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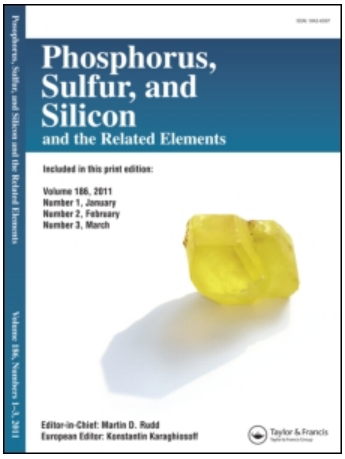

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REACTIONS OF ORGANOMETALLIC REAGENTS WITH SULFONYL HALIDES. V. ACTION OF p-TOLUENESULFONYL IODIDE ON SELECTED DIARYLCADMIUM COMPOUNDS

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REACTIONS OF ORGANOMETALLIC REAGENTS WITH SULFONYL HALIDES. V. ACTION OF *p*-TOLUENESULFONYL IODIDE ON SELECTED DIARYLCADMIUM COMPOUNDS

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Interaction of *p*-toluenesulfonyl iodide (**1**) with diarylcadmium compounds (**2–6**) gave in all cases *p*-tolyl *p*-toluenethiosulfonate and *p*-toluenesulfonic acid in addition to the corresponding iodoarenes, diaryls and other hydrocarbons.

Plausible mechanisms including the intermediacy of aryl and *p*-toluenesulfonyl radicals were suggested for explaining our findings.

The results show that the behaviour of arylsulfonyl iodides towards diarylcadmium compounds is much different from that of the corresponding fluorides or chlorides.

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INTRODUCTION

In continuation to our previous studies[1–4] on the behaviour of sulfonyl halides towards organometallic reagents, the present investigation deals with the action of arenesulfonyl iodides with diarylcadmium compounds. Cadmium reagents were found to be unreactive towards sulfonyl fluorides whereas Grignard reagents afforded sulfones in good yield upon interaction with the same sulfonyl fluorides.[4] On the other hand, organocadmium reagents react smoothly with sulfonyl chlorides[1–3] giving sulfones in moderate to poor yield in addition to other products such as chloroarenes, biaryls, sulfinic acids and sulfonic acids. A suitable mechanism was suggested for the different reaction pathways.

RESULTS AND DISCUSSION

The reactivity of sulfonyl iodide compared with sulfonyl fluorides and sulfonyl chlorides was studied via interaction of *p*-toluenesulfonyl iodide (**1**) with diphenylcadmium (**2**), di(*p*-tolyl) cadmium (**3**), di(*p*-anisyl) cadmium (**4**), di(α-naphthyl) cadmium (**5**) and dibenzylcadmium (**6**). Separation and analysis of the reaction products gave *p*-tolyl *p*-toluenethiosulfonate (**7**, 67.7–77.9%) and *p*-toluenesulfonic

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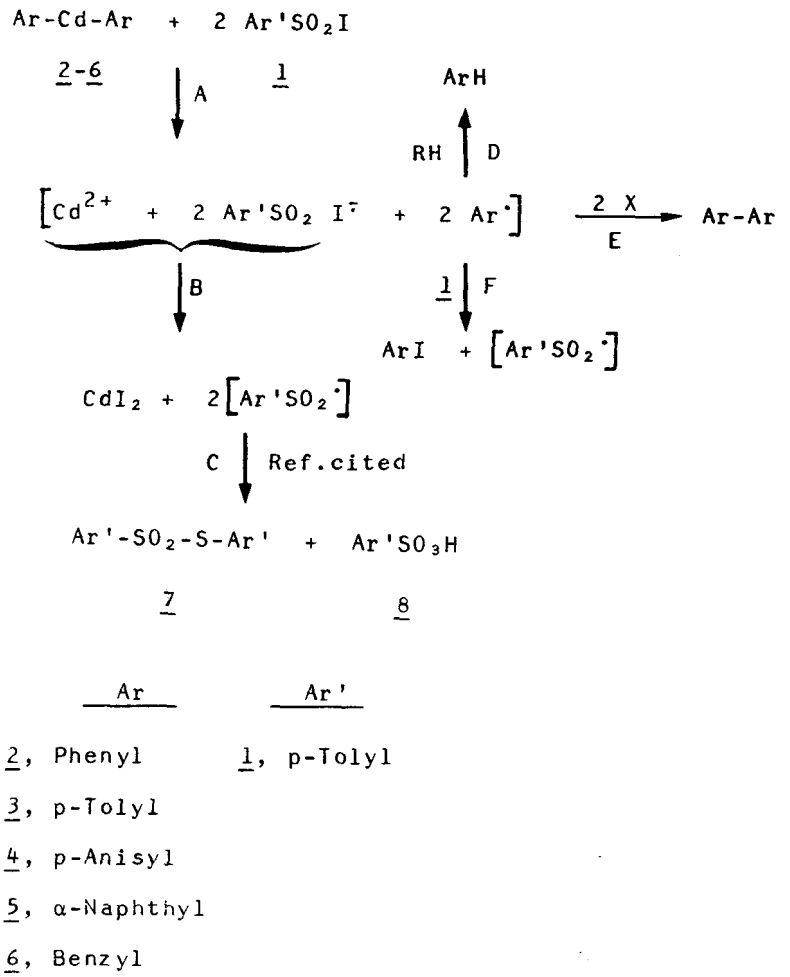
acid (**8**, 13%) in all cases whatever a cadmium reagent was used. Also, the corresponding iodoarenes, biaryls and hydrocarbons were isolated.

The isolated products indicate a radical reaction including the formation of *p*-toluenesulfonyl radicals[5-10] and aryl radicals (Scheme 1). However in the present case, generation of *p*-toluenesulfonyl radicals is expected to be through electron transfer with the formation of the radical anion (p-$CH_3C_6H_4S\dot{O}_2I^{\ominus}$), cadmium cation ($Cd^{2\oplus}$) and aryl radical (Ar) (Scheme 1-A). The aromatic hydrocarbons, may be generated from aryl radicals via hydrogen abstraction (Scheme 1-D) and/or from hydrolysis of the diarylcadmium compound or by dimerization of aryl radicals (Scheme 1-E) to diaryl. Iodine abstraction from iodoarenes according to Schemes 1-B and 1-F results in formation of sulfonyl radicals. The produced *p*-toluenesulfonyl radicals prefer to couple in a head-to-tail reaction[5] forming $CH_3C_6H_4S(O_2)—O—S(O)—C_6H_4CH_3$ **A** rather than α-disulfone[6,7] $CH_3C_6H_4—S(O_2)—$



Ar	Ar'
2, Phenyl	1, p-Tolyl
3, p-Tolyl	
4, p-Anisyl	
5, α-Naphthyl	
6, Benzyl	

SCHEME 1

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$S(O_2)$—$C_6H_4CH_3$. Compound A, in turn, generates sulfonate-($CH_3C_6H_4SO_2O$) and sulfinyl-($CH_3C_6H_4SO$) radicals. Dimerization of the sulfinyl radical should give the intermediate $CH_3C_6H_4$—S(O)—O—S—$C_6H_4CH_3$ B, which undergoes intramolecular rearrangement to *p*-tolyl *p*-toluenethiosulfonate (**7**). *p*-Toluenesulfonic acid (**8**) may be formed from *p*-toluenesulfonate radical via hydrogen abstraction and/or through hydrolysis of its anhydride.[5,7]

The suggested mechanism is supported by the observation that refluxing of *p*-toluenesulfonyl iodide alone or in the presence of $MgCl_2$ and/or $CdCl_2$ under the same reaction conditions gave only unchanged *p*-toluenesulfonyl iodide.

It is noteworthy to mention that Wedekind and Schenk[11] observed the formation of thiosulfonate ester ($ArSO_2SAr$) in addition to, as reported by Hepworth and Clapham,[12] sulfones ($ArSO_2Ar'$), sulfoxides (ArSOAr') and sulfides (ArSAr'), during the reaction of sulfonyl chlorides ($ArSO_2Cl$) with some organomagnesium halides (Ar'MgX). Also, Gilman and Fothergill[13] reported that the reaction of *p*-toluenesulfonyl iodide with phenylmagnesium bromide gave iodobenzene (56%) and *p*-toluenesulfinic acid (21%).

It may be suggested from the results of this study that the type of metal of the organometallic compound as well as the type of the halogen atom in the sulfonyl halide have a pronounced effect on the rate as well as on the path-way of the reaction of organometallic compounds with sulfonyl halides.

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EXPERIMENTAL

Instrumentals. GLC analysis were carried out using an Aerograph gas chromatograph (HI-Fi) model 600 D equipped with a flame ionization detector and an integrating recorder (Servo/Riter II, Texas Instruments, Inc.). Product were identified by direct comparison with authentic samples using 8′ × $\frac{1}{8}$″ column packed with SE 30 over chromosorb. All fractional distillations were carried out on a 2 ft. Podbielniak[14] column with partial head, packed with spiral Nichrome wire and heated by an externally heated jacket. All melting points are uncorrected and were determined using Kofler melting point apparatus.

Starting materials and authentic samples: *p*-Toluenesulfonyl iodide (**1**) was prepared according to the reported procedure[15] in 90% yield.

Iodoarenes: were prepared as described[16] from the corresponding diazonium salt and potassium iodide. *p*-Iodotoluene (mp 35°C, lit.[16] mp 36–7°C) was formed in 86%, *p*-iodoanisole (mp 50°C, lit[16] mp 51°C) was obtained in 80% and α-iodonaphthalene was collected at 135°C/2 mmHg, picrate mp 127°C, lit.[17] 127°C. Iodobenzene was purchased from Fluka company and was chromatographically pure. Authentic samples of diphenl, di-*p*-tolyl, di-*p*-anisyl and dibenzyl were also available.[1-3]

General Procedure. In a typical run, diarylcadmium reagent was prepared from haloarene (0.027 mole), 0.66 g (0.027 g · atom) magnesium turnings and 2.8 g (0.019 mole) of cadmium chloride according to the published procedure.[3] To the diarylcadmium reagent, a solution of 6.0 g (0.027 mole) *p*-toluenesulfonyl iodide in 50 ml ether was added rapidly and the reaction mixture was refluxed for two hours, cooled and decomposed with ice–HCl mixture. The organic layer was separated and the aqueous layer was extracted several times with ether. After evaporation of ether, the residue was subjected to steam distillation. The aqueous distillate was extracted with ether, the extracts were dried over magnesium sulfate, filtered and the solvent was evaporated on a water bath. The residue was then distilled under vacuum and the obtained iodoarenes, hydrocarbons and diaryls were weighed up and checked with GLC analysis, mp, mmp or bp using authentic samples.

The steam distillation flask was cooled whereby a solid material crystallized out. Separation and recrystallization from ethanol gave *p*-tolyl *p*-toluenethiosulfonate (67.7—77.9% yield), mp 76°C, lit.[18] mp 76°C. Anal. Cald. for $C_{14}H_{14}S_2O_2$: C, 60.43%; H = 5.00%; S, 23.02%; Found: C, 60.0%; H, 5.0; S, 23.0%.

The aqueous solution was evaporated to dryness and the residue was p-toluenesulfonic acid, which was converted to *p*-toluenesulfonamide for identification, mp and mmp 137°C, lit.[19] mp 137.5°C. Results are found in Table I.

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TABLE I

Reaction of *p*-toluenesulfonyl iodide with diarylcadmium compounds

Exp.	Cadmium Reagent	p-Tolyl p-toluenethio-sulfonate (%)	Iodoarenes		Diaryls		$CH_3C_6H_4SO_3H$ %
			Name	%	Name	%	
1	Diphenylcadmium	74.4	Iodobenzene	26.0	Diphenyl	30	13
2	Di(*p*-tolyl)cadmium	74.7	*p*-Iodotoluene	43.3	*p*,*p'*-Ditolyl	20	13
3	Di(*p*-anisyl)cadmium	74.4	*p*-Iodoanisole	46.5	*pp'*-Dianisyl	10	13
4	Di(α-naphthyl)cadmium*	67.7	α-Iodonaphthalene	30.0	—	—	13
5	Dibenzylcadmium	77.9	—	—	Dibenzyl	75	13

*Naphthalene was isolated in 17% from the steam distillable fraction, the other hydrocarbons (benzene, toluene, anisole) were also formed and detected by GLC analysis of the original reaction product.

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