Desulfonylation of Aromatic Sulfonyl Halides Catalyzed by Some Platinum–Metal Complexes

JOCHANAN BLUM AND GAD SCHARF

Department of Organic Chemistry, Hebrew University, Jerusalem, Israel

Received October 14, 1969

The catalytic desulfonylation of arenesulfonyl chlorides and bromides by $RhCl(PPh_3)_3$ (**1**), $RhCl(CO)(PPh_3)_2$ (**2**), $IrCl(CO)(PPh_3)_2$ (**3**), $RuCl_2(PPh_3)_3$ (**4**), $Pt(PPh_3)_4$ (**5**), and $PdCl_2$ (**6**) has been investigated. The desulfonylation is assumed to proceed mainly by a metal ion promoted mechanism and to a smaller extent *via* homolytic decomposition. A theory of the former mechanism has been suggested which accounts for the observations made in this study. The essential features of the theory are the steps $ArSO_2IrCl_2(CO)(PPh_3)_2$ (**7**) → $ArSO_2IrCl_2(CO)(PPh_3)$ (**8**) → $ArIrCl_2(CO)(SO_2)(PPh_3)$ (**9**) and loss of sulfur dioxide from the last compound. Several new rhodium and iridium complexes are described.

In a preliminary communication[1] we reported that chlorotris(triphenylphosphine)rhodium(I), $RhCl(PPh_3)_3$ (**1**), catalyzes the conversion of arenesulfonyl chlorides into the corresponding aryl chlorides.

We have studied now the applicability of this homogeneous catalytic desulfonylation to a variety of aromatic sulfonyl halides, using various complexes of the platinum group (Tables I and II) as catalysts. In addition, we investigated the nature of some catalyst–substrate complexes that are assumed to be intermediates in the process.

TABLE I

DESULFONYLATION OF BENZENE- AND *p*-CHLOROBENZENESULFONYL CHLORIDE BY VARIOUS CATALYSTS

Sulfonyl chloride	Wt, g	Catalyst	Method[a]	Maximum yield of pure aryl halide, %
Benzene-	17.6	$RhCl(PPh_3)_3$ (**1**)	A	79
Benzene-	15	$RhCl(PPh_3)_3$ (**1**)	B	88
Benzene-	5	$RhCl(PPh_3)_3$ (**1**)	C	75
Benzene-	10.7	*trans*-$RhCl(CO)(PPh_3)_2$ (**2**)	A	32
Benzene	5	*trans*-$RhCl(CO)(PPh_3)_2$ (**2**)	C	59
Benzene-	15	*trans*-$IrCl(CO)(PPh_3)_2$ (**3**)	A	36
Benzene-	17.2	*trans*-$IrCl(CO)(PPh_3)_2$ (**3**)	C	74
Benzene-	10	$RuCl_2(PPh_3)_3$ (**4**)	B	37
Benzene-	5.5	$RuCl_2(PPh_3)_3$ (**4**)	C	50
Benzene-	10	$Pt(PPh_3)_4$ (**5**)	B	20
Benzene-	10.6	$Pt(PPh_3)_4$ (**5**)	C	50
Benzene-	10.4	$PdCl_2$ (**6**)	A	27
Benzene-	10	$PdCl_2$ (**6**)	C	65
p-Chlorobenzene-	10	$RhCl(PPh_3)_3$ (**1**)	A	85
p-Chlorobenzene-	15	$RhCl(PPh_3)_3$ (**1**)	B	67
p-Chlorobenzene-	5	$RhCl(PPh_3)_3$ (**1**)	C	97
p-Chlorobenzene-	10	*trans*-$RhCl(CO)(PPh_3)_2$ (**2**)	A	35
p-Chlorobenzene-	10	*trans*-$RhCl(CO)(PPh_3)_2$ (**2**)	C	71
p-Chlorobenzene-	10	*trans*-$IrCl(CO)(PPh_3)_2$ (**3**)	A	37
p-Chlorobenzene-	14.2	*trans*-$IrCl(CO)(PPh_3)_2$ (**3**)	C	74
p-Chlorobenzene-	15	$RuCl_2(PPh_3)_3$ (**4**)	B	55
p-Chlorobenzene-	5	$RuCl_2(PPh_3)_3$ (**4**)	C	60
p-Chlorobenzene-	15	$Pt(PPh_3)_4$ (**5**)	B	46
p-Chlorobenzene-	5	$Pt(PPh_3)_4$ (**5**)	C	55

[a] See Experimental Section: A, simple distillation; B, under nitrogen; C, in hexachlorobenzene.

In Table I, the results obtained with benzene- and *p*-chlorobenzenesulfonyl chloride and several catalysts are summarized. The figures indicate that the rhodium complex **1** is the best of these catalysts: the rate of desulfonylation is high in comparison with that of the competing homolytic noncatalytic decomposition of the sulfonyl chlorides.[2] When chlorocarbonylbis(triphenylphosphine)rhodium(I), $RhCl(CO)(PPh_3)_2$ (**2**), chlorocarbonylbis(triphenylphosphine)iridium(I), $IrCl(CO)(PPh_3)_2$ (**3**), dichlorotris(triphenylphosphine)ruthenium(II), $RuCl_2(PPh_3)_3$ (**4**), tetrakis(triphenylphosphine) platinum(0), $Pt(PPh_3)_4$ (**5**), and palladium dichloride (**6**) were used, the undesired side reactions became more and more predominant.

The homolytic decomposition could generally be reduced by dilution of the reaction mixture with hexachlorobenzene.

In Table II some representative experiments using **1** as catalyst are summarized. The results obtained with simple derivatives of benzenesulfonyl chloride and bromide are comparable with those obtained by heterogeneous catalyses.[3]

In these cases the noncatalyzed thermal decomposition is slow and the desulfonylation is believed to

---

(1) J. Blum, *Tetrahedron Lett.*, 3041 (1966).

(2) *Cf.* P. J. Bain, E. J. Blackman, W. Cummings, S. A. Hughes, E. R. Lynch, E. B. McCall, and R. J. Roberts, *Proc. Chem. Soc.*, 186 (1962).

(3) Monsanto Chemicals Ltd., British Patents 948,281 and 976,438; *Chem. Abstr.*, **62**, 7681e (1965); French Patent 1,340,833; *Chem. Abstr.*, **60**, 5393e (1964).

TABLE II

DESULFONYLATION OF ARENESULFONYL HALIDES BY 1

Expt	Sulfonyl halide (g)	Method[a]	Reaction time, min	Aryl halides formed (best yield obtained, %)
1	$\mathrm{C_6H_5SO_2Br}$ (4.7)	C	5	$\mathrm{C_6H_5Br}$ (60)
2	p-$\mathrm{CH_3C_6H_4SO_2F}$ (15)	A, D	180	No aryl fluoride
3	p-$\mathrm{CH_3C_6H_4SO_2Cl}$ (15)	A	30	p-$\mathrm{ClC_6H_4CH_3}$ (72)
4	p-$\mathrm{CH_3C_6H_4SO_2Br}$ (7)	A	5	No aryl bromide
5	p-$\mathrm{CH_3C_6H_4SO_2Br}$ (27)	C	5	p-$\mathrm{BrC_6H_4CH_3}$ (45) p-$\mathrm{ClC_6H_4CH_3}$ (traces)
6	2,4,6-$\mathrm{(CH_3)_3C_6H_2SO_2Cl}$ (3)	C	4	2-Chloromesitylene (27)
7	p-$\mathrm{CH_3OC_6H_4SO_2Cl}$ (15)	A	40	p-$\mathrm{ClC_6H_4OCH_3}$ (40)
8	p-$\mathrm{FC_6H_4SO_2Cl}$ (15)	A	240	p-$\mathrm{ClC_6H_4F}$ (61)
9	p-$\mathrm{FC_6H_4SO_2Br}$ (3.9)	C	15	p-$\mathrm{BrC_6H_4F}$ (50), p-$\mathrm{ClC_6H_4F}$ (traces)
10	p-$\mathrm{ClC_6H_4SO_2F}$ (4)	D	330	p-$\mathrm{ClC_6H_4F}$ (traces)
11	2,5-$\mathrm{Cl_2C_6H_3SO_2Cl}$ (10)	A	25	1,2,5-$\mathrm{C_6H_3Cl_3}$ (65)
12	p-$\mathrm{BrC_6H_5SO_2Cl}$ (15)	A, B	20	p-$\mathrm{C_6H_4Cl_2}$ (18) p-$\mathrm{BrC_6H_4Cl}$ (34) p-$\mathrm{C_6H_4Br_2}$ (17)
13	p-$\mathrm{BrC_6H_4SO_2Cl}$ (3)[b]	C	20	p-$\mathrm{C_6H_4Cl_2}$ (8) p-$\mathrm{BrC_6H_4Cl}$ (14) p-$\mathrm{C_6H_4Br_2}$ (3)
14	p-$\mathrm{BrC_6H_4SO_2Cl}$ (3)[c]	D	20	p-$\mathrm{C_6H_4Cl_2}$ (6.5) p-$\mathrm{BrC_6H_4Cl}$ (9) p-$\mathrm{C_6H_4Br_2}$ (2.8)
15	p-$\mathrm{BrC_6H_4SO_2Br}$ (3)[d]	A	7	p-$\mathrm{C_6H_4Br_2}$ (60)
16	p-$\mathrm{BrC_6H_4SO_2Br}$ (3)[e]	C	20	p-$\mathrm{C_6H_4Cl_2}$ (12) p-$\mathrm{BrC_6H_4Cl}$ (32) p-$\mathrm{C_6H_4Br_2}$ (29)
17	p-$\mathrm{IC_6H_4SO_2Cl}$ (10)[f]	C	15	p-$\mathrm{C_6H_4Cl_2}$ (6), p-$\mathrm{ClC_6H_4I}$ (29) p-$\mathrm{C_6H_4I_2}$ (16)
18	o-$\mathrm{O_2NC_6H_4SO_2Cl}$ (5)	D	90	o-$\mathrm{ClC_6H_4NO_2}$ (3)
19	m-$\mathrm{C_6H_4(SO_2Cl)_2}$ (10)	A	15	m-$\mathrm{C_6H_4Cl_2}$ (62)
20	1,3,5-$\mathrm{C_6H_3(SO_2Cl)_3}$ (3)	A	10	1,3,5-$\mathrm{C_6H_3Cl_3}$ (33)
21	α-$\mathrm{C_{10}H_7SO_2Cl}$ (5)	A	30	α-$\mathrm{C_{10}H_7Cl}$ (17)
22	β-$\mathrm{C_{10}H_7SO_2F}$ (10)	D	180	β-$\mathrm{C_{10}H_7F}$ (10)
23	β-$\mathrm{C_{10}H_7SO_2Cl}$ (6)	A[g]	20	β-$\mathrm{C_{10}H_7Cl}$ (69)
24	β-$\mathrm{C_{10}H_7SO_2Cl}$ (5)	D	30	β-$\mathrm{C_{10}H_7Cl}$ (53)
25	4-$\mathrm{FC_{10}H_6}$-1-$\mathrm{SO_2Cl}$ (5)	A[g]	20	1-$\mathrm{ClC_{10}H_6}$-4-F (70)
26	8-$\mathrm{ClC_{10}H_6}$-1-$\mathrm{SO_2Cl}$ (4)	D	20	1,8-$\mathrm{C_{10}H_6Cl_2}$ (27)
27	2-Fluorenesulfonyl chloride (0.9)	D[h]	10	2-Chlorofluorene (6)
28	1-Anthracenesulfonyl chloride (2.9)	D	10	1-Chloroanthracene (9)
29	6-Chrysenesulfonyl fluoride (1.3)	D	270	6-Fluorochrysene (traces)
30	6-Chrysenesulfonyl chloride (2)[i]	D	15	6-Chlorochrysene (50)

[a] See Experimental Section: A, B, and C as in Table I; D, in hexachlorobenzene but under reflux. [b] When **3** was used as catalyst, the products and yields were as follows: p-$\mathrm{C_6H_4Cl_2}$ (3); p-$\mathrm{BrC_6H_4Cl}$ (18); p-$\mathrm{C_6H_4Br_2}$ (6). [c] In the absence of catalyst: p-$\mathrm{C_6H_4Cl_2}$ (12); p-$\mathrm{BrC_6H_4Cl}$ (11); p-$\mathrm{C_6H_4Br_2}$ (2). [d] In the absence of catalyst, 40%. [e] In the absence of catalyst: p-$\mathrm{C_6H_4Cl_2}$ (1); p-$\mathrm{BrC_6H_4Cl}$ (16); p-$\mathrm{C_6H_4Br_2}$ (30). [f] Similar results were obtained without catalyst. [g] The reaction was carried out under reduced pressure, which permits the reaction mixture to boil between 255 and 275°. [h] Under nitrogen. [i] In the absence of catalyst 6.5% 6-chlorochrysene was formed.

proceed mainly by metal-ion promotion. The sulfonyl halides of lower stability, *i.e.*, those that split homolytically at, or below, the threshold temperature for *catalytic* desulfonylation,[1] give lower yields of the expected aryl halides.

The sulfonyl bromides belong to the latter category and do not yield aryl bromides by simple distillation over the catalyst (method A), but dilution of the reaction mixtures with a tenfold excess of hexachlorobenzene (method C) permits the formation of the aryl bromides (expt 1, 5, and 9).

That the desulfonylation of the sulfonyl bromides proceeds, at least to a small extent, by a free-radical mechanism is shown by the fact that both p-toluene- and p-fluorobenzenesulfonyl bromide react with the perchlorinated solvent and form small quantities of p-chlorotoluene and p-dichlorobenzene, respectively. Moreover, when p-bromobenzenesulfonyl bromide—whose tendency to undergo homolytic decomposition is also shown below—is heated with **1** in perfluorobiphenyl or in Perfluoroalkane-225 (Peninsular ChemResearch Inc.), fluorobenzene and p-bromofluorobenzene are formed along with the expected p-dibromobenzene.

While fluoro- and chlorobenzenesulfonyl chloride do not decompose thermally in the absence of the catalyst to a considerable extent, the bromo and especially the

TABLE III

PHYSICAL DATA AND ANALYSES FOR IRIDIUM AND RHODIUM COMPOUNDS

Compd	Approx mp, °C dec	C, %		H, %		Cl, %		P, %		S, %		$\tilde{\nu}_{CO}$[a] cm^{-1}
		Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	
$C_{44}H_{37}Cl_2IrO_3P_2S$ (7, Ar = p-$CH_3C_6H_4$)[b]	290	53.9	53.4	3.7	3.8			6.9	6.4	3.7	3.3	2080
$C_{26}H_{22}Cl_2IrO_3PS$ (8 or 9, Ar = p-$CH_3C_6H_4$)	260	43.9	44.1	3.5	3.1	10.0	10.0	4.4	4.4	4.2	4.5	2098
$C_{43}H_{34}Cl_3IrO_3P_2S$ (7, Ar = p-ClC_6H_4)[b]	205	52.1	52.2	4.4	3.4	11.4	10.8			3.7	3.2	2080
$C_{25}H_{19}Cl_3IrO_3PS$ (8 or 9, Ar = p-ClC_6H_4)	250	41.3	41.2	2.8	2.6	14.4	14.6	4.2	4.3	4.0	4.4	2090
$C_{43}H_{34}Cl_3IrOP_2$ (11, Ar = p-ClC_6H_4)	285	55.4	55.7	3.6	3.7	12.3	12.5	6.5	6.7	0.0	0.0	2020
$C_{25}H_{19}Cl_2IrO_3PS$ (12 or 13, Ar = p-ClC_6H_4)[c]	200	43.8	43.3	2.8	2.7			4.6	4.5	4.5	4.6	2105
$C_{50}H_{38}Cl_6Ir_2O_4P_2S$ (14)[c]	282	43.4	43.1	2.8	2.7	15.0	15.4			2.7	2.3	2040 br
$C_{47}H_{37}Cl_2IrO_3P_2S$ (7, Ar = β-$C_{10}H_7$)	210	55.9	56.0	3.7	3.7	7.5	7.1	6.5	6.2			2080
$C_{29}H_{22}Cl_2IrOP$ (10, Ar = β-$C_{10}H_7$)	>300	51.6	51.1	3.3	3.2	10.0	10.4	4.4	4.7	0.0	0.0	2070
$C_{29}H_{22}ClIrO_3PS$ (12 or 13, Ar = β-$C_{10}H_7$)[c]	>300	49.0	49.0	3.3	3.1	5.2	5.0	4.3	4.3	4.4	4.4	2050
$C_{35}H_{28}Cl_2IrO_3PS$ (15)		51.1	51.2	3.3	3.4			3.8	3.8	4.1	3.9	2095
$C_{47}H_{37}ClFIrO_3P_2S$ (16)	204	56.8	56.9	3.9	3.7			6.1	6.3	3.0	3.2	2080
$C_{25}H_{22}Cl_2O_2PRhS$ (17, Ar = p-$CH_3C_6H_4$)	283	51.0	50.8	3.7	3.7	12.4	12.0	5.2	5.2			
$C_{28}H_{22}Cl_2O_2PRhS$ (17, Ar = β-$C_{10}H_7$)	218	53.5	53.5	4.2	3.5	11.6	11.3	4.6	4.9			

[a] In Nujol. [b] *Cf.* ref 6. [c] Paramagnetic.

iodo derivatives undergo extensive homolytic fragmentation at their boiling points. Thus, *e.g.*, *p*-bromobenzenesulfonyl chloride is converted after 20 min at reflux into 0.4% *p*-dichlorobenzene, 12% *p*-bromochlorobenzene, and 8.5% *p*-dibromobenzene, and in the presence of hexachlorobenzene to 12, 11, and 2% of these dihalides, respectively. Addition of catalytic amounts of either **1** or **3** lowers the degree of interaction with the solvent (expt 13 and 14). The formation of *p*-dichloro- and *p*-dibromobenzene does not result from disproportionation of *p*-bromochlorobenzene, as the latter is unaffected by **1**. Similar radical-type disproportionation and interaction with the solvent were observed with *p*-bromobenzenesulfonyl bromide (expt 15 and 16).

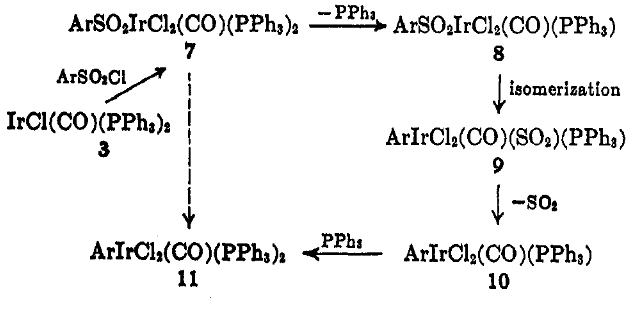
Arenedi- and -trisulfonyl chlorides are desulfonylated at 240–250° in fair yields (expt 19 and 20), while higher temperatures lead to extensive polymerization.

Naphthalenesulfonyl chlorides could be converted catalytically into the corresponding chloronaphthalenes when the reaction temperature was carefully controlled (below 275°). The polycyclic sulfonyl chlorides are polymerized by **1**, when heated in the absence of hexachlorobenzene, while in the presence of this solvent some quantities of the polycyclic aryl chlorides are formed. 6-Chrysenesulfonyl chloride is exceptional in that it yields up to 50% 6-chlorochrysene together with varying amounts of chrysene (up to 36%). Thermal decomposition of 6-chrysenesulfonyl chloride (without **1**) gave up to 6.5% aryl halide.

The desulfonylation of sulfonyl fluorides, which has been reported to be successful in some heterogeneous catalyses,[3] generally failed under our experimental conditions: benzene- and *p*-toluenesulfonyl fluoride did not give any fluorides on refluxing with **1** for many hours. *p*-Chlorobenzene- and 6-chrysenesulfonyl fluoride yielded up to 2% the expected fluoride, probably as a result of homolytic fission, and 2-naphthalenesulfonyl fluoride could be converted into 2-fluoronaphthalene in 10% yield.

Following our experience in the field of catalytic decarbonylation,[4] we attempted to study the mechanism of the catalytic desulfonylation by treating several sulfonyl halides with the catalysts at various temperatures between 78 and 160°. The rhodium catalyst **1** gave only a small number of defined addition complexes, one, $Rh_2Cl_2(SO_2)(PPh_3)_2$,[1] being an adduct of sulfur dioxide and dissociated **1** [*cf.* the formation of $RhCl(SO_2)(PPh_3)_2$ directly from **1** and liquid sulfur dioxide].[5] The Vaska complex $IrCl(CO)(PPh_3)_2$ (**3**) that has been shown above to catalyze the desulfonylation reaction (though less effectively than **1**), however, reacts smoothly with several sulfonyl halides to give the 12 complexes listed in Table III.

In a previous study, Collman and Roper[6] reported that a number of sulfonyl chlorides react with **3** to give iridium sulfinate complexes of type **7**, two of which (Ar = C_6H_5 and Ar = p-$CH_3C_6H_4$) could be transformed into **11** by heating at 110°. It could thus be assumed that the conversion of arenesulfonyl halides into aryl halides is based on this simple reaction **7** → **11**. However, while the analogous decarbonylation reaction of, *e.g.*, $CH_3COIrBr_2(CO)(PPhEt_2)_2$ to $CH_3IrBr_2(CO)(PPhEt_2)_2$,[7] and the desulfonylation of some platinum(0) sulfinate complexes[8] could be rationalized as one- and two-step processes, respectively, the direct



$ArSO_2IrCl(CO)(PPh_3)$ **12**

$ArIrCl(CO)(SO_2)(PPh_3)$ **13**

$[p\text{-}ClC_6H_4IrCl_2(CO)(PPh_3)]_2SO_2$ **14**

$\beta\text{-}C_{10}H_7SO_2IrCl_2(CO)(PPh_3)\cdot C_6H_6$ **15**

$\beta\text{-}C_{10}H_7SO_2IrClF(CO)(PPh_3)_2$ **16**

$ArSO_2RhCl_2(PPh_3)$ **17**

---

(4) J. Blum, E. Oppenheimer, and E. D. Bergmann, *J. Amer. Chem. Soc.*, **89**, 2338 (1967).

(5) J. J. Levison and S. D. Robinson, *Inorg. Nucl. Chem. Lett.*, **4**, 407 (1968).

(6) J. P. Collman and W. R. Roper, *J. Amer. Chem. Soc.*, **88**, 180 (1966).

(7) J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc., A*, 604 (1967).

(8) C. D. Cook and G. S. Jauhal, *Can. J. Chem.*, **45**, 301 (1967).

desulfonylation of **7** seems improbable (unless a seven-coordinated iridium intermediate were formed), and our experiments provide evidence that the transformation **7** → **11** is a multistep process. Initial loss of PPh_3 yields **8**, which isomerizes to **9** and by loss of SO_2 gives **10**. The latter recombines with PPh_3 to give aryldichlorocarbonylbis(triphenylphosphine)iridium (**11**).

In our experience *p*-toluene-, *p*-chlorobenzene-, and *β*-naphthalenesulfonyl chloride reacted with **3** in aromatic hydrocarbons to give complexes of type **7** only in very poor yields and in an impure state. The main products in these reactions were complexes of type **8** (or **9**). *β*-Naphthalenesulfonyl chloride in benzene gave the benzene solvate **15**. Addition of triphenylphosphine to the reaction mixture led, however, in all cases to reasonable yields of **7**.

The reaction of **3** with equimolar quantities (or with a small excess) of *β*-naphthalenesulfonyl chloride in boiling benzene led to the formation of the desulfonylated complex **10**. *p*-Chlorobenzenesulfonyl chloride gave under these conditions a divalent iridium compound of structure **12** (or **13**), which may arise from **8** (or **9**) by loss of a chlorine atom. The analogous *β*-naphthyliridium(II) compound crystallized from the boiling mixture of equimolar amounts of **3** and *β*-naphthalenesulfonyl chloride in mesitylene.

The analyses of several complexes isolated show an S to Ir ratio of 1:2. The formation of such compounds—one of which is **14**—is easily rationalized by the reaction pathway described above.

It is noteworthy that from the reaction mixture of chloride-free *β*-naphthalenesulfonyl *fluoride*, **3**, and PPh_3 in boiling mesitylene, some dichlorosulfinate, **7** (Ar = β-$C_{10}H_7$), was isolated in addition to the expected fluoro compound **16**. The complexity of the reaction, including the extensive ligand exchange, is evidenced by the fact that upon concentration of the mother liquor from this reaction, we obtained a mixture showing six distinctive M–CO bands in the infrared.

The rhodium analog of **3**, chlorocarbonylbis(triphenylphosphine)rhodium (**2**), gave with the sulfonyl chlorides complex mixtures. Two compounds which could be separated in fairly pure state, *viz.* **17**, Ar = *p*-$CH_3C_6H_4$, and **17**, Ar = β-$C_{10}H_7$, surprisingly, had lost the CO group. The desulfonylation of the probable initial rhodium–sulfinate complex $ArSO_2RhCl_2(CO)(PPh_3)_2$ might thus proceed either after extrusion of one molecule of PPh_3 or, alternatively, by loss of carbon monoxide in the well-known decarbonylation pathway.

In conclusion, we feel that although not all complexes isolated in this study are necessarily intermediates in the *catalytic* desulfonylation, and, although catalysts **1**, **2**, **4**, **5**, and **6** might react differently from **3**, the essential features of the catalysis are the formation of a metal–sulfinate complex and loss of SO_2. Elimination of ArX and recombination of the remaining metal compound with the sulfonyl halide then concludes the catalytic cycle.

Experimental Section

Chlorotris(triphenylphosphine)rhodium(I) (**1**),[9] *trans*-chlorocarbonylbis(triphenylphosphine)rhodium(I) (**2**),[10] *trans*-chlorocarbonylbis(triphenylphosphine)iridium(I) (**3**),[10,11] dichlorotris(triphenylphosphine)ruthenium(II) (**4**),[12] and tetrakis(triphenylphosphine)platinum(0) (**5**)[13] have been prepared by methods described in the literature. The different methods used for the desulfonylation reactions (see Tables I and II) are illustrated by the following examples.

Method A. *p*-Dichlorobenzene from *p*-Chlorobenzenesulfonyl Chloride.—A mixture of 10.0 g of freshly distilled *p*-chlorobenzenesulfonyl chloride and 0.1 g of chlorotris(triphenylphosphine)rhodium(I) (**1**) was heated in a Claisen flask equipped with a 25-cm-long Vigreux column, so as to permit distillation at 166–172° of the *p*-dichlorobenzene formed. After 25 min no more of this compound was collected; a polymer remained in the distillation flask. The crude distillate was taken up with methylene chloride and the solution was washed with alkali, neutralized, dried, and distilled, yield 5.9 g (85%) of pure *p*-dichlorobenzene, mp 53°, bp 168°.

Method B. Chlorobenzene from Benzenesulfonyl Chloride.—A slow stream of nitrogen was passed through the system described above, in which a mixture of 10.0 g of freshly distilled benzenesulfonyl chloride and 0.1 g of dichlorotris(triphenylphosphine)ruthenium(II) (**4**) was heated at 240° (wax bath). Chlorobenzene distilled over during 75 min, and much polymer was left in the flask. The distillate was worked up as above, yielding 2.35 g (37%) of pure chlorobenzene, bp 131°.

Method C. *p*-Bromofluorobenzene from *p*-Fluorobenzenesulfonyl Bromide.—In the same apparatus as in method A, there was placed 3.9 g of *p*-fluorobenzenesulfonyl bromide (see below), 60 mg of **1**, and 12 g of purified hexachlorobenzene. Upon gentle heating 2.2 g of material distilled, which was worked up in the usual manner. The crude product was analyzed by vapor phase chromatography on a 2 m × 6.4 mm column packed with 20% SE-30 on Chromosorb W and on a 1 m × 6.4 mm column packed with 10% Apiezon L on Chromosorb W, and was found to contain traces of fluorobenzene and 0.5% *p*-chlorofluorobenzene. The yield of *p*-bromofluorobenzene was 47%.

Method D. Desulfonylation of *β*-Naphthalenesulfonyl Fluoride.—A mixture of 10.0 g of *chloride-free* *β*-naphthalenesulfonyl fluoride (prepared in 90% yield from the sulfonyl *chloride* and potassium fluoride[14]), 20 g of hexachlorobenzene, and 125 mg of **1** was heated with stirring at 260° (wax bath) for 3 hr. The powdered reaction mixture was digested with 100 ml of hot benzene, filtered, and concentrated. The residue was freed from hexachlorobenzene by extraction with methanol. Vapor phase chromatography analysis on a 2.6-m-long column packed with 10% Apiezon L on Chromosorb W (condition for separation of naphthalene and 2-fluoronaphthalene) showed that 10% 2-fluoronaphthalene had been formed.

***p*-Fluorobenzenesulfonyl Bromide.**—A stirred mixture of 29.8 g of sodium *p*-fluorobenzenesulfonate, 27.1 g of red phosphorus, and 16 g of bromine was heated on the water bath until a homogeneous liquid was formed. After cooling, the reaction mixture was poured onto crushed ice and chloroform. The organic layer was washed with cold water, dried, and concentrated. The residue was distilled at 66° (0.1 mm), affording 13 g (54%) of *p*-fluorobenzenesulfonyl bromide as a colorless oil that darkened upon exposure to air.

Anal. Calcd for $C_6H_4FBrO_2S$: C, 30.1; H, 1.7; F, 7.9. Found: C, 30.1; H, 1.6; F, 7.9.

6-Chrysenesulfonyl Fluoride.—To a stirred solution of 5 g of chrysene in 200 ml of chloroform, 15 ml of fluorosulfonic acid was added at −50 to −20° during 75 min. The cold bath was removed and stirring was continued for 22 hr at room temperature. Crushed ice and chloroform were added and the organic layer was separated, washed several times with cold water, and dried. The solvent was removed and the oily residue was triturated with a mixture of chloroform and hexane. Thus 2.1 g (31%) of 6-chrysenesulfonyl fluoride, mp 175–179° (from cyclohexane), was obtained.

Anal. Calcd for $C_{18}H_{11}FO_2S$: C, 69.6; H, 3.6; F, 6.1. Found: C, 69.9; H, 3.1; F, 6.0.

Dichlorocarbonyl-*p*-tolylsulfinatobis(triphenylphosphine)iridium(III) (7, Ar = *p*-$CH_3C_6H_4$).—A stirred mixture of 600 mg of *p*-toluenesulfonyl chloride, 300 mg of **3**, 1.1 g of triphenyl-

---

[9] J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc., A*, 1711 (1966).

[10] J. Blum, J. Y. Becker, H. Rosenman, and E. D. Bergmann, *ibid.*, *B*, 1000 (1969).

[11] F. D. Mango and I. Dvoretzky, *J. Amer. Chem. Soc.*, **88**, 1654 (1966).

[12] T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **28**, 945 (1966).

[13] L. Malatesta and C. Cariello, *J. Chem. Soc.*, 2323 1958).

[14] W. Davies and J. H. Dick, *J. Amer. Chem. Soc.*, **53**, 2104 (1931).

phosphine, and 20 ml of benzene was refluxed under nitrogen for 7 hr. The precipitate was filtered and successively washed with hot ethanol and hot acetone to yield the pale yellow complex: mp 290° dec, $\bar{\nu}^{\text{Nujol}}$ 1070 and 1230 (SO) and 2080 cm^{-1} (CO). The compound could not be freed from traces of impurities having bands at 1040, 1170, 1190, and 2020 cm^{-1}.

Dichlorocarbonyl-*p*-tolylsulfinato(triphenylphosphine)iridium(III) (8, Ar = *p*-$CH_3C_6H_4$).—A solution of 600 mg of *p*-toluenesulfonyl chloride and 310 mg of **3** in 20 ml of benzene was refluxed for 7 hr, and the light tan crystals which separated were filtered off and washed with cold acetone to yield a cream-colored complex that darkened at 220° and melted with decomposition at 259–260°, $\bar{\nu}^{\text{Nujol}}$ 1070 and 1268 (SO) and 2095 cm^{-1} (CO).

Reactions of *p*-Chlorobenzenesulfonyl Chloride and 3 in Benzene. A.—A stirred solution of 500 mg of *p*-chlorobenzenesulfonyl chloride and 400 mg of **3** in 40 ml of benzene was refluxed under nitrogen for 90 min. From the clear solution, a few crystals separated. They were filtered off and washed with hot acetone and proved to be **dichlorocarbonyl-*p*-chlorophenylsulfinatobis(triphenylphosphine)iridium(III)** (7, Ar = *p*-ClC_6H_4): mp 205° dec; $\bar{\nu}^{\text{Nujol}}$ 1062, 1220, and 1238 (SO) and 2080 cm^{-1} (CO). The *filtrate* was treated with light petroleum ether (bp 40–60°) and the voluminous precipitate was filtered and recrystallized several times from a mixture of benzene and cyclohexane, yielding light tan crystals of **chlorocarbonyl-*p*-chlorophenylsulfinato(triphenylphosphine)iridium(II)** (**12**, **Ar** = *p*-ClC_6H_4), mp 200°. In the esr measurement of the solid sample a very strong signal at $g = 2.03$ was observed.

B.—On refluxing a mixture of 600 mg of *p*-chlorobenzenesulfonyl chloride, 300 mg of 3 and 1.1 g of triphenylphosphine in 20 ml of benzene, a precipitate was formed, which was filtered off and treated with hot acetone. The pale yellow, *insoluble* **dichlorocarbonyl-*p*-chlorophenylbis(triphenylphosphine)iridium(III)** (11, Ar = *p*-ClC_6H_4) thus obtained decomposed at 285°.

Reaction of *p*-Chlorobenzenesulfonyl Chloride and 3 in Mesitylene.—*p*-Chlorobenzenesulfonyl chloride (600 mg) and 300 mg of **3** were heated in 20 ml of mesitylene at 80° for 90 min. Then the temperature was gradually raised to 160°. A solid separated, and the mixture was refluxed for an additional 3 hr. The precipitate was treated with boiling toluene. The *least soluble*, colorless fraction proved to be **dichlorocarbonyl-*p*-chlorophenylsulfinato(triphenylphosphine)iridium(III) (8, Ar = *p*-ClC_6H_4)**. It turns deep yellow at 246° and decomposes at 250°: $\bar{\nu}^{\text{Nujol}}$ 1073, 1235, and 1263 (SO) and 2090 cm^{-1} (CO).

The fraction *soluble* in toluene was treated with petroleum ether (bp 40–60°) and recrystallized from benzene and cyclohexane, giving the correct analysis for **14**, mp 280–285° dec. The solid sample gave a signal at $g = 2.03$ in the esr spectrum.

Dichlorocarbonyl-β-naphthylsulfinato(triphenylphosphine)iridium(III)·C_6H_6 (15).—A mixture of 600 mg of β-naphthalenesulfonyl chloride, 300 mg of **3**, and 15 ml of benzene was refluxed with stirring. The mixture soon became homogeneous, and then a heavy precipitate was formed. After 5.5 hr the solid was filtered and washed with acetone to yield pale yellow crystals of **15**: $\bar{\nu}^{\text{Nujol}}$ 1085 and 1265 (SO) and 2095 (CO) cm^{-1}.

Dichlorocarbonyl-β-naphthyl(triphenylphosphine)iridium(III) (10, Ar = β-$C_{10}H_7$).—A solution of 182 mg of β-naphthalenesulfonyl chloride, 300 mg of **3**, and 20 ml of toluene was refluxed for 6 hr. (Alternatively, 20 ml of benzene was used and the mixture was refluxed for 11 hr.) The solution was diluted with hexane and the precipitate formed was refluxed with benzene for 5 min. The insoluble pale green crystals were sulfur-free and did not melt below 300°.

Chlorocarbonyl-β-naphthylsulfinato(triphenylphosphine)iridium(II) (12, Ar = β-$C_{10}H_7$).—A mixture of 182 mg of β-naphthalenesulfonyl chloride, 300 mg of **3**, and 20 ml of benzene was refluxed for 11 hr under nitrogen. The precipitate was refluxed with benzene for 5 min. The greenish, insoluble crystals obtained did not melt below 300°: $\bar{\nu}^{\text{Nujol}}$ 1075, 1270, and 1280 (SO) and 2050 cm^{-1} (CO). In the esr spectrum of the solid sample a strong signal at $g = 2.03$ was observed.

Chlorocarbonylfluoro-β-naphthylsulfinatobis(triphenylphosphine)iridium(III) (16) was obtained when 600 mg of β-naphthalenesulfonyl fluoride, 300 mg of **3**, and 20 ml of benzene were refluxed under nitrogen for 10 hr. The insoluble material was freed from some **dichlorocarbonyl-β-naphthylsulfinatobis(triphenylphosphine)iridium(III) (7, Ar = β-$C_{10}H_7$)** by heating with a mixture of benzene and acetone in which the latter is insoluble. This dichloro complex, mp 210°, was identical with a sample obtained by a procedure similar to that described for **7**, Ar = *p*-$CH_3C_6H_4$. The insoluble fluoro compound melted at 204°.

Dichloro-*p*-tolylsulfinato(triphenylphosphine)rhodium(III) (17, Ar = *p*-$CH_3C_6H_4$).—A mixture of 170 mg of *p*-toluenesulfonyl chloride, 300 mg of chlorocarbonylbis(triphenylphosphine)rhodium(I) (**2**), and 20 ml of benzene was refluxed under nitrogen for 3 hr. The orange precipitate did not dissolve in benzene and had no carbonyl bands in the infrared spectrum, mp 280–285°.

The soluble fraction proved to be a mixture of carbonyl-containing rhodium compounds.

Dichloro-β-naphthylsulfinato(triphenylphosphine)rhodium(III) (17, Ar = β-$C_{10}H_7$) was obtained by the same procedure as an orange-brown solid, mp 218° dec.

Registry No.—**1**, 14694-95-2; **2**, 13938-94-8; **3**, 14871-41-1; **4**, 15529-49-4; **5**, 14221-02-4; **6**, 7647-10-1; **7**, Ar = *p*-$CH_3C_6H_4$, 15629-10-4; **7**, Ar = *p*-ClC_6H_4, 15712-63-7; **7**, Ar = β-$C_{10}H_7$, 23916-65-6; **8**, Ar = *p*-$CH_3C_6H_4$, 23916-66-7; **8**, Ar = *p*-ClC_6H_4, 23916-67-8; **9**, Ar = *p*-$CH_3C_6H_4$, 24012-12-2; **9**, Ar = *p*-ClC_6H_4, 24012-13-3; **10**, Ar = β-$C_{10}H_7$, 23957-31-5; **11**, Ar = *p*-ClC_6H_4, 23957-32-6; **12**, Ar = *p*-ClC_6H_4, 23916-68-9; **12**, Ar = β-$C_{10}H_7$, 23916-69-0; **13**, Ar = *p*-ClC_6H_4, 24012-14-4; **13**, Ar = β-$C_{10}H_7$, 24012-15-5; **14**, 23957-33-7; **15**, 23916-70-3; **16**, 23916-71-4; **17**, Ar = *p*-$CH_3C_6H_4$, 24073-54-9; **17**, Ar = β-$C_{10}H_7$, 24035-14-1; 6-chrysenesulfonyl fluoride, 23924-10-9; benzenesulfonyl chloride, 98-09-9; *p*-chlorobenzenesulfonyl chloride, 98-60-2.

Acknowledgment.—We wish to thank Professor Ernst D. Bergmann for his advice in these studies.