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Reactions of Diphenylsulfanuric Chloride with Amines

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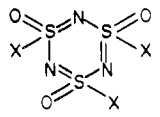
Diphenylsulfanuric chloride (1-chloro-3,5-diphenyl-1*H*,3*H*,5*H*-1,3,5,2,4,6-trithiatriazine 1,3,5-trioxide), $(NSO)_3(C_6H_5)_2Cl$, reacts with secondary amines by nucleophilic substitution to give diphenylsulfanuric amides without cleavage of the trithiatriazine ring. Reaction with triethylamine or pyridine in the presence of water gives amine salts of diphenylsulfanuric acid, which hydrolyze to ring-opened products. Diphenylsulfanuric chloride also reacts with trimethylamine in the presence or absence of water to give the diphenylsulfanuric amide of dimethylamine, but with methanol and trimethylamine the tetramethylammonium salt of diphenylsulfanuric acid is formed.

Symmetrical six-membered triaza heterocycles of phosphorus (phosphazenes)[1] and carbon (triazines)[2] have been studied extensively. Considerably less is known about their sulfur analogues, the trithiatriazines.[3] Sulfanuric halides, **1**



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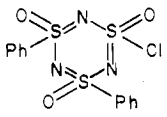
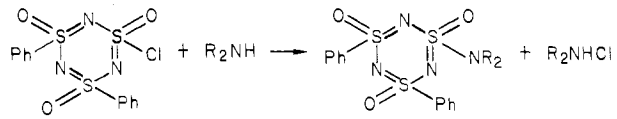


2

(symmetrical trihalotrithiatriazine trioxides), react with a variety of nucleophiles.[3-10] The trifluorides[3,5-7] have received more attention because they are more stable than the chlorides and do not suffer ring cleavage with nucleophiles. The sulfur–nitrogen ring stays intact for sulfanuric chloride (**1a**, X = Cl) only upon reaction with weaker nucleophiles like morpholine[4] and diphenylmercury.[8] With the amines all three chlorines may be substituted, but only two are replaced by diphenylmercury. The product obtained, diphenylsulfanuric chloride (1-chloro-3,5-diphenyl-1*H*,3*H*,5*H*-1,3,5,2,4,6-trithiatriazine 1,3,5-trioxide, **2**), was reported to resist attempts of further substitution with excess diphenylmercury,[8] phenyllithium,[8] or potassium thiocyanate.[10] However, contrary to the implications of these results, we have found that **2** reacts further with a variety of amines.[11] This report contains results of those studies with full experimental details.

Results

Reaction with Secondary Amines. Treatment of a solution of **2** (ca. 0.03 M) in benzene or acetonitrile with morpholine



2 **3**

at room temperature resulted in the formation of 1-morpholido-3,5-diphenyl-1*H*,3*H*,5*H*-1,3,5,2,4,6-trithiatriazine 1,3,5-trioxide (**3a**, 70 and 65% yield, respectively). Piperidine and diethylamine reacted similarly. However, ethylenimine gave polymeric material while diethanolamine and bis(2-chloroethyl)amine gave no isolable adducts. No effort was made to optimize conditions with these compounds.

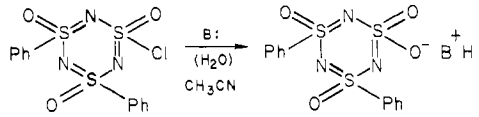
The effects of amine structure and concentration, the nature of the solvent, and the presence of a common ion on reaction times (for disappearance of **2**) and yields are summarized in Table I. The more nucleophilic piperidine and diethylamine had shorter reaction times than morpholine. Doubling the concentration of amine also decreased the reaction times. Reaction times were shorter in benzene than in acetonitrile; however, the products precipitated from benzene and not from acetonitrile. The addition of tetraethylammonium chloride (as a source of "common" chloride ions) to the reaction of **2** with diethylamine in acetonitrile caused a slight decrease in the reaction time.

Table I. Reaction of Diphenylsulfanuric Chloride (**2**) with Secondary Amines

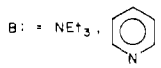
amine	product	solvent	reaction time, h [2:amine] 1:3	1:6	% yield[a]
morpholine	**3a**	C_6H_6	8.5	2.0	76
morpholine	**3a**	CH_3CN	115	2.5	65
piperidine	**3b**	C_6H_6	0.5	0.25	80
piperidine	**3b**	CH_3CN	106	2.2	78
diethylamine	**3c**	C_6H_6	1.4	0.2	67
diethylamine	**3c**	CH_3CN	36	2.3	45
diethylamine	**3c**	CH_3CN		1.5[b]	

[a] Yields are reported for reactions with a ratio of **2**:amine of 1:6. [b] Reaction time with **2**, $NHEt_2$, and Et_4NCl in the ratio of 1:6:6.

Reaction with Tertiary Amines. Diphenylsulfanuric chloride (**2**) also reacted with tertiary amines such as triethylamine, trimethylamine, and pyridine. Treatment of an aqueous or



2 **4**



methanolic solution of **2** in acetonitrile with triethylamine, followed by workup, afforded the triethylammonium salt of diphenylsulfanuric acid (3,5-diphenyl-1-hydroxy-1*H*,3*H*,5*H*-1,3,5,2,4,6-trithiatriazine 1,3,5-trioxide), **4a**. The structure is based on elemental analysis and spectral data. The compound analyzed for $C_{18}H_{26}N_4S_3O_4$. The IR spectrum had an absorption band corresponding to the N–H group. The NMR spectrum had unresolved multiplets at δ 8.01 and 7.42 corresponding to one amino and ten phenyl protons, a quartet at δ 2.85 and a triplet at δ 1.00 assigned to the ethyl groups. The addition of a drop of trifluoroacetic acid resulted in splitting of the ethyl methylene protons into a multiplet, a behavior typical of compounds containing the triethylammonium moiety. Efforts to obtain a mass spectrum of the compound were fruitless. Reaction of **2** with pyridine and water gave a similar product (**4b**). Attempts to isolate a quaternary ammonium intermediate (**5a**) from the reaction of **2** with triethylamine under anhydrous conditions were unsuccessful. After repeated efforts at purification of the reaction mixture in a drybox, the only isolated product was **4a**.

Attempts to convert **4** to its conjugate acid **6** failed. Treatment with cation-exchange resin gave no isolable product. However, treatment of **4a** with 1 M HCl gave a white solid, the analysis of which is consistent with structure **7**. Heating an aqueous solution of **4a** or **4b** gave primarily benzenesulfonamide.

Reaction of **2** with trimethylamine gave different products depending upon the reaction conditions. In anhydrous or

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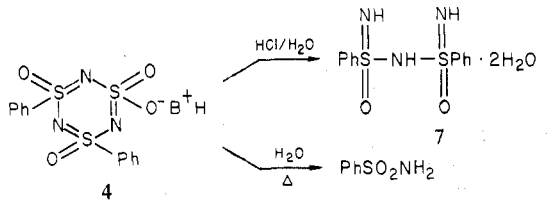
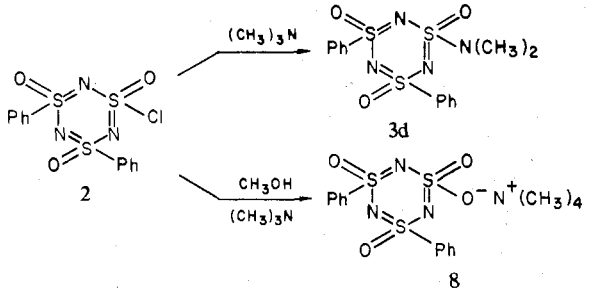


aqueous acetonitrile it gave the dimethylaminodiphenylsulfanuric amide derivative, **3d**. However, in methanolic acetonitrile the tetramethylammonium salt of diphenylsulfanuric acid, **8**, was isolated.

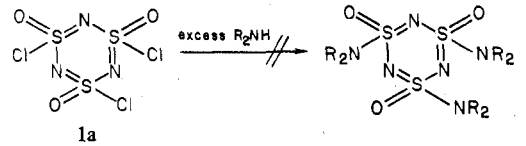


Reaction of **2** with *N*,*N*-dimethylaniline gave a deep blue oil from which no product was isolated.

Reaction with Primary Amines. Attempts were made to prepare substitution products of diphenylsulfanuric chloride (**2**) with anhydrous ammonia, aniline, and *n*-butylamine. Limited experiments produced no pure products in these cases.

If crystalline products were not isolated in our various experiments, liquid chromatography on silica gel was seldom effective because of streaking.

Reactions of Sulfanuric Chloride with Secondary Amines. Several attempts were made to prepare trisubstituted secondary amine derivatives of α-sulfanuric chloride,[3] **1a** (chlorine atoms all cis), as potential antitumor agents. We employed the mild



1a

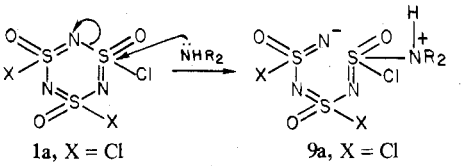
$R_2NH = CH_2{-}CH_2$ (N, H), $(CH_3)_2NH$, $HN(CH_2CH_2OH)_2$, $HN(CH_2CH_2Cl)_2$

conditions which had previously[4] been successful for morpholine and **1a** to ethylenimine, dimethylamine, diethanolamine, and bis(2-chloroethyl)amine, but only intractable oils were produced.

Discussion

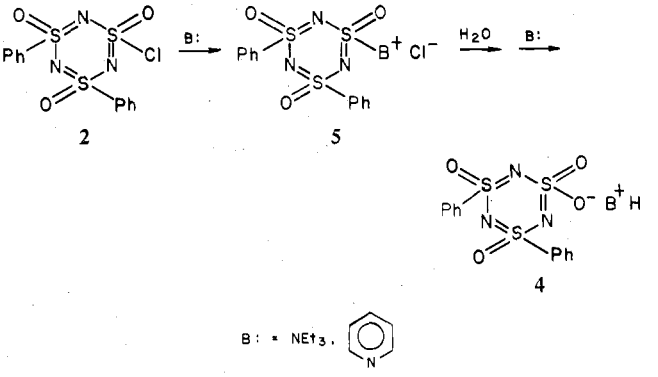
Analysis of results for the reaction of diphenylsulfanuric chloride (**2**) with secondary amines (Table I) suggests that substitution occurs by an S_N2 mechanism. Decreased reaction times with higher concentrations of amine and the absence of a common ion effect due to addition of tetraethylammonium chloride certainly argue against an S_N1 mechanism. While the solvent effect does not support the S_N1 mechanism, the shorter reaction times and higher yields from benzene may represent an anomaly because of precipitation of the products. No hard kinetic data is available, however, to confirm an S_N2 mechanism.

The successful substitution of **2** by even a stronger nucleophile like diethylamine without ring cleavage suggests a stabilizing effect of the phenyl groups in **2** compared with chlorine in **1a**. It seems reasonable that the competition between substitution with ring cleavage vs. that without cleavage may be a comparison of the relative stabilities of a ring-opened imide anion (**9**) vs. the chloride ion, respectively. Ring cleavage of **1a** would give a more stable anion, **9a** (X = Cl), than that (**9b**, X = Ph) produced from **2**. Another

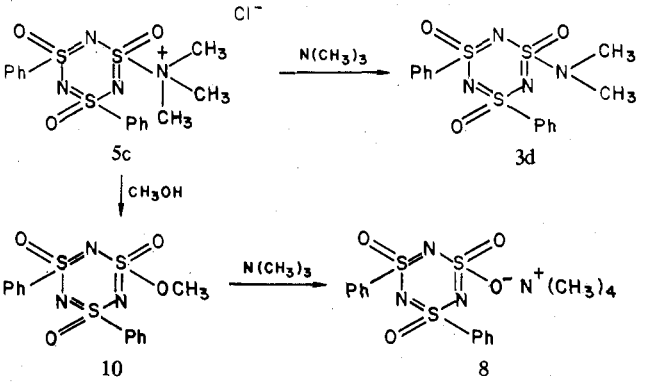


factor which could be even more important is the ability of **9** to eliminate X^-. Loss of Cl^- is reasonable, but loss of Ph^- is not. Loss of Cl^- could result in irreversible ring cleavage. This explanation is also compatible with the much greater stability of the sulfanuric fluorides.[5] The stronger S–F bonds would be much less likely to cleave. An alternative mechanism for cleavage could involve nucleophilic attack at an electrophilic chlorine atom.

The composite of results for reaction of diphenylsulfanuric chloride (**2**) with tertiary amines supports an initial quaternary ammonium complex (**5**) in each case. With triethylamine and pyridine the complex is subsequently hydrolyzed to the amine salt of diphenylsulfanuric acid (**4**). Further hydrolysis of **4** with acid to **7** or hot water to benzenesulfonamide is reasonable for its structure. When the nucleophile is trimethylamine,



another reaction of the complex, **5c**, becomes competitive with hydrolysis. Demethylation of **5c** occurs to produce the amide, **3d**, in the presence or absence of water. However, methanol



apparently solvolyzes the complex to produce an alkylating methyl ester of diphenylsulfanuric acid (**10**), which reacts with trimethylamine to give **8**. This latter reaction has a precedent with sulfanuric fluoride (**1b**).[6] The formation of **4** from water and triethylamine or pyridine is analogous to the methanol reaction but has not been reported for **1b**.

$$(NSOF)_3 + CH_3OH + 2N(CH_3)_3 \xrightarrow[\text{ether}]{-20\ ^\circ C} [N_3S_3O_3F_2O]^-[N(CH_3)_4]^+ + [N(CH_3)_3H]F$$

1b

Conclusions

We have demonstrated that the replacement of two chloro groups of sulfanuric chloride (**1a**) by phenyl produces a sulfanuric derivative that is much less prone to ring cleavage upon nucleophilic substitution. It also appears that monosubstitution reactions that occur with sulfanuric fluoride (**1b**) will proceed in like manner for diphenylsulfanuric chloride (**2**). Thus, a new route to varied derivatives of diaryl (and perhaps dialkyl) sulfanuric compounds has been found.

Experimental Section

All chemicals used were of reagent grade quality. Phosphorus pentachloride (Aldrich) and sulfamoyl chloride (American Hoechst) were powdered in a drybox prior to use. All moisture-sensitive compounds were handled and stored in a drybox. The *n*-heptane used for extraction of sulfanuric and diphenylsulfanuric chloride was purified by passing it through a 15 by 3.5 in. column of alumina. Eastman Chromagram thin-layer sheets coated with silica gel containing a fluorescent indicator were used. Melting points were determined on a Thomas-Hoover apparatus and are uncorrected. Microanalyses were performed by Robertson Laboratory of Florham Park, N.J.

Trichlorophosphazosulfonyl Chloride. The procedure of Kirsanov[12] was modified by replacing sulfamic acid by sulfamoyl chloride and reducing the amount of phosphorus pentachloride to 1 equiv. This procedure avoids the formation of phosphorus oxychloride as a byproduct and gives higher yields.

To a 1-L, three-necked flask containing 200 mL of carbon tetrachloride and equipped with an inlet tube, drying tube, and mechanical stirrer was added 332 g (1.59 mol) of PCl_5 through gooch tubing. This was followed by 174 g (1.51 mol) of sulfamoyl chloride added in the same manner. After stirring of the mixture for 1 h at room temperature, the drying tube was replaced by a condenser and the slush was refluxed for 2 h to give a clear yellow solution. After removal of the solvent in vacuo, the residue crystallized on standing in a refrigerator for 24 h. The solid was filtered in a drybox and washed with 50 mL of cold *n*-heptane to give 250 g of product, mp 30–33 °C. An additional 40 g (total yield 77%) was recovered from the chilled filtrate.

Sulfanuric Chloride. Pyrolysis of 290 g of trichlorophosphazosulfonyl chloride by Kirsanov's procedure[12] gave 26 g of α-sulfanuric chloride (mp 145–146 °C) and 12 g of β-sulfanuric chloride (mp 45–47 °C) for a combined yield of 34%.

Diphenylsulfanuric Chloride (2). Reaction of 11.1 g (38 mmol) of α-sulfanuric chloride[13] with 27 g (76 mmol) of diphenylmercury (Eastman) according to the procedure of McKenney and Fetter[8] gave 9 g of crude **2**. Thin-layer chromatography (TLC) of the crude product on silica gel (eluted with benzene) showed **2** (R_f = 0.83), a non-UV-absorbing spot with lower R_f and a UV-absorbing spot at the origin. Chromatography of the crude mixture on a 22 by 3 in. silica gel column eluted with benzene–hexane (7:3) gave 6.9 g of pure **2** (one spot on TLC).

1-Morpholido-3,5-diphenyl-1*H*,3*H*,5*H*-1,3,5,2,4,6-trithiatriazine 1,3,5-Trioxide (3a). To a stirred solution of 1.15 g (0.4 mmol) of diphenylsulfanuric chloride (**2**) in 15 mL of benzene contained in a 25-mL round-bottom flask equipped with a drying tube was added 0.2 mL (2.4 mmol) of morpholine. The progress of the reaction was followed by TLC eluted with benzene and was judged complete after 2 h when the spot corresponding to diphenylsulfanuric chloride (R_f = 0.83) had disappeared completely. The white solid which precipitated during this period was filtered, washed with brine, and crystallized from ethanol–hexane to give 130 mg (76%) of **3a**: mp 140–141 °C; NMR [$(CD_3)_2S{=}O$] δ 7.95 and 7.55 (m, 10 H), 3.75 (m, 4 H), 3.05 (m, 4 H); IR (KBr) 3.38, 3.53, 3.65, 6.90, 8.10, 8.25, 8.90, 9.05, 9.25, 9.35, 9.62, 9.90, 10.10, 13.25, 13.50, 14.15 μm.

Anal. Calcd: C, 45.08; H, 4.22; N, 13.14; S, 22.56. Found: C, 44.82; H, 4.67; N, 12.92; S, 22.31.

In a second run, 0.1 mL (1.2 mmol) of morpholine was allowed to react with **2** in a similar manner. The reaction was completed in 8.5 h.

In a third run, 0.15 g (0.4 mmol) of **2** reacted completely with 0.2 mL (2.4 mmol) of morpholine in 15 mL of acetonitrile after 2.5 h. This reaction was homogeneous throughout. Acetonitrile was removed in vacuo, and the concentrate was dissolved in chloroform, washed with brine, dried over $MgSO_4$, and crystallized from ethanol–hexane to give 0.115 g (65%) of **3a**, mp 140–141 °C. A mixture melting point between this sample and the one obtained from benzene was not depressed.

In a fourth run, 0.1 mL (1.2 mmol) of morpholine was allowed to react with 0.15 g (0.4 mmol) of **2** in 15 mL of acetonitrile. The reaction was completed after 115 h.

1-Piperidino-3,5-diphenyl-1*H*,3*H*,5*H*-1,3,5,2,4,6-trithiatriazine 1,3,5-Trioxide (3b). To a stirred solution of **2** in 15 mL of benzene was added 0.24 mL (1.4 mmol) of piperidine. After 0.5 h the solvent was removed in vacuo and the resulting white solid was washed with brine and crystallized from ethanol–hexane to give 0.14 g (80%) of **3b**: mp 151.5–152.5 °C; NMR [$(CD_3)_2S{=}O$] δ 7.95 and 7.50 (m, 10 H), 2.90 (m, 4 H), 1.45 (m, 6 H); IR (KBr) 3.39, 3.52, 6.95, 8.10, 8.20, 9.03, 9.35, 9.88, 13.20, 14.25 μm.

Anal. Calcd: C, 48.11; H, 4.71; N, 13.20; S, 22.67. Found: C, 48.17; H, 4.99; N, 12.91; S, 22.37.

Results from additional runs with different ratios of piperidine to **2** in benzene and acetonitrile are summarized in Table I.

1-Diethylamino-3,5-diphenyl-1*H*,3*H*,5*H*-1,3,5,2,4,6-trithiatriazine 1,3,5-Trioxide (3c). In a similar manner to the preparations of **3a** and **3b**, 0.11 g (67%) of **3c**, mp 127–128 °C, was obtained after 0.2 h from a 6 to 1 ratio of amine to **2** in benzene. NMR [$(CD_3)_2S{=}O$]: δ 7.85 and 7.55 (m, 10 H), 2.82 (q, 4 H), 108 (t, 6 H). IR (KBr): 6.85, 7.99, 8.20, 9.05, 9.58, 9.88, 10.10, 13.20, 14.20 μm.

Anal. Calcd: C, 46.60; H, 4.85; N, 13.59; S, 23.30. Found: C, 46.52; H, 5.62; N, 13.37; S, 23.24.

Results from additional runs with different ratios of ethylamine to **2** in benzene and acetonitrile are summarized in Table I.

Reaction of 2 with Triethylamine. To a stirred solution of 0.2 g (0.53 mmol) of **2** in 10 mL of acetonitrile and 0.5 mL water was added 0.44 mL (3.2 mmol) of triethylamine. After 15 h the solvent was removed in vacuo and the resulting yellow oil was dissolved in chloroform, washed with cold water, and dried over $MgSO_4$. Removal of the solvent in vacuo gave a yellow oil which crystallized from ethanol–hexane to give 180 mg of a white solid: mp 122–123 °C; NMR ($CDCl_3$) δ 8.01 and 7.42 (m, 11 H, 2 Ph, and 1 N^+–H), 2.85 (q, 6H, 3 CH_2), 1.00 (t, 9 H, 3 CH_3); ($CDCl_3$, CF_3COOH) same as above except δ 2.85 is a multiplet instead of a quartet; IR (KBr) 3.34, 3.72, 3.76, 6.95, 8.25, 9.2, 9.6, 10.3, 13.9, 14.5 μm.

Anal. Calcd: $C_{18}H_{26}N_4S_3O_4$: C, 47.16; H, 5.67; N, 12.22; S, 20.96. Found: C, 47.83; H, 6.00; N, 12.56; S, 21.43.

Reaction of 2 with Trimethylamine in Acetonitrile–Methanol. To an ice-cold stirred solution of 0.430 g (1.2 mmol) of **2** in 10 mL of acetonitrile and 1 mL of methanol was added an excess of trimethylamine (1 mL). After 7 h, removal of excess of trimethylamine and solvents gave a wet solid weighing 0.455 g. A portion of this (0.200 g) was crystallized from methanol to give 160 mg of **8** as a white solid, mp 117–119 °C. A second crystallization from methanol raised the melting point to 119–120 °C. NMR [$(CD_3)_2S{=}O$]: δ 7.93 and 7.60 (m, 10 H), 3.02 (s, 12 H). IR (KBr): 6.74, 6.91, 7.88, 8.09, 9.00, 9.40, 12.1 μm.

Anal. Calcd for $C_{16}H_{22}N_4S_3O_4$: C, 44.65; H, 5.12; N, 13.02; S, 22.32. Found: C, 44.72; H, 5.25; N, 12.78; S, 22.49.

Reaction of 2 with Trimethylamine in Aqueous Acetonitrile. To an ice-cold, stirred solution of 230 mg (0.6 mmol) of **2** in 10 mL of acetonitrile containing 0.5 mL of water was added an excess of trimethylamine (0.6 mL). After 8 h, removal of excess trimethylamine and solvents gave a mushy solid, which was dissolved in chloroform, washed with cold water, and dried over $MgSO_4$. Removal of the solvent and crystallization of the resulting concentrate from ethanol afforded 130 mg of **3d**, as a white solid. TLC of this solid on silica gel eluted with chloroform revealed the presence of one UV-absorbing spot. However, development with iodine showed the presence of another component at the origin. The solid was placed on a short silica gel column and eluted with chloroform. The resulting solid had no spot at the origin and appeared as a single spot on TLC: mp 87–88 °C; NMR ($CDCl_3$) δ 8.18 and 7.63 (m, 10 H), 2.72 (s, 6 H); IR (KBr) 6.90, 7.95, 8.90, 10.7, 12.0 μm.

Anal. Calcd for $C_{14}H_{16}N_4S_3O_3$: C, 43.75; H, 4.16; N, 14.57; S, 25.02. Found: C, 43.56; H, 4.31; N, 14.32; S, 25.15.

Reaction of 2 with Pyridine. To a solution of 440 mg of **2** in 10 mL of acetonitrile containing 1 mL of water was added 0.3 mL of pyridine and the solution was stirred overnight. The white solid (**4b**) which precipitated during this time was filtered and crystallized twice from ethanol and weighed 350 mg: mp 119.5–121 °C; NMR [$(CD_3)_2S{=}O$] δ 8.65 (2 pyridinium protons next to the nitrogen), 7.81 (14 H; 10 aromatic, 3 pyridinium, and 1 NH^+); IR (KBr) 3.03,

3.40, 7.85, 8.00, 8.98, 10.9, 13.9, 14.8 μm.

Anal. Calcd for $C_{17}H_{16}N_4S_3O_4 \cdot 2H_2O$: C, 43.24; H, 4.23; N, 11.86; S, 20.38. Found: C, 42.86; H, 4.39; N, 11.77; S, 20.50.

Treatment of 4a with Water. A suspension of 100 mg of **4a** in 2 mL of distilled water was heated on a steam bath for 30 min. The resulting clear solution was then left overnight at room temperature. The white solid which precipitated during this period was filtered, weighed (55 mg), and identified as benzenesulfonamide, mp 152–154 °C.

Treatment of 4a with 1 M HCl. On treatment of 200 mg of **4a** with 1 M HCl, a white solid precipitated which was filtered, washed with brine, and crystallized from ethanol to give 60 mg of **7**: mp 131.5–133 °C; NMR [$(CD_3)_2S{=}O$] δ 8.04 and 7.78 (aromatic), 2.52 (NH); IR (KBr) 2.98, 3.50, 6.89, 7.78, 7.94, 8.97, 10.6, 13.2, 14.6 μm.

Anal. Calcd for $C_{12}H_{13}N_3S_2O_2 \cdot 2H_2O$: C, 43.50; H, 5.13; N, 12.68; S, 19.38. Found: C, 43.66; H, 4.46; N, 12.62; S, 19.06.

Treatment of 4b with Water. A 50-mg sample of **4b**, dissolved in 1 mL of water, was heated for 30 min on a steam bath. The solution was then left at room temperature for several hours. The white solid, which precipitated, was filtered, weighed (20 mg), and identified as benzenesulfonamide, mp 151–153 °C.

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Registry No. **2**, 28464-34-8; **3a**, 63823-93-8; **3b**, 64051-75-8; **3c**, 63823-94-9; **3d**, 69069-47-2; **4a**, 69069-49-4; **4b**, 69069-50-7; **7**, 69069-51-8; **8**, 69069-53-0; trichlorophosphazosulfonyl chloride, 14700-21-1; PCl_5, 10026-13-8; sulfamoyl chloride, 7778-42-9; morpholine, 110-91-8; piperidine, 110-89-4; diethylamine, 109-89-7; triethylamine, 121-44-8; trimethylamine, 75-50-3; pyridine, 110-86-1; benzenesulfonamide, 98-10-2.

References and Notes

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Kinetics and Mechanism of Oxidative Addition of Aryl Iodides to Iridium(I) Complexes

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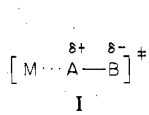
The kinetics of oxidative addition of aryl iodides to *trans*-$IrCl(CO)L_2$ (L = tertiary phosphine) are governed by a two-term rate law, $R = \{k_1 + k_2[ArI]\}[Ir]$, similar in form to the equation describing substitution reactions of square-planar complexes. The second-order path is decreased by added phosphine. Electron-withdrawing groups in either the aryl halide or the complex enhance the rate of reaction. Linear free energy relationships were found between k_2 and the Hammett σ_p for substituents in the aryl iodide ($\rho = +0.6$) and between k_2 and the Kabachnik $\sum\sigma^{ph}$ for substituents on the phosphine ($\rho = +0.4$). A two-step mechanism is suggested for the second-order path involving predissociation of the phosphine ligand. These data are compared with prevailing ideas concerning the mechanisms of oxidative addition reactions of d^8 square-planar complexes.

Introduction

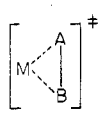
Since the classic study of Chock and Halpern,[3] the reactions of Vaska's compound *trans*-$IrCl(CO)(PPh_3)_2$ and its analogues have held a central position in efforts to elucidate the mechanism of oxidative addition of small molecules to d^8 transition-metal complexes (1). In spite of the intense activity

$$\textit{trans}\text{-}IrCl(CO)L_2 + AB \rightarrow \textit{trans}\text{-}IrCl(A)(B)(CO)L_2 \quad (1)$$
$$L = \text{triphenylphosphine}$$

in this field numerous questions remain unanswered. The nature of the transition state remains a controversial topic. Both linear (I) and three-center (II) transition states have been

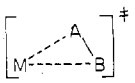


I



II

suggested. The original proposal[3-6] that homopolar oxidants (A = B) react via a symmetrical transition state (I) whereas polar oxidants (A ≠ B) react via a linear transition state (II) has recently been modified.[7] An unsymmetrical three-center transition state (III) which may be regarded as a gradation



III

between forms I and II has been proposed. Evidence favoring this view was adduced from the findings[6] that the activation parameters for the addition of a variety of molecules of Vaska's compound could be accommodated by a single smooth curve, with an isokinetic temperature. Many authors[4,7-10] have cited evidence that inclusion of electron-releasing functional groups in the coordinated phosphine ligands enhances the reactivity of the complex toward oxidative addition. The analogous rhodium(I) complex $RhCl(CO)(PAr_3)$ was shown to behave similarly.[11] However, no great reactivity differences were found for the addition of H_2 to *trans*-$IrCl(CO)L_2$ (L = tertiary phosphine).[4]

The influence of electronic factors in the addend molecule has previously been investigated for the addition of substituted benzyl chlorides.[4] We have recently shown[12] that aryl halides may be added to Vaska's compound and its analogues. In this system the bond activated by the iridium(I) complex is an aromatic carbon–iodide linkage, which should be expected to be particularly sensitive to the electronic effects of substituents

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