromatographed on a 60 cm x 1 cm column packed with 80 g neutral alumina. The following compounds were obtained:  $\alpha,\alpha'$ -dinaphthyl (0.8 g, 12%) eluted with petr. ether (40–60); mp 155–156° and  $\alpha$ -naphthyl phenyl sulfone (2.4 g, 20%), eluted with a mixture of petr. ether (60–80) and benzene (2 : 3); mp 100, lit.<sup>9</sup> 97–99°.

#### Action of *p*-Toluenesulfonyl Chloride on Di- $\alpha$ -naphthylcadmium

The products of this reaction were separated in the same way as in the preceding reaction. The following compounds were obtained: naphthalene (1.0 g, 18%),  $\alpha,\alpha'$ -dinaphthyl (1.0 g, 14.5%),  $\alpha$ -chloronaphthalene (1.7 g, 19%) and  $\alpha$ -naphthyl *p*-tolyl sulfone (4 g, 30%).

#### Action of Benzenesulfonyl Chloride on Di-*p*-anisylcadmium

This reaction was carried out as usual to give finally anisole (1.1 g, 18%) and *p*-chloroanisole (4.4 g, 57%) as steam distillable products. The non-distillable products were separated by chromatography on neutral alumina to give *p,p'*-dianisyl (0.4 g, 6.7%); mp 172°, lit.<sup>10</sup> 171–173°, and *p*-anisyl phenyl sulfone (4.6%).

#### Action of *p*-Toluenesulfonyl Chloride on Di-*p*-anisylcadmium

This reaction was similar to the preceding one and the following products were obtained: anisole (1.0 g, 16.6%), *p*-chloroanisole (4.0 g, 50%), *p,p'*-dianisyl (0.4 g, 7%) and *p*-anisyl *p'*-tolyl sulfone (0.6 g, 4.5%).

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† The yields of these compounds are shown in Tables I and II and will not be repeated here.