The uv spectrum showed a λ_{max} of 440 nm (only, except for the typical end absorption of **3** in CCl$_4$, Figure 1) with A_{440} being 6.784 (0.424, corrected for dilution of 0.20 to 3.20 ml). The entire 125-ml solution was photolyzed in a quartz flask attached to a reflux condenser for 20 min. Appearance of a new λ_{max} at 520 nm indicated formation of I$_2$. A 10.00-ml aliquot of the resulting solution was washed with 15.00 ml of 0.0559 *N* Na$_2$S$_2$O$_3$, which then consumed 8.52 ml of 0.0508 *N* KI$_3$, indicating the formation

of 5 mequiv of I$_2$ presumably from 5 mequiv of sulfenyl iodide (yield, at least $\sim$70%).

Coupling, Carbonylation, and Vinylation Reactions of Aromatic Sulfinic Acids *via* Organopalladium Intermediates

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The expulsion of sulfur dioxide from arenesulfinic acids and their salts by palladous salts in a variety of solvents is reported. The aryl groups couple to form a biaryl in 35% yield, and Pd^{2+} is reduced to metallic palladium. Mercuric chloride acts as a catalyst and doubles the yield of the biaryl. The reaction presumably proceeds by formation of an arylpalladium complex. In the presence of carbon monoxide, olefins, or nitriles insertion reactions take place leading to carbonylation, vinylation, or acylation of arenesulfinate anions in low to medium yields.

Recently the formation of arylpalladium complexes from arylmercuric chloride and palladium chloride was postulated.[1] Owing to the low stability of the organometallic intermediate only the products of subsequent reactions, biaryls and palladium metal or insertion products in the presence of CO or olefins, were isolated. Likewise, benzeneboronic acid and palladium acetate yielded biphenyl and palladium metal,[2] presumably *via* a phenylpalladium complex obtained by electrophilic displacement of boron. Substitution of aromatic hydrogen by palladium salts to give similar intermediates was considered as a first step in coupling reactions of benzene and toluene.[2-4] The present work was undertaken in order to explore whether arylpalladium complexes could be prepared by desulfination of aromatic sulfinic acids. Sulfur dioxide eliminations of arenesulfinate complexes of transition metals have been reported,[5,6] and the preparation of arylmercuric chlorides from aromatic sulfinic acids and mercuric chloride (eq 1) has been known since 1905.[7]

$$\text{ArSO}_2\text{H} + \text{HgCl}_2 \xrightarrow[\text{78°}]{\text{H}_2\text{O-EtOH}} \text{ArHgCl} + \text{SO}_2 + \text{HCl} \quad (1)$$
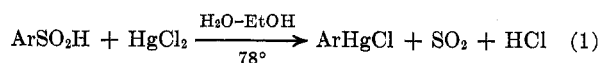
Attempts to replace HgCl$_2$ by thallic chloride in reaction 1 were unsuccessful.[8] Crystalline palladium arenesulfinate complexes have been prepared,[9,10] but their chemistry was not explored.

The present work shows that the addition of palladium salts to aromatic sulfinic acids in heated solution leads to evolution of sulfur dioxide, most likely by an electrophilic substitution process. The expected de-

composition products of the presumed arylpalladium intermediates, namely biaryls and palladium metal, were isolated. In Table I the experimental conditions and results of this new coupling reaction of sulfinic acids are summarized. The biaryls formed (biphenyl or *p,p'*-bitolyl) were identified by melting point, mixture melting point, ir, and glpc. Accordingly, the main reaction can be expressed as in eq 2. The yields

$$\text{2ArSO}_2\text{Na} + \text{Na}_2\text{PdCl}_4 \longrightarrow$$
$$\text{ArAr} + \text{2SO}_2 + \text{Pd} + \text{4NaCl} \quad (2)$$

of the by-products, aromatic hydrocarbon, arylchloride, and various sulfur products, depend strongly upon solvent and anion. Benzylacetate formed in entry 7 is a secondary product, derived from oxidation of toluene.

Mercuric chloride catalyzed the coupling reaction of aromatic sulfinic acids in aqueous solution, as reflected in the higher conversions to biaryls in Table II. The production of *p*-bromotoluene in entry 7, apparently derived by a ligand transfer reaction, prompted attempts to synthesize other *para*-substituted toluenes from *p*-toluenesulfinic acid, palladium chloride, and certain anions. However, experiments involving the anions X$^-$ = F$^-$, CN$^-$, OCN$^-$, N$_3^-$, or NO$_2^-$ did not yield any *p*-CH$_3$C$_6$H$_4$X. Entry 8 shows that a catalytic amount of palladium salt is sufficient in the presence of a reoxidizing agent like cupric chloride.

The intermediate formation of arylpalladium complexes in the desulfination of arenesulfinic acids with PdCl$_2$ was further substantiated by isolating the expected[1b] insertion products with carbon monoxide and olefins. The conversions in Table III again reflect strong solvent effects. Only the double insertion products (two *p*-tolyl groups per olefin) were formed with 1 atm of ethylene (entries 3 and 4). Occasionally the solvent added to the initial olefin or the olefinic product (entries 3, 5, and 8). The last two reactions represent additions of the *p*-tolylpalladium complex into CN triple bonds, a new type of insertion reaction of transition metal aryl complexes. The ketones isolated are

(1) (a) P. M. Henry, *Tetrahedron Lett.*, 2285 (1968). (b) R. F. Heck, *J. Amer. Chem. Soc.*, **90**, 5518 (1968), and subsequent papers. (c) M. O. Unger and R. A. Fouty, *J. Org. Chem.*, **34**, 18 (1969).

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(9) B. Chiswell and L. M. Venanzi, *J. Chem. Soc. A*, 1246 (1966).

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TABLE I
REACTIONS OF ARENESULFINIC ACIDS WITH PALLADIUM(II) SALTS[a]

| Entry	Sulfinate	Pd Salt	Solvent	Temp., °C	Conversion to biaryl, %	Conversion to other products
1	$C_6H_5SO_2Na$[b]	Na_2PdCl_4	H_2O	100	35	3.5% $ArSO_2SAr$, 1% ArCl
2	$p\text{-}CH_3C_6H_4SO_2H$	Na_2PdCl_4[c]	$H_2O\text{-}EtOH$	81	27	0.7% Ar_2S
3	$p\text{-}CH_3C_6H_4SO_2Na$[d]	Na_2PdCl_4	H_2O	100	19	Trace of Ar_2S
4	$p\text{-}CH_3C_6H_4SO_2Na$[d]	Na_2PdCl_4	EtOH	79	27	Traces of Ar_2S, ArCl
5	$p\text{-}CH_3C_6H_4SO_2Na$[d]	Na_2PdCl_4	HOAc	116	36	
6	$p\text{-}CH_3C_6H_4SO_2Na$[d]	Na_2PdCl_4	CF_3COOH	71	1.7	15% Ar_2S, toluene
7	$p\text{-}CH_3C_6H_4SO_2Na$[d]	$Pd(OAc)_2$	HOAc	116	9.5	22% $C_6H_5CH_2OAc$, sulfur products

[a] 0.01 mol of Pd salt and 0.02 mol of sulfinate in 40 ml of solvent. [b] All ingredients heated together. [c] Pd salt solution (20 ml) added dropwise to the boiling sulfinate solution (20 ml). [d] Sulfinate solution (20 ml) added dropwise to the boiling solution of the Pd salt.

TABLE II
REACTIONS OF ARENESULFINIC ACIDS WITH PALLADIUM(II) SALTS AND MERCURIC CHLORIDE[a]

| Entry	Sulfinate	Pd Salt	Solvent	Temp, °C	Conversion to biaryl, %	Conversion to other products
1	$C_6H_5SO_2Na$[b]	Na_2PdCl_4	H_2O	100	71	2% $ArSO_2SAr$, trace of ArCl
2	$p\text{-}CH_3C_6H_4SO_2Na$	Na_2PdCl_4[c]	H_2O	100	61	1% Ar_2SO_2
3	$p\text{-}CH_3C_6H_4SO_2Na$[d]	Na_2PdCl_4	H_2O	100	63	Traces
4	$p\text{-}CH_3C_6H_4SO_2Na$[d]	Na_2PdCl_4	CH_3OH	66	23	
5	$p\text{-}CH_3C_6H_4SO_2Na$[d]	Na_2PdCl_4	HOAc	116	28	
6	$p\text{-}CH_3C_6H_4SO_2Na$[d]	$Pd(OAc)_2$	H_2O	100	26	9% Ar_2S, 2% Ar_2SO_2
7	$p\text{-}CH_3C_6H_4SO_2Na$[d]	$Na_2(PdBr_2Cl_2)$	H_2O	100	51	9% ArBr, traces
8	$p\text{-}CH_3C_6H_4SO_2Na$[d]	Na_2PdCl $+ CuCl_2$[e]	H_2O	100	380	

[a] 0.01 mol of Pd salt, 0.02 mol of sulfinate, and 0.001 mol of $HgCl_2$ in 40 ml of solvent. [b] All ingredients heated together. [c] Pd salt solution (20 ml) added dropwise to the boiling sulfinate solution (20 ml). [d] Sulfinate solution (20 ml) added dropwise to the boiling solution of the other ingredients (20 ml). [e] 0.001 mol of Pd salt and 0.01 mol of $CuCl_2$.

TABLE III
REACTIONS OF p-TOLUENESULFINATE ANION AND PALLADIUM(II) SALTS WITH DOUBLE AND TRIPLE BONDS[a]

Entry	Pd Salt	Compound with multiple bond	Solvent	Temp, °C	Conversion to p,p'-bitolyl, %	Conversion to insertion product	Conversion to other products
1	Na_2PdCl_4[b]	CO	CH_3OH	66	Trace	29% $ArCOOCH_3$, 5% Ar_2CO	1.4% ArCl, 1.8% Ar_2S
2	Na_2PdCl_4[b]	CO	H_2O	100	27	2% ArCOOH, 10% Ar_2CO	Traces
3	Na_2PdCl_4[b]	C_2H_4	CH_3OH	63	Trace	11% ArCH=CHAr (trans), 30% $ArCH(CH_3)OCH_3$	12% $ArCH(OCH_3)CH_2Ar$, traces
4	Na_2PdCl_4	C_2H_4	$CH_3CN\text{-}H_2O$	76	Trace	48% ArCH=CHAr (trans)	Traces
5	Li_2PdCl_4	$i\text{-}C_4H_8$	$(CH_3)_2CO\text{-}H_2O$	63	4	25% $ArCH=C(CH_3)_2$, 20% $ArCH(OH)CH(CH_3)_2$	Traces
6	Na_2PdCl_4[b]	$c\text{-}C_5H_8$	EtOH	58	Trace	28% Ar—⬠ + isomers	Traces
7	Na_2PdCl_4[b]	$c\text{-}C_6H_{10}$	EtOH	71	Trace	22% Ar—⬡ + isomers	Traces
8	Na_2PdCl_4[b]	$PhCH=CH_2$	CH_3OH	66		47% ArCH=CHPh (trans)	17% $PhCH(CH_3)OCH_3$, 44% $PhCH_2CH(OCH_3)_2$
9	Li_2PdCl_4[b]	$Ph_2C=CH_2$	Dioxane-H_2O	91		33% $ArCH=CPh_2$	1.7% Ph_2CO, traces
10	Na_2PdCl_4	$CH_3C≡N$	$CH_3CN\text{-}H_2O$	80	18	14% $ArCOCH_3$	Traces
11	Li_2PdCl	$PhC≡N$	$PhCN\text{-}H_2O$	100	Trace	4% ArCOPh	68% $PhCONH_2$

[a] 0.01 mol of Pd salt and 0.05 mol of olefin in 20 ml of solvent were added dropwise to the boiling solution of 0.01 mol of the sulfinate (20 ml). Gaseous olefins and CO were introduced continuously at 1 atm. [b] In the presence of 0.001 mol of $HgCl_2$.

subsequently formed during the aqueous–acidic work-up (eq 3).

$$ArPdCl + R\text{—}C≡N \longrightarrow Ar\text{—}C\underset{N\text{—}PdCl}{\overset{R}{\diagup}} \xrightarrow{H_2O} ArCOR \quad (3)$$
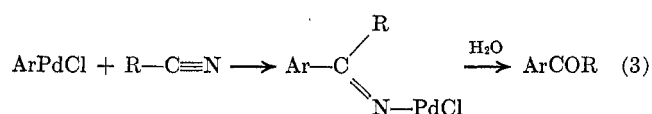
Experimental Section

All chemicals were of reagent grade quality and used without further purification. The sulfinates were obtained from K & K Laboratories. Experimental procedures are given in the Tables. Additions of one reagent to another took 1–6 hr and were followed by a reflux period of 1–16 hr. Conversions were not affected by the duration of the reactions. Work-up consisted

of removal of the solution from the palladium metal precipitate, extraction of organic products into ether, washing, drying, and evaporation of the ether. The products were analyzed by glpc on a 2-ft column of 20% SE-60 (silicon rubber) on Chromosorb W, at 100° + 15°/min to 290° with 30 cc of He/min. Samples of pure products (of Table III) were obtained by recrystallization, distillation, and/or preparative glpc and identified by melting point, ir and nmr spectra, and mass determination. The identity of chromatographically pure biaryls was confirmed by melting point, mixture melting point, ir and nmr spectra. In addition,

the purity of p,p'-bitolyl was proved by glpc on a 15-ft column of 5% Apiezon N on Chromosorb W, operated at 225° with 60 cc of He/min, which separated all $C_{14}H_{14}$ isomers. Conversions were based on palladium salt and obtained from glpc peak areas.

Stereochemistry of Amine Additions to Acetylenic and Allenic Sulfones and Sulfoxides

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Additions of ethylenimine to *nonterminal* acetylenic sulfones and sulfoxides ($RC\equiv CSO_2R'$ and $RC\equiv CSOR'$) proceed nonstereoselectively to give mixtures of conjugated adducts. Allenic sulfones and sulfoxides react with ethylenimine to give the nonconjugated adducts, which do not isomerize under the reaction conditions to the conjugated adducts. A solvent effect and a temperature effect show the *trans* addition process to be kinetically favored and the *cis* process to give the more stable *trans* adduct. Both the R and R′ groups in $RC\equiv CSO_2R'$ affect the *cis–trans* ratio of adducts in the ethylenimine additions. Theories to explain these results are given.

Several years ago, a study in this laboratory of the stereochemistry of additions of amines to acetylenic sulfones and carboxylic esters was reported.[1] This and other work in the area of amine additions to activated acetylenes registered over the last few years, was facilitated by the utility of nmr analysis for configurational determinations[1–3] and the unique advantage of ethylenimine as a nucleophile in producing adducts which resist *cis–trans* isomerization under the reaction conditions.[1,3,4] For example, ethylenimine adds to p-tolylsulfonylacetylene giving ≥95% *cis*-1-ethylenimino-2-(p-tolylsulfonyl)ethene (eq 1) while simple

$$HC\equiv CSO_2Ar + \underset{}{\triangleright}NH \longrightarrow$$
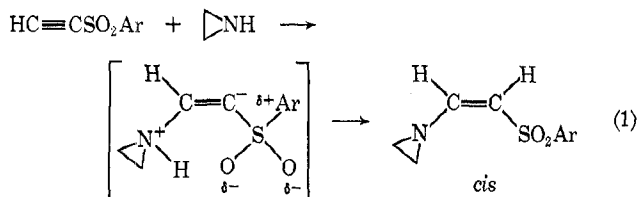
secondary amines as well as primary amines give the *trans* adduct *via* isomerization of the initially produced *cis* isomer.

Ethyl and methyl propiolate undergo nonstereoselective addition with ethylenimine giving both *cis* and *trans* adducts.[1,3,4] It was suggested[1] that the ethyl propiolate–ethylenimine addition involves the formation of a dipolar intermediate which has a linear resonance stabilized carbanion center (eq 2). Protonation from

$$HC\equiv CCO_2Et + \underset{}{\triangleright}NH \longrightarrow$$
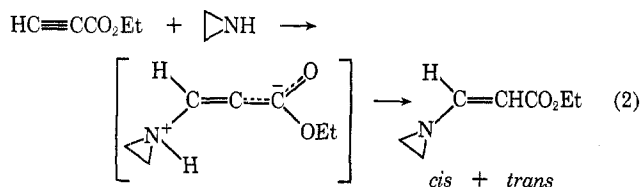
either side accounts for the nonstereoselectivity of the addition. It was proposed that the p-tolylsulfonyl-

acetylene–ethylenimine intermediate has an angular carbanion center with the *cis* configuration being stabilized by electrostatic and/or hydrogen-bonding forces (eq 1), thereby accounting for predominant *trans* addition.

Results and Discussion

Amine additions to *nonterminal* acetylenes of the form $RC\equiv CZ$ (where R = CH_3 and CH_2CH_3 and Z = SO_2Et, $SO_2C_6H_4CH_3$-p, and SOEt) needed careful examination and constitute part of the basis for this report. In the nonstereoselective reaction, there was the possibility that isomerization and subsequent addition to the allene, $CH_2=C=CHSO_2Et$, was competing

$$\underset{}{\triangleright}NH + CH_3C\equiv CSO_2Et \longrightarrow$$
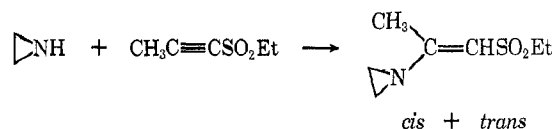
with addition to the conjugated acetylene.[1,2] Hence the nature of additions of ethylenimine to two allenic sulfones and an allenic sulfoxide as well as two propargyl sulfones and one propargyl sulfoxide was studied and is described herein.

Allenic sulfones have been prepared by isomerization of the propargyl sulfones with either triethylamine or basic alumina.[2,5] Allenic sulfoxides have not been reported, but we have found them to be accessible also in this manner (eq 3). The propargyl and 1-propynyl

$$HC\equiv CCH_2SOEt + Al_2O_3 \xrightarrow{CH_2Cl_2} CH_2=C=CHSOEt \quad (3)$$
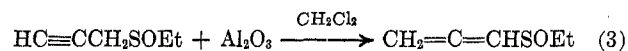
sulfoxides were prepared by oxidation of the corresponding sulfide with 1 equiv of sodium metaperiodate or 1 equiv of *m*-chloroperbenzoic acid.

Addition of ethylenimine to the allenic and propargylic sulfones and sulfoxides led to the formation of the nonconjugated adduct, by 1,2 addition to the allene directly or through initial isomerization of the

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(4) R. Huisgen, B. Giese, and H. Huber, *Tetrahedron Lett.*, 1883 (1967).

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