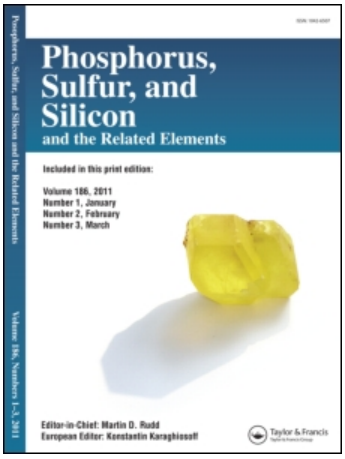

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REACTION OF ORGANOCADMIUM REAGENTS WITH SULFONYL HALIDES III. ACTION OF ALKANESULFONYL CHLORIDES ON SELECTED DIARYLCADMIUM COMPOUNDS

by

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ABSTRACT

The reaction of methane- and ethanesulfonyl chloride with selected diarylcadmium compounds was investigated. In contrast with arenesulfonyl chlorides which react with diarylcadmium to give sulfones in appreciable yields, ethanesulfonyl chloride did not yield sulfones. Methanesulfonyl chloride gave sulfones in very poor yields. The major products were haloarenes, alkanesulfinic acids and biaryls.

Cross-over experiments revealed that the formation of biaryls involve an inter- *not* intramolecular reaction (*cf.* eq. 4).

Studies on the course of the reaction of organocadmium reagents with sulfonyl halides appear to be limited to previous investigations in our laboratory.[1,2] In these studies, we have found that diarylcadmium compounds react with arenesulfonyl chlorides (benzene- and toluenesulfonyl chloride) in benzene or ether solutions to give several products. These products include: biaryls, diaryl sulfones, sulfinic acids and haloarenes. In an extension of this work, we have investigated the reaction of five different organocadmium reagents with some alkanesulfonyl chlorides-(methane- and ethanesulfonyl chloride).

Results and Discussion

Diphenylcadmium was found to react with methanesulfonyl chloride, under the general conditions reported earlier[2] to give biphenyl, chlorobenzene, methanesulfinic acid and methyl phenyl sulfone. Similarly, di-*p*-tolylcadmium reacted under the same conditions with methanesulfonyl chloride to yield, *p,p'*-bitolyl, *p*-chlorotoluene, methanesulfinic acid and methyl *p*-tolyl sulfone. When the reaction was repeated using dibenzylcadmium, di-α-naphthylcadmium or di-*p*-anisylcadmium, the comparable products were obtained. These results are summarized in Table I.

Similar results were obtained when the reactions were repeated using ethanesulfonyl chloride instead of methanesulfonyl chloride (*cf.* Table II), except that in this case no appreciable amounts of the corresponding sulfone could be isolated among the reaction products.

While these results are similar to those reported earlier[2] for the reaction of organocadmium reagents with arenesulfonyl chlorides, comparison of the results shown in Tables I and II with those reported earlier reveal that the yields of the sulfones are considerably decreased whereas the yields of the haloarenes are appreciably increased. In the previous communications we have suggested that the following competing reactions are involved:

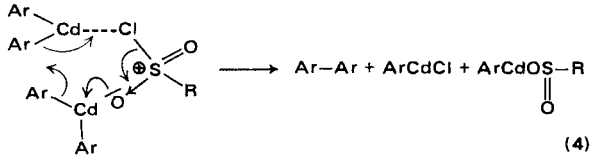
$$(C_6H_5)_2Cd + 2RSO_2Cl \rightarrow 2RSO_2C_6H_5 + CdCl_2 \quad (1)$$

$$(C_6H_5)_2Cd + 2RSO_2Cl \rightarrow 2C_6H_5Cl + (RSO_2)_2Cd \quad (2)$$

$$(C_6H_5)_2Cd + RSO_2Cl \rightarrow C_6H_5{-}C_6H_5 + RSO_2CdCl \; [(RSO_2)_2Cd + CdCl_2] \quad (3)$$

From the results presented above it seems that reaction 1 is not as important with alkanesulfonyl chlorides.

The formation of biaryls in these reactions is of particular interest. We have suggested previously that biaryls are formed *via* a charge-transfer complex which may either collapse or react with another molecule of the organocadmium reagent as follows:



(4)

TABLE I

Reaction Products of Diarylcadmium with Methanesulfonyl Chloride

		Sulfone [$ArSO_2CH_3$]							
Run	Cadmium reagent	Ar	Yield[a], %	Biaryl	Yield[a], %	Haloarene	Yield[a], %	Methanesulfinic acid, %	Methanesulfonic acid[b], %
1	Diphenylcadmium	Phenyl	5.7	Biphenyl	26.5	Chlorobenzene	45	35	36
2	Di-*p*-tolylcadmium	*p*-Tolyl	5.5	*p,p'*-Bitolyl	23.5	*p*-Chlorotoluene	42	37	34
3	Dibenzylcadmium	Benzyl	0.9	Bibenzyl	50	Benzyl chloride	32	44	38
4	Di-α-naphthylcadmium	α-Naphthyl	0.6	α,α'-Binaphthyl	–	α-Chloronaphthalene	57.5	39	40
5	Di-*p*-anisylcadmium	*p*-Anisyl	0.6	*p,p'*-Dianisyl	–	*p*-Chloroanisole	62	49	41

a Isolated yield.

b Formed by hydrolysis of unreacted methanesulfonyl chloride during steam distillation.

TABLE II

Reaction Products of Diarylcadmium with Ethanesulfonyl Chloride

		Sulfone [$ArSO_2C_2H_5$]							
Run	Cadmium reagent	Ar	Yield[a], %	Biaryl	Yield[a], %	Haloarene	Yield[a], %	Ethanesulfinic, acid, %	Ethanesulfonic acid[b], %
1	Diphenylcadmium	Phenyl	–	Biphenyl	26.5	Chlorobenzene	44	41	33.5
2	Di-*p*-tolylcadmium	*p*-Tolyl	–	*p,p'*-Bitolyl	24	*p*-Chlorobenzene	47	41	42
3	Dibenzylcadmium	Benzyl	–	Bibenzyl	48	Benzyl chloride	34	39.5	36.5
2	Di-α-naphthylcadmium	α-Naphthyl	–	α,α'-Binaphthyl	–	α-Chloronaphthalene	50	43	30

a Isolated yield.

b Formed by hydrolysis of unreacted ethanesulfonyl chloride during steam distillation.

In order to differentiate between these two possibilities we have prepared solutions of diphenylcadmium and di-*p*-tolylcadmium. These two solutions were mixed together and the mixture was allowed to react with methanesulfonyl chloride under the usual conditions. Examination of the products of this reaction revealed the presence of biphenyl, *p,p'*-bitolyl and 4-methylbiphenyl, this result excluded the first possibility and supports that shown in eq 4.

Experimental Section

General Procedure

The cadmium reagents were prepared from bromoarenes (0.055 moles) according to the published procedure.[3] To solution of these reagents in benzene or ether, there was added in one portion a solution of 0.0435 mole of methanesulfonyl chloride (or ethanesulfonyl 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-cooled sulfuric (or hydrochloric) acid. The organic layer was extracted twice with ether.

The combined organic solution was extracted twice with 20-ml portions of a cold 5% sodium hydroxide solution.

The alkaline extracts were added to the original aqueous solution and the combined solutions were neutralized with hydrochloric acid and then continuously extracted with ether for 24 hrs. The sulfinic acid† was converted to the corresponding benzyl sulfone by the published procedure.[4]

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

From the produced benzyl sulfone the yield of sulfinic acid was calculated assuming the reaction was 80% complete. The amount of sulfonic acids was calculated by difference.

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.

Action of Methanesulfonyl Chloride on Diphenylcadmium

Distillation of the steam distillable products gave 0.8 g (18.9%) benzene, 2.8 g (45%) chlorobenzene and 1.0 g (26.5%) biphenyl. Recrystallization of the residue from steam distillation gave 0.4 g (5.7%) of methyl phenyl sulfone, mp 88°. All these products were identical in all respects with authentic samples.

Action of Ethanesulfonyl Chloride on Diphenylcadmium

In this run, benzene (0.8 g, 19%), chlorobenzene (2.7 g, 43%) and biphenyl (1.0, 26.5%) were separated from the steam distillable fraction. No ethyl phenyl sulfone was obtained.

Action of Methanesulfonyl Chloride on Di-*p*-tolylcadmium

p-Ditolylcadmium (prepared from 9.4 g *p*-chlorotoluene) reacted with methanesulfonyl chloride according to the general procedure described above. Fractional distillation of the steam distillable products gave 0.9 g (17.6%) of toluene, 2.9 g (42%) of *p*-chlorotoluene, 1.15 g (23.5%) of *p,p'*-bitolyl. Methyl *p*-tolyl sulfone (0.4 g, 5.5%) was obtained from the residue left after steam distillation; M^+, m/e 170.

Action of Ethanesulfonyl Chloride on Di-*p*-tolylcadmium

The steam distillable products from this reaction were: toluene (0.9 g, 17.6%), *p*-chlorotoluene (3.2g, 47%) and *p,p'*-bitolyl (1.2 g, 24%). No residue was obtained after steam distillation.

Action of Methanesulfonyl Chloride on Dibenzylcadmium

The steam distillable products from this reaction were: toluene (1 g, 19.5%), benzyl chloride (2 g, 32%) and bibenzyl (2.4 g, 50%). The residue remaining after steam distillation was recrystallized to give 0.06 g (0.9%) benzyl methyl sulfone, mp 128°; lit.[5] mp 127°.

Action of Ethanesulfonyl Chloride on Dibenzylcadmium

The following compounds were separated from the steam distillable products of this reaction: Toluene (1 g, 19.6%), benzyl chloride (2.3 g, 34%) and bibenzyl (2.4 g, 48%). No benzyl sulfone was obtained in this run.

Action of Methanesulfonyl Chloride on Di-α-naphthylcadmium

Di-α-naphthylcadmium (prepared from 11.4 g, 0.055 mol, α-bromonaphthalene) was treated with methanesulfonyl chloride according to our general procedure. After separation of methanesulfinic and sulfonic acids, the following compounds were separated from the steam distillable portion of the products: naphthalene (1.0 g, 19%) and α-chloronaphthalene (5.1 g, 57.5%).

The non-steam distillable materials (0.12 g) were separated by chromatography on a column packed with 20 g neutral alumina. The first fraction was eluted with petr. ether (40–60) and the presence of α,α'-binaphthyl in this fraction was confirmed by tlc using authentic sample. A 0.05 g of methyl α-naphthyl sulfone was eluted with petr. ether (60–80) and benzene (1 : 9). Recrystallized from water, mp 102°, lit.[6] mp 110.5–102°.

Action of Ethanesulfonyl Chloride on Di-α-naphthylcadmium

The products of this reaction were separated by a similar manner as described in the preceding reaction. Only, the following compounds were obtained: naphthalene (1.15 g, 22%) and α-chloronaphthalene (4.4 g, 50%).

Action of Methanesulfonyl Chloride with Di-*p*-anisylcadmium

This reaction was carried out as usual to give finally anisole (1.3 g, 22%) and *p*-chloroanisole (4.8 g, 62%) as steam distillable products. The non-distillable products were separated by chromatography on neutral alumina to give *p,p'*-bianisyl (as proved by tlc) and 0.05 g (0.6%) of *p*-anisyl methyl sulfone; m.p. 124–125°, lit.[7] mp. 121°.

References

1. A. I. Khodair, A. Osman, and A. A. Abdel-Wahab, *Int. J. Sulfur Chem.*, 8, No. 4 (1974).
2. A. I. Khodair, A. Swelim, and A. A. Abdel-Wahab, See previous paper.
3. J. Cason and H. Rapoport, "Laboratory Text in Organic Chemistry", 2nd Edition, 465 (1962).
4. W. Bardley, *J. Chem. Soc.*, 458 (1938).
5. "Dictionary of Organic Compounds", Vol. III (1943).
6. I. H. Bohme, *Chem. Ber.*, **69B**, 1610–1615 (1936).
7. M. E. Hepenstall and S. Smiles, *J. Chem. Soc.*, 899 (1938).