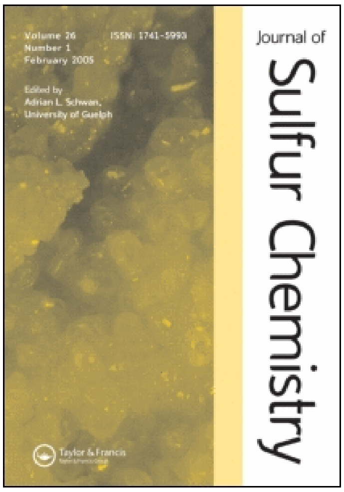

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Azosulfones: Versatile Precursors for Aryl Radicals, Aryl Cations, Aryl Anions, Carbenes, and Benzynes

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AZOSULFONES: VERSATILE PRECURSORS FOR ARYL RADICALS, ARYL CATIONS, ARYL ANIONS, CARBENES, AND BENZYNES

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The preparation, physical properties, and reactions of arylazo aryl sulfones are described. The mechanism of the decomposition of arylazo aryl sulfones is discussed. Arylazo aryl sulfones afford aryl cations, aryl radicals, and aryl anions under strongly acidic, weakly basic, and strongly basic conditions, respectively. Carbenes are formed from alkenylazo sulfones while cyclic azosulfones such as 1,2,3-benzothiazole 1,1-dioxides, afford benzynes. Tosylazocyclohexene reacts with enamines to give [2 + 3] cycloadducts.

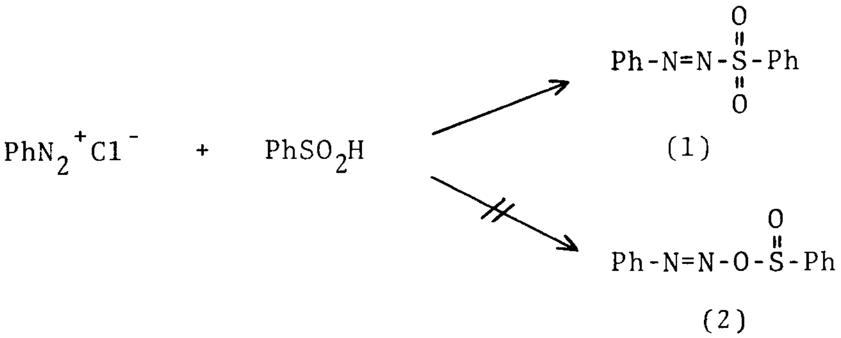
INTRODUCTION

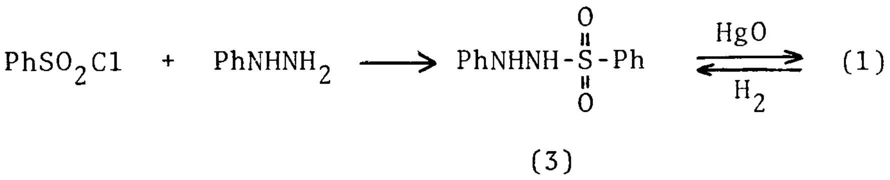
Sulfonyl diimides or azosulfones with the general formula $RSO_2N{=}NR'$ show a variety of reactions depending on the reaction conditions. For instance, arylazo aryl sulfones, the earliest known members of this family of compounds, can be used to generate aryl cations, aryl anions, or aryl free radical by proper choice of the reaction conditions. Alkenylazo sulfones afford carbenes and some cyclic azosulfones such as 1,2,3-benzothiazole 1,1-dioxides, yield benzynes. Thus, azosulfones are versatile precursors of these reactive intermediates and constitute a powerful tool in synthetic organic chemistry.

This short review describes the preparation, physical properties, and reactions of azosulfones. Industrial uses of the azosulfones such as the initiation of radical polymerization,[1] film coating,[2] and coupling in diazo copying[3] are not included.

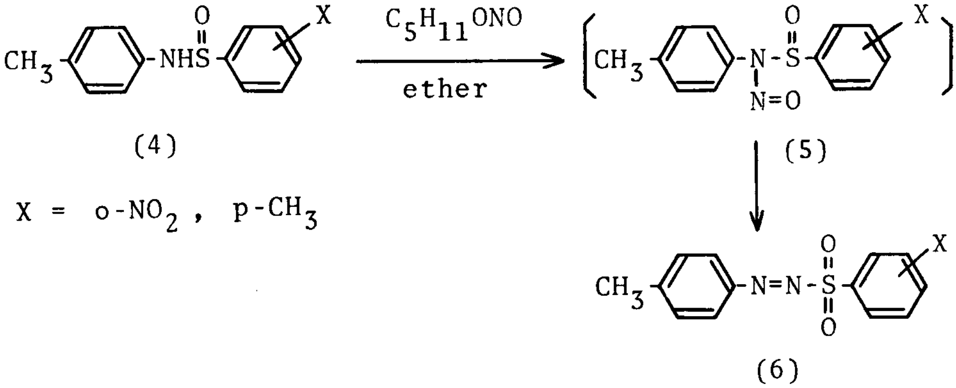
I. PREPARATION OF AZOSULFONES

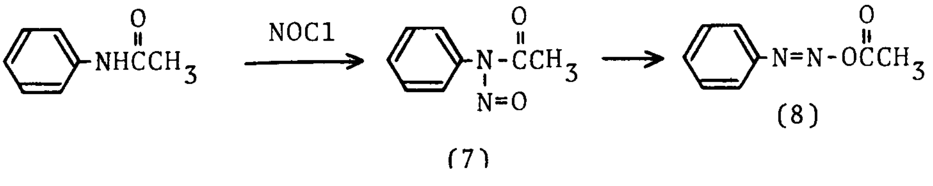
In 1887, Koenigs first prepared phenylazo phenyl sulfone (1) by reaction of benzenediazonium ion with benzenesulfinic acid.[4] The structure assigned was not that of the sulfinate (2)' but of the sulfone (1) since (1) could also be obtained by oxidation of *N*-benzenesulfonyl-*N'*-phenylhydrazine (3) with mercury (II) oxide and could be reduced to (3).



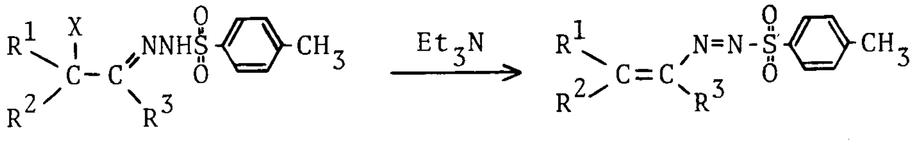


Coupling of diazonium salts with sulfinates and the oxidation of sulfonylhydrazines are still the major general synthetic methods for azosulfones. Meerwein *et al.*[5] obtained the azosulfones (6) by reaction of sulfinamides (4) with amyl nitrite in ether. The mechanism of this reaction involves most likely the formation of the *N*-nitrososulfonamide (5) as an intermediate which in turn rearranges to an azosulfone, similar to the formation of phenyl diazoacetate (8) from *N*-nitrosoacetanilide (7).[6]



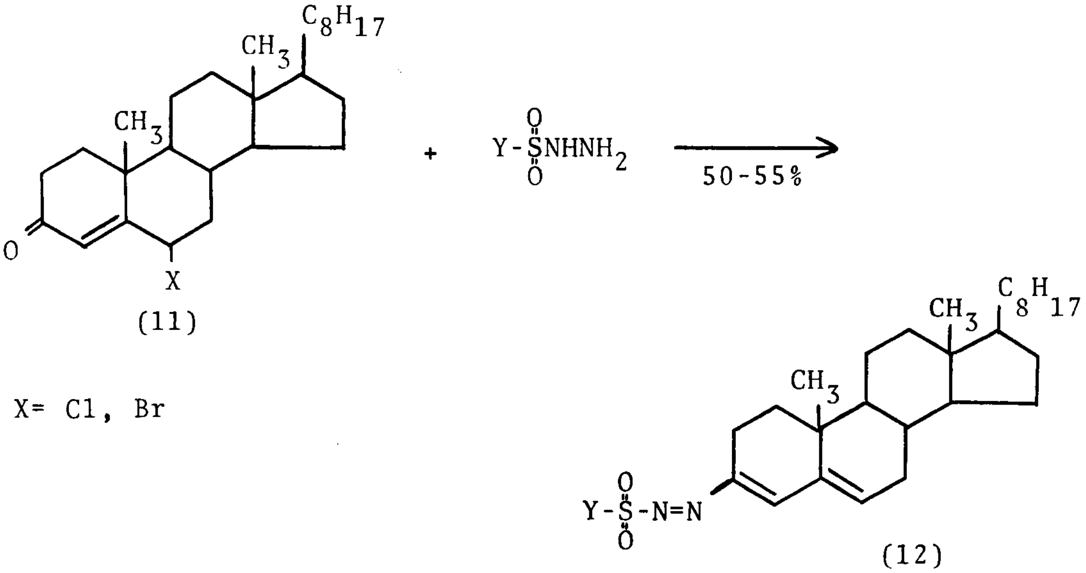


The tosylazoalkenes (10) have been prepared by dehydrohalogenation-rearrangement of the *N*′-(*p*-tolylsulfonyl)-hydrazones (9) with triethylamine.[7]



(9) (10)

Similarly, the conjugated sulfonylazo alkenes (12) and (14) have been prepared[8,9] from (11) and (13), respectively.

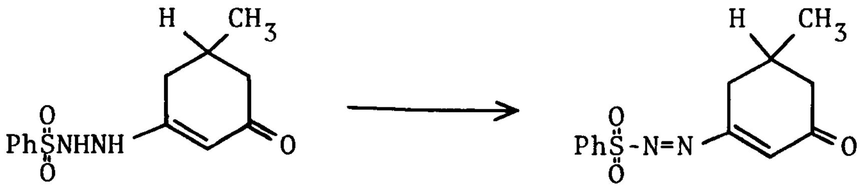


(11)

X= Cl, Br

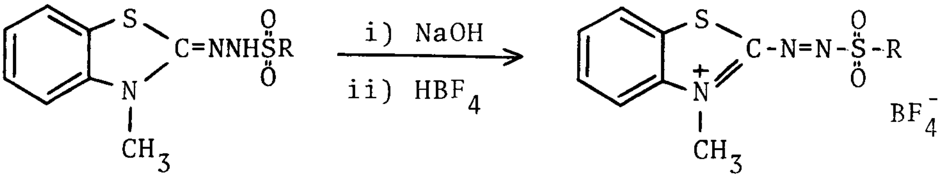
(12)

			mp (°C)
a:	Y=	CH_3	90
b:	Y=	C_6H_5	160
c:	Y=	p-$CH_3C_6H_4$	115
d:	Y=	p-ClC_6H_4	104.5



(13) (14)

The quaternary heterocyclic azosulfones (16) were prepared from the 3-methyl-2-benzothiazolinone hydrazones (15) by successive treatment with sodium hydroxide and tetrafluoroboric acid.[10]



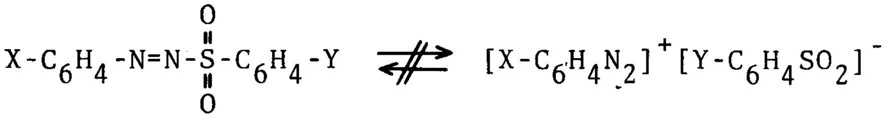
(15) (16)

R	Yield(%)	mp(°C)
CH_3	86	129
Ph	88	182

The azosulfones prepared by these methods are summarized in Tables I and II.

II. STRUCTURE OF ARYLAZO ARYL SULFONES

Azosulfones are covalent compounds and some evidence against any appreciable isomerism between azosulfone (17) and diazonium sulfinate (18) has been presented.[14]



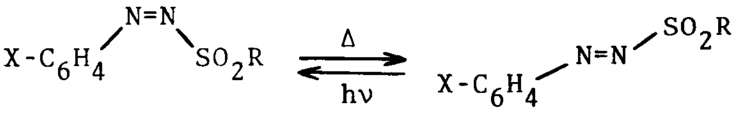
$$X\text{-}C_6H_4\text{-}N{=}N\text{-}\overset{O}{\underset{O}{S}}\text{-}C_6H_4\text{-}Y \;\not\rightleftarrows\; [X\text{-}C_6H_4N_2]^+[Y\text{-}C_6H_4SO_2]^-$$

(17) (18)

$X = Y = o\text{-}NO_2$

However, in methanol, as Ritchie, Satiel, and Lewis have demonstrated,[15] arylazo aryl sulfones are in equilibrium with the corresponding diazonium and sulfinate ions (X = m-Cl, p-Cl, p-Br, p-CH_3, H, m-CF_3, p-CN, p-NO_2; Y = H, p-CH_3, p-Br, m-NO_2, p-NO_2).

The dipole moments and the electronic spectra of arylazo aryl sulfones have been reported (Table III).[16] Azosulfones are in general considered to adopt the transoid geometry. A recent study by flash spectroscopy of a solution of (19) established the existence of a reversible cis-trans isomerization, and the first-order rate constants for this isomerization have been determined.[17] As shown in Table IV the rate depends strongly on the substituents.



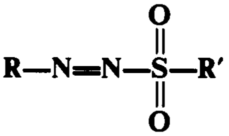
(19a) (19b)

III. KINETIC STUDIES OF THE THERMAL DECOMPOSITION OF AZOSULFONES

Kinetic studies of the thermal decomposition of aryl, benzyl, and methyl arylazo sulfones have been reported by several groups.

TABLE I

Arylazo Aryl Sulfones



$R{-}N{=}N{-}S(=O)_2{-}R'$ (1)

R	R′	mp(°C)	reference
Ph	o-NO_2—C_6H_4	76	5
Ph	p-Me—C_6H_4	85	5
Ph	p-MeO—C_6H_4	125	5
2,5-$(OEt)_2$-4-PhCONH—C_6H_2	p-MeCONH—C_6H_4	110	11
Ph	p-Me—C_6H_4	83	12
2,4-Me_2—C_6H_3	p-Me—C_6H_4	90	12
p-MeO—C_6H_4	p-Me—C_6H_4	94	12
1-$C_{10}H_7$	p-Me—C_6H_4	102	12
2-$C_{10}H_7$	p-Me—C_6H_4	112	12
Ph	2-$C_{10}H_7$	86	12
p-MeO—C_6H_4	2-$C_{10}H_7$	94	12
p-Me_2N—C_6H_4	p-Me—C_6H_4	130	13
p-MeO—C_6H_4	p-Me—C_6H_4	110	13
p-Me—C_6H_4	p-Me—C_6H_4	96	5, 13
p-Cl—C_6H_4	p-Me—C_6H_4	118	13
p-NO_2—C_6H_4	p-Me—C_6H_4	135	13
m-MeO—C_6H_4	p-Me—C_6H_4	84	13
m-Me—C_6H_4	p-Me—C_6H_4	69	13
m-NO_2—C_6H_4	p-Me—C_6H_4	113	13
Ph	p-Me—C_6H_4	90	13
Ph	Ph	76	13
Ph	p-Cl—C_6H_4	94	13
Ph	m-NO_2—C_6H_4	89	13
o-NO_2—C_6H_4	p-Me—C_6H_4	85	5

III.1. Arylazo aryl sulfones

Rosenthal and Overberger investigated the thermal decomposition of phenylazo phenyl sulfone (1) in several solvents and found that the decomposition rates were accelerated by an acidic product or by addition of benzenesulfinic acid.[18] The autocatalyzed decomposition could be inhibited with calcium oxide suspended in the solvent. It was pointed out

TABLE II

Tosylazoolefins (10) from *N*-Tosylhydrazone (9)

Hydrazone (9)					
R^1	R^2	R^3	X	Yield (%)	mp (°C)
Br	Br	H	Br	26	91
Cl	Cl	CH_3	Cl	68	108
t-Bu	Cl	H	Cl	69	70
t-Bu	Br	H	Br	67	72
Ph	H	Ph	H	65	84
Ph	H	CH_2Ph	H	60	84
Ph	Ph	H	H	72	90
$—(CH_2)_4$		H	H	64	54

later that pyridine or quinoline is a much better inhibitor than calcium oxide.[19] The products of the thermal decomposition of (1) were studied (Table V) and their formation found to be consistent with a mechanism which involves the decomposition of (1) into a phenyldiazenyl and a benzenesulfonyl radical, radical attack on the solvent molecules, induced decomposition of (1) by the primary or the solvent derived radicals, and combination of all possible radicals.[20] Compound (1) initiates the polymerization of styrene, methyl methacrylate, vinyl acetate, and acrylonitrile, and under suitable conditions high-molecular weight polymers can be obtained.[21]

The rates of decomposition of phenylazo *p*-tolyl sulfone (20) were carefully determined in ethylbenzene, anisole, chlorobenzene, nitrobenzene, pyridine, and DMF in the presence of pyridine, and are shown in Table VI. The activation enthalpy and entropy are found

TABLE III

Dipole Moments and Electronic Spectra of Arylazo Aryl Sulfones (1)

$R—N{=}N—SO_2R'$				
R	R′	mp(°C)	λ_{max}(log ε)	μ(D)
Ph	Ph	78	295(4.1), 425(2.3)	4.20
o-$Cl—C_6H_4$	Ph	98	296(4.0), 435(2.35)	—
p-$Cl—C_6H_4$	Ph	107	295(4.4), 415(3.1)	4.39
p-$Br—C_6H_4$	Ph	115	280(4.1), 450(2.6)	4.40
p-$NO_2—C_6H_4$	Ph	136	260(4.8), 410(3.0)	4.76
2,4,6-$Br_3—C_6H_2$	Ph	121	260(3.8), 445(2.8)	4.59

TABLE IV

Rate Constants of the cis-trans Isomerization of Azosulfones[a]

$$(19a) \xrightleftharpoons[k_2]{k_1} (19b)$$

$X—C_6H_4—N{=}N—SO_2R$		λ_{max}(nm)				
			trans	cis	$k_1 \times 10^{-2}$	$k_2 \times 10^{-2}$
X	R	π-π*	n-π*	n-π*	(s^{-1})	(s^{-1})
p-Cl	*p*-Cl—C_6H_4	312	431	478	15.7	15.9
p-Cl	*p*-Me—C_6H_4	311	433	480	2.2	3.4
p-MeO	*p*-Cl—C_6H_4	348	422	475	250	213
p-Cl	$PhCH_2$	308	434	480	2.5	2.3
p-MeO	$PhCH_2$	345	428	485	19.3	19.8

[a] in dioxane

TABLE V

Decomposition Products of Phenylazo Phenyl Sulfone (1) in Benzene (78° C) and in *p*-Xylene (138° C)

Product	Yield (mol per mol of (1))	
	in Benzene	in *p*-Xylene
Benzene	(solvent)	0.20
Biphenyl	0.45	—
2,5-Dimethylbiphenyl	—	0.26
Azobenzene	0.02	—
N-Phenyl-*N'*-(*p*-biphenylyl)-diimide	0.005	—
Diphenyl disulfide	—	0.01
Phenyl sulfone	0.05	0.03
Diphenyl disulfone	—	0.022
Benzenesulfinic acid	0.27	0.013
Phenyl *p*-methylbenzyl sulfone	—	0.16
Nitrogen	0.85	0.95

TABLE VI

First-Order Rate Constants of the Decomposition of (20) in the Presence of Pyridine[a]

Temp, (°C) \ Solvent	Ethylbenzene	Anisole	Chlorobenzene	Pyridine	Nitrobenzene	DMF
	$k_1 \times 10^4$ (sec^{-1})					
80.0	1.32		0.49	0.49	0.67	0.59
85.4	1.97	0.79	1.08	1.04	1.16	1.11
90.6	5.06	1.51	2.52	1.79	2.24	3.78
93.1	5.92					
95.6		2.94	5.38	3.42	5.15	5.33
99.1		4.82				

[a] $[(1)]_0 = 0.05$ mol/l, $[\text{pyridine}]_0/[(1)]_0 = 2 \sim 4$ except for the decomposition in pyridine

to change remarkably with the solvent (Table VII). This is in striking contrast to the results reported concerning the thermal decomposition of 2,2′-azobisisobutyronitrile, in which the maximum difference between the activation parameters determined in several solvents is found to be $\Delta\Delta H^{\neq} = 1.78$ kcal/mol and $\Delta\Delta S^{\neq} = 4.96$ e.u.[21] An isokinetic relationship was found to hold for activation parameters in these solvents, and the isokinetic temperature β was estimated to be 88.6°C.[19] The decomposition of the arylazo aryl sulfones (17) was studied in chlorobenzene (in the presence of pyridine in order to suppress any acid catalysis) at 80–118°C, and found to follow first-order kinetics (Table VIII). An isokinetic relationship was found to hold between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ ($\beta = 101.0$°C) in this case, too. Substituents at the benzenesulfonyl group influence the rate very little, whereas substituents at the phenylazo group decrease the rates (especially electron-releasing substituents).[13]

TABLE VII

Activation Parameters for the Decomposition of (20) in the Presence of Pyridine

Solvent	$\Delta H^{\neq}$ (kcal/mol)	$\Delta S^{\neq}$ (e.u.)
Ethylbenzene	30.8	10.7
Pyridine	32.2	12.3
Nitrobenzene	32.6	14.1
Anisole	35.9	22.2
Chlorobenzene	39.4	32.8
DMF	39.6	34.4

TABLE VIII

Results of the Decomposition of Arylazo Aryl Sulfones in Chlorobenzene in the Presence of Pyridine

$X—C_6H_4—N{=}N—SO_2—C_6H_4—Y$		$k_1 \times 10^4$ (sec^{-1})							
		Temp (° C)						ΔH$^{\neq}$	ΔS$^{\neq}$
X	Y	80.0	85.4	90.6	95.6	99.4	102.7	(Kcal/mol)	(e.u.)
p-MeO	*p*-Me			0.697	1.38	2.24	4.21	39.4	30.0
p-Me	*p*-Me		0.638	1.41	2.85	4.07		38.7	29.9
p-Cl	*p*-Me		0.696	1.39	2.09	5.06		37.7	27.2
p-NO_2	*p*-Me		1.16	2.08	4.06	6.81		33.1	15.2
m-MeO	*p*-Me		0.797	1.51	2.84	6.13		37.1	25.9
m-Me	*p*-Me		0.961	1.66	3.45	6.72	10.8	38.1	28.5
m-NO_2	*p*-Me		0.897	1.58	3.12	5.48		33.7	16.5
H	*p*-Me	0.494	1.08	2.52	5.38			39.4	32.8
H	H	0.536	1.16	2.68	4.63			36.0	23.5
H	*p*-Me	0.494	1.08	2.52	5.38			39.4	32.8
H	*p*-Cl			2.07	4.14	6.93	10.86	36.5	24.5
H	*m*-NO_2		1.35	2.46	4.73	9.38		38.4	30.2
p-Me_2N	*p*-Me		1.13 (105.0°C)	2.17 (109.0°C)	5.36 (115.0°C)	7.23 (118.0°C)		41.8	33.5

TABLE IX

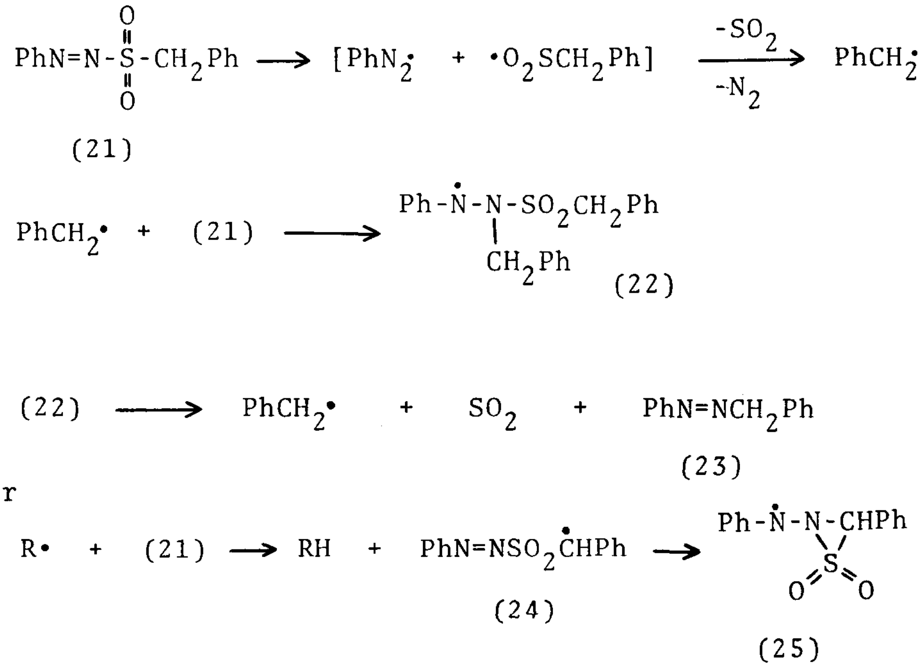
Thermal Decomposition Products of (22) in Non-Polar Solvents

Products	Yield (mol per mol of (21))		
	in Benzene[a]	in Cumene[b]	in Diphenylmethane[c]
Sulfur dioxide	0.66	0.57	0.80
Benzaldehyde phenylhydrazone	0.55	0.46	0.34
Benzaldehyde *N'*-benzyl *N'*-phenylhydrazone	0.06	0.12	0.16
Biphenyl	0.02	—	—
Azobenzene	<0.01	—	—
Toluene	0	0.01	0.05
Benzene	(solvent)	0.11	0.15

[a]at 55°C, [b]at 80°C, [c]at 80°C

III.2. Phenylazo benzyl sulfone

The thermal decomposition of phenylazo benzyl sulfone (21) has been examined[22] in benzene, cumene, and diphenylmethane the products being shown in Table IX. The following induced homolytic decomposition mechanism has been proposed:



$$PhN{=}N{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}CH_2Ph \longrightarrow [PhN_2^{\bullet} + {}^{\bullet}O_2SCH_2Ph] \xrightarrow[-N_2]{-SO_2} PhCH_2^{\bullet} + Ph^{\bullet}$$

(21)

$$PhCH_2^{\bullet} + (21) \longrightarrow Ph{-}\dot{N}{-}\underset{CH_2Ph}{\underset{|}{N}}{-}SO_2CH_2Ph$$

(22)

$$(22) \longrightarrow PhCH_2^{\bullet} + SO_2 + PhN{=}NCH_2Ph$$

(23)

or

$$R^{\bullet} + (21) \longrightarrow RH + PhN{=}NSO_2\dot{C}HPh \longrightarrow$$

(24)

(25)

$$(25) \longrightarrow SO_2 + \underset{(26)}{PhN{=}N{-}\dot{C}HPh}$$

$$(26) + (21) \longrightarrow PhN{=}N{-}SO_2\dot{C}HPh + PhNHN{=}CHPh + (23)$$

The first-order rate constants of the thermal decomposition of (21) have been determined spectrophotometrically in six solvents at 45–70°C using the free-radical scavenging technique with a stable Koelsch free radical (Table X).[23] The activation parameters in non-polar solvents such as benzene, toluene, anisole, and chlorobenzene were almost the same, but in the two polar solvents pyridine and nitrobenzene the activation entropies decreased significantly compared to those in the non-polar solvents (Table XI), indicating a strong solvation by pyridine or nitrobenzene of the transition state. Since the decomposition reaction of (21) is endothermic the transition state resembles the products (in this case the sulfonyl and the diazenyl radical) more than the starting material, according to the Hammond postulate.[24] The polar character of the transition state can be explained by contributions of the charge-transfer resonance form shown below.

TABLE X

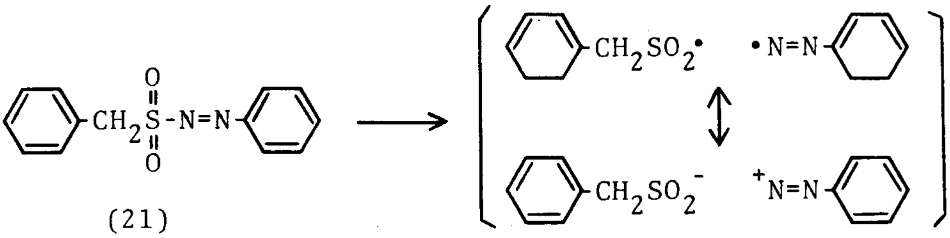
First-Order Rate Constants for Thermal Decomposition of Phenylazo Benzyl Sulfone (21) in Solutions (60°C)

Solvent	$k_1 \times 10^6$ (sec^{-1})
Benzene	17.9
Toluene	17.9
Anisole	10.4
Chlorobenzene	11.4
Pyridine	12.6
Nitrobenzene	3.01

TABLE XI

Activation Parameters for the Thermal Decomposition of (21) in Solutions

Solvent	H^{*} (Kcal/mol)	S^{*} (e.u.)
Benzene	34.8	23.9
Toluene	34.4	22.7
Anisole	35.7	25.6
Chlorobenzene	35.0	23.8
Pyridine	29.3	6.8
Nitrobenzene	30.7	8.2

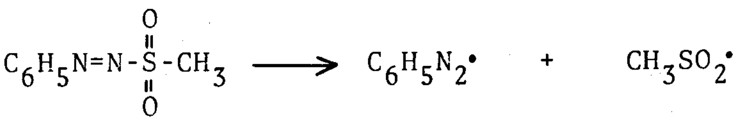


(21)

In the thermal decomposition of alkyl arylazo sulfides (alkyl—S—N=N—Ar), significant changes of the activation parameters with solvent have been observed[25] and explained by the formation of the ion pair, alkyl—S^- ^+N=N—Ar. An isokinetic relationship was found between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ ($\beta = 30°C$).

III.3. *Phenylazo methyl sulfone*

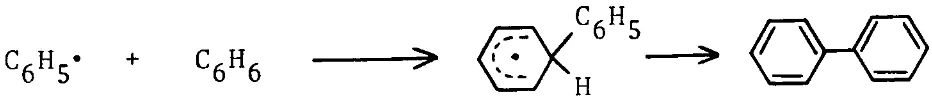
The thermal decomposition of phenylazo methyl sulfone (27) has been investigated in several solvents.[26] In the non-polar solvents benzene, cumene, and diphenylmethane the major decomposition products to be isolated (Table XII) are most easily interpreted as arising from the initial homolytic dissociation of (27) and free-radical intermediates.



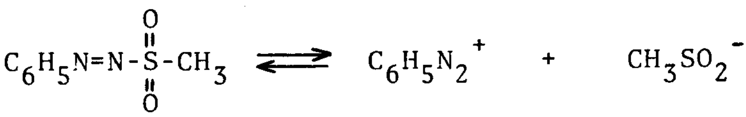
$$C_6H_5N{=}N{-}S(=O)_2{-}CH_3 \longrightarrow C_6H_5N_2\cdot + CH_3SO_2\cdot$$

(27)

$$C_6H_5N_2\cdot \longrightarrow C_6H_5\cdot + N_2$$



In the aprotic polar solvent acetonitrile, on the other hand, the principal decomposition product is thought to arise via an initial heterolytic dissociation of (27) into sulfinate and benzenediazonium ion and reaction of the latter with the solvent in the manner shown below.



$$C_6H_5N{=}N{-}S(=O)_2{-}CH_3 \rightleftharpoons C_6H_5N_2^+ + CH_3SO_2^-$$

(27)

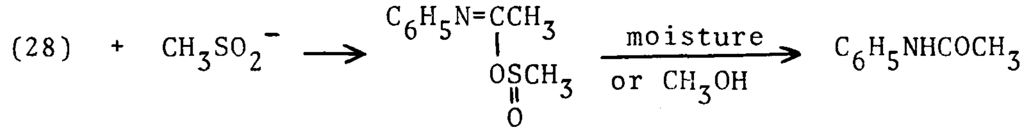
$$C_6H_5N_2^+ + CH_3CN \longrightarrow C_6H_5\overset{+}{N}{\equiv}CCH_3 + N_2$$

(28)

TABLE XII

Thermal Decomposition Products of (27) in Non-Polar Solvents

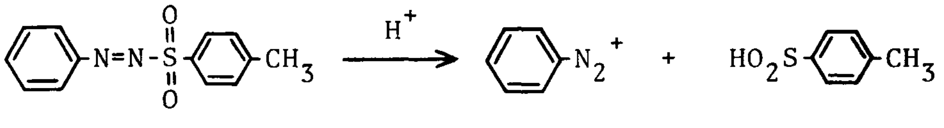
	Yield (mol per mol of (27))			
Product	Benzene	Benzene + CaO	Cumene	Diphenylmethane
SO_2	0.14	0.14	0.03	0.11
Biphenyl	0.26	0.32	—	—
Azobenzene	0.14	0.03	—	—
Benzene	(solvent)	(solvent)	0.24	0.23
$CH_3SO_3C_6H_5$	0.07	0.00	0.07	0.00
Bis-(methanesulfonyl)-phenylhydrazine	0.05	—	—	—
p-Phenylazobenzene	0.00	0.02	—	—
Benzhydryl methyl sulfone	—	—	—	0.11
sym-Tetraphenylethane	—	—	—	0.065
o- and *p*-Phenyldiphenyl methane	—	—	—	0.08
Bicumyl	—	—	0.12	—



$$(28) + CH_3SO_2^- \longrightarrow \begin{array}{c} C_6H_5N{=}CCH_3 \\ | \\ OSCH_3 \\ \| \\ O \end{array} \xrightarrow[\text{or } CH_3OH]{\text{moisture}} C_6H_5NHCOCH_3$$

III.4. Phenylazo p-tolyl sulfone

The decomposition of phenylazo *p*-tolyl sulfone (20) was studied in benzene in the presence of trifluoroacetic acid.[27] The decomposition is first-order, but becomes faster with increasing concentration of trifluoroacetic acid (Table XIII). The rate constants obtained under these conditions are much greater than those obtained under basic conditions (in the presence of pyridine, Table VI). The rate acceleration by addition of trifluoroacetic acid is ascribed to the ionic decomposition initiated by protonation to afford benzenediazonium ion and *p*-toluenesulfinic acid.



(20)

Actually, when trifluoroacetic acid was added to a benzene solution of (20), a new IR

TABLE XIII

First-Order Rate Constants for the Decomposition of Phenylazo *p*-Tolyl Sulfone (20) in C_6H_6—CF_3CO_2H

Temp. (° C)	$k_1 \times 10^4(sec^{-1})$[a]	Temp. (°C)	$k_1 \times 10^4(sec^{-1})$[b]
40.5	5.39	45.6	6.24
34.9	2.34	40.7	2.94
30.0	1.11	35.5	1.19
25.5	0.53		
Ea = 28.7 kcal/mol		Ea = 32.3 kcal/mol	
$\Delta S^{\neq}$ = 16.0 e.u.		$\Delta S^{\neq}$ = 26.1 e.u.	

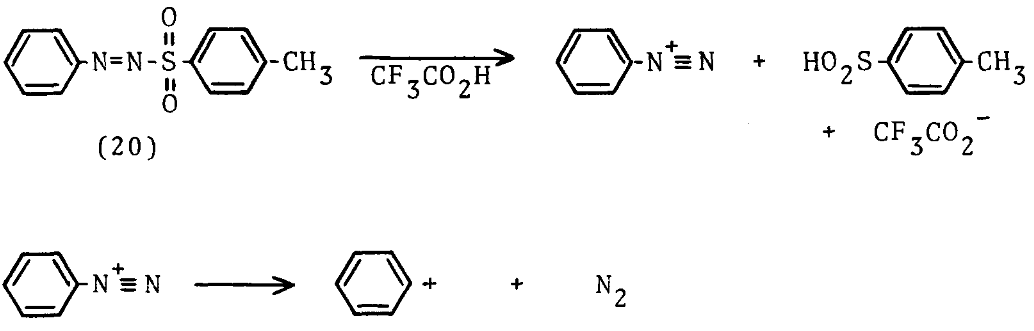
[a] $[(20)]/[CF_3CO_2H]$ = 5.89 mol/mol
[b] $[(20)]/[CF_3CO_2H]$ = 2.95 mol/mol

absorption corresponding to Ar—$N^+\equiv N$ was observed at 2280 cm^{-1} which gradually disappeared with evolution of nitrogen.

IV. REACTIONS OF AZOSULFONES

IV.1. Aryl cation formation

The reaction of (20) with substituted benzenes in the presence of trifluoroacetic acid gives biphenyl derivatives.[27] The partial rate factors for this arylation are quite different from those for the corresponding arylation with phenyl radicals generated by decomposition of benzoyl peroxide,[28] *N*-nitrosoacetanilide,[29] or phenylazotriphenylmethane,[30] and similar to those of the arylation with phenyl cations generated via benzenediazonium salts.[31] The results suggest that phenyl cations (28) are formed from (20) in very strongly acidic media.



(20)

(28)

X = OCH_3, CH_2CH_3, Cl, CO_2CH_3, NO_2

Since arylazo aryl sulfones are readily soluble in various solvents, including non-polar solvents, in contrast to the diazonium salts, they are a very useful source of aryl cations.

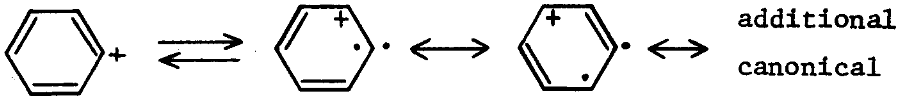
TABLE XIV

Partial Rate Factors For the Phenylation of Substituted Benzenes

		Phenylating Reagents				
X in PhX		(2) + CF_3CO_2H (40°C)	$PhN_2^+BF_4^-$ (40°C)	NAA[a] (20°C)	PAT[b] (60°C)	BPO[c] (80°C)
MeO	k_o/k	2.66	3.14	3.56	4.16	2.4
	k_m/k	0.18	0.68	0.93	1.44	0.7
	k_p/k	1.55	3.50	1.29	1.32	1.1
Me	k_o/k		1.32	3.7		2.5
	k_m/k		0.61	0.9		0.71
	k_p/k		1.84	1.1		1.0
Et	k_o/k	1.32	1.31		1.98	
	k_m/k	0.59	0.83		1.50	
	k_p/k	1.17	1.40		1.28	
Cl	k_o/k	0.61	1.02	3.09	3.83	1.6
	k_m/k	0.07	0.51	0.51	1.45	1.0
	k_p/k	0.35	1.17	1.48	2.32	1.2
CO_2Me	k_o/k	0.48	0.40		6.83	3.04
	k_m/k	0.41	0.40		1.03	0.93
	k_p/k	0.19	0.25		4.55	2.72
NO_2	k_o/k	0.07	0.29	9.38	9.58	5.5
	k_m/k	0.21	0.37	1.16	1.14	0.86
	k_p/k	0.03	0.21	9.15	3.04	4.9

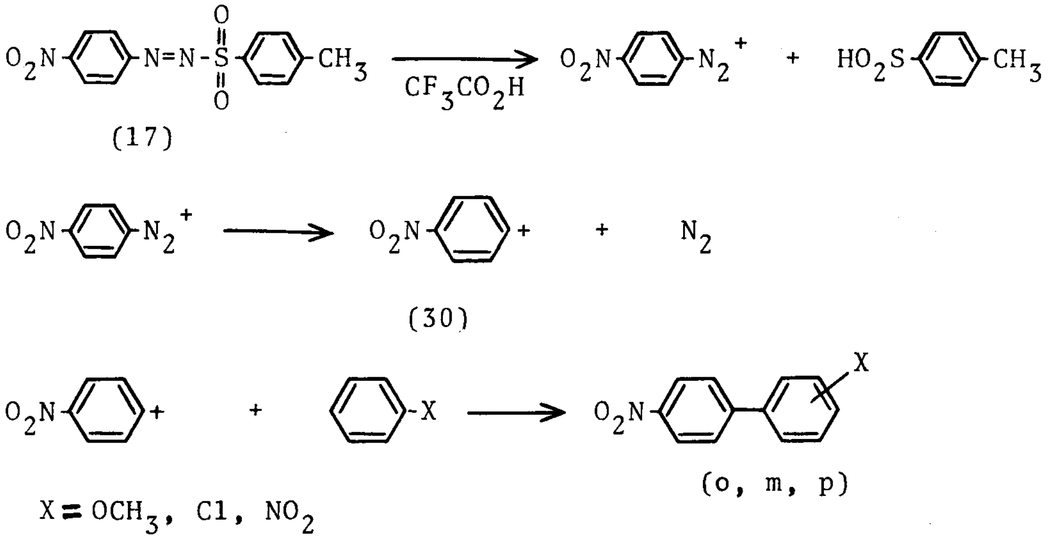
[a] *N*-Nitrosoacetanilide
[b] Phenylazotriphenylmethane
[c] Benzoyl peroxide

The partial rate factors for the meta and the para position shown in Table XIV are better correlated with σ^+ values than with σ values. However, the reaction constant ρ is very small ($\rho = -1.0$) compared to the ρ values for the usual electrophilic aromatic substitution reactions.[32] It has been suggested that the phenyl cation has a diradical cation structure (29) arising by transfer of one π-electron to the vacant sp^2 orbital.[31,33]



(28) (29a) (29b)

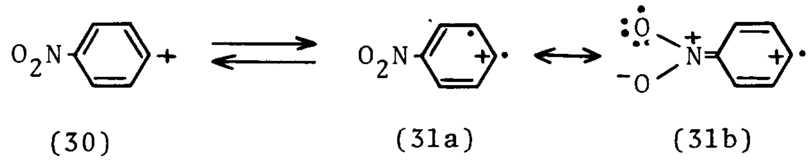
The arylation of substituted benzenes with *p*-nitrophenylazo *p*-tolyl sulfone (17) ($X = p\text{-}NO_2$, $Y = p\text{-}CH_3$) in the presence of trifluoroacetic acid has also been studied.[34]



(17)

(30)

The partial rate factors for the arylation show that the reaction is electrophilic (Table XV), and the results indicate formation of the *p*-nitrophenyl cation as the reactive intermediate. The fact that the *p*-nitrophenyl cation is more selective and less reactive than the phenyl cation in reactions with arenes may be explained as follows. If the phenyl cation and the *p*-nitrophenyl cation do not possess a diradical cation nature, the *p*-nitrophenyl cation would certainly be less stable and more reactive than the phenyl cation. On the other hand, if the *p*-nitrophenyl cation has a diradical structure, it may be stabilized by resonance as shown below and should be less reactive than the phenyl cation.



(30) (31a) (31b)

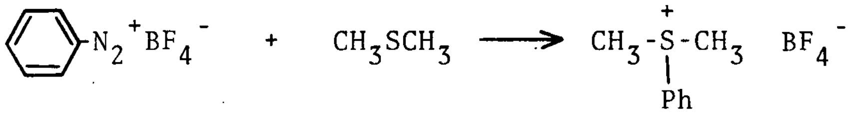
The reaction of benzenediazonium tetrafluoroborate with dimethyl sulfide to give dimethylphenylsulfonium tetrafluoroborate (32) suggests that the singlet phenyl cation is subject to nucleophilic attack by dimethyl sulfide.[35]

TABLE XV

Partial Rate Factors for the *p*-Nitrophenylation of Substituted Benzenes with *p*-Nitrophenylazo *p*-Tolyl Sulfone in the Presence of CF_3CO_2H at 60°C

X in PhX		*p*-Nitrophenylating Reagent	
		NPATS[a]	NNAA[b]
	k_o/k	3.97	5.17
MeO	k_m/k	0.51	0.84
	k_p/k	1.27	2.30
	k_o/k	1.46	1.53
Cl	k_m/k	0.53	0.65
	k_p/k	0.60	1.01
	k_o/k	0.88	0.93
NO_2	k_m/k	0.12	0.35
	k_p/k	0.13	1.53

[a] *p*-Nitrophenylazo *p*-tolyl sulfone and CF_3CO_2H
[b] *p*-Nitro-*N*-nitrosoacetanilide

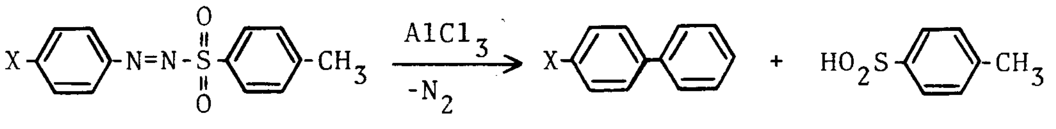


(32)

Ab initio molecular orbital calculations for the singlet ($^1A_1$) and triplet ($^3B_1$, $^3A_2$) states of the phenyl cation have been carried out by Schleyer *et al.*[36] The singlet cation is highly distorted with a C—C$^+$—C angle of 145°, while the triplet geometries are close to those of benzene. Gleiter, Hoffmann, and Stehrer concluded that the triplet diradical phenyl cation is less stable than the singlet state by molecular orbital calculations.[37] In substituted phenyl cations, the singlet state is best stabilized by σ-donors, but π-donors are also effective. The triplet state is expected to be stabilized by π-donors.

Recently, esr spectra of triplet aryl cations have been observed, and indicate that the lowering of the energy level of the triplet state (relative to the almost isoenergetic singlet level) to become the ground state is promoted by the presence of electron-releasing groups such as NR_2, OR, SR, and SAr. It was concluded that ab initio calculations cannot deal adequately with the subtlety of the effects responsible for the stabilization of triplet aryl cations.[38]

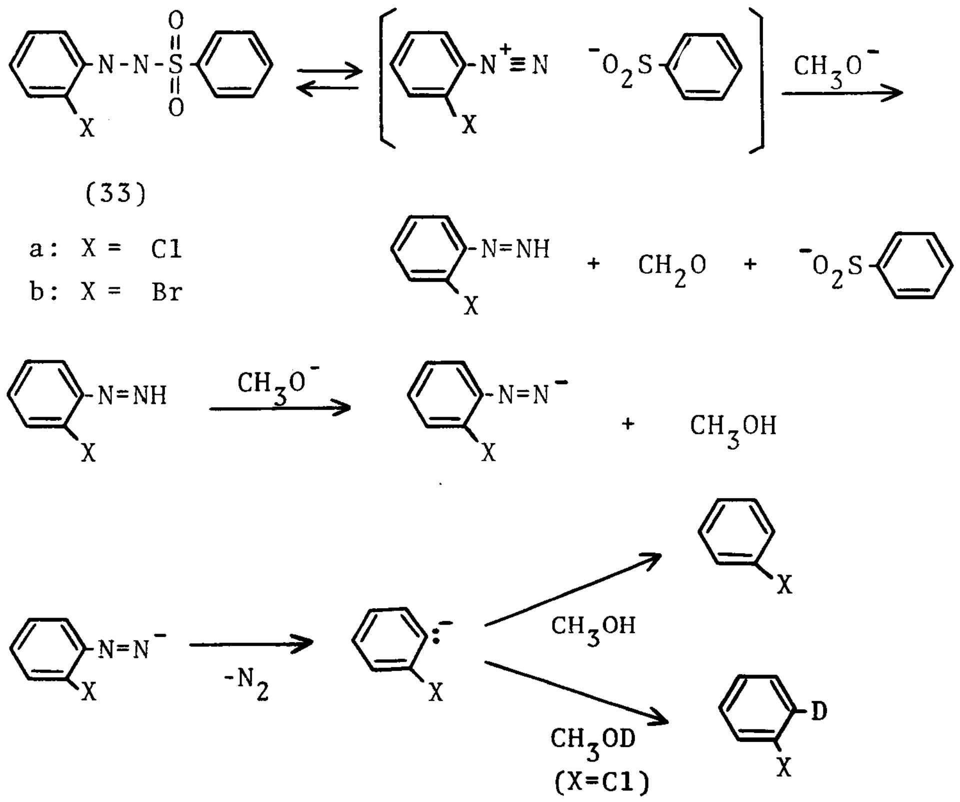
The reaction of arylazo *p*-tolyl sulfones (17) (X = H, CH_3, OCH_3, NO_2, CH_3CONCH_3, $(CH_3)_2N$; Y = CH_3) with benzene under the influence of $AlCl_3$ to give mainly biphenyls involves elimination of *p*-toluenesulfinic acid, followed by evolution of nitrogen.[39]



(17)

IV.2. Aryl anion formation

Bunnett and Happer reported that under strongly basic reaction conditions arylazo aryl sulfones form aryl anions.[40] When ortho-halophenylazo phenyl sulfones (33) were treated with 1.2 M sodium methoxide, halobenzenes were formed, and chlorobenzene-2-d (34) was obtained when *o*-chlorophenylazo phenyl sulfone (33b) was treated with a CH_3OD solution. A reaction mechanism via an *o*-halophenyl anion was postulated.



(33)

a: X = Cl
b: X = Br

However, in very dilute sodium methoxide solution the halobenzenes are considered to be formed by a radical mechanism, since the chlorobenzene formed in the reaction of (33a) in CH_3OD contained no deuterium.

IV.3. Aryl radical formation

IV.3.A. Arylation Thermal[19] and photochemical[41] phenylation of substituted benzenes with phenylazo *p*-tolyl sulfone (20) in the presence of pyridine has been studied. The partial rate factors for the phenylation shown in Table XVI are quite similar to those obtained

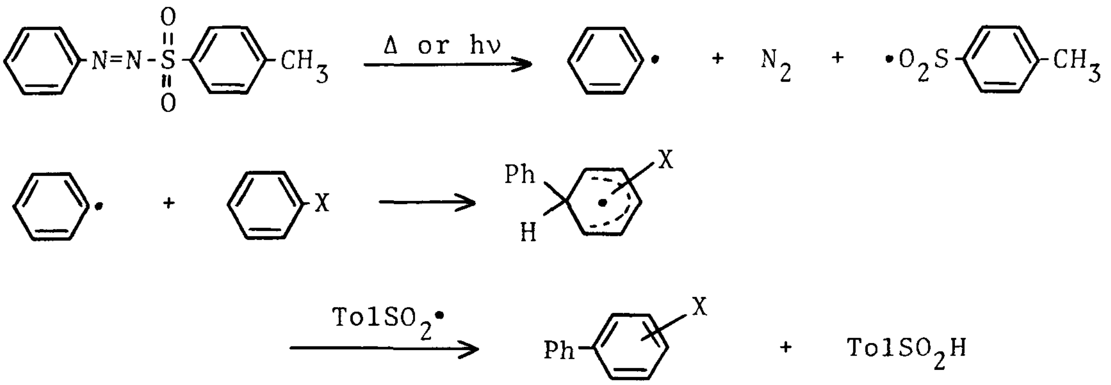
TABLE XVI

Partial Rate Factors for the Thermal and Photochemical Phenylation of Substituted Benzenes with (20) in the Presence of Pyridine[a]

	Thermal Reaction[b]			Photochemical Reaction[c]		
X in PhX	k_o/k	k_m/k	k_p/k	k_o/k	k_m/k	k_p/k
MeO	4.91	1.69	1.89	4.99	0.94	1.92
Et	2.00	1.33	1.49	2.41	1.30	1.37
Cl	3.32	1.31	2.16	2.95	1.06	1.42
CN	2.68[d]	1.16[d]	2.75[d]	3.64	1.46	4.37
NO_2	10.36	1.26	8.70	5.34	1.14	4.37

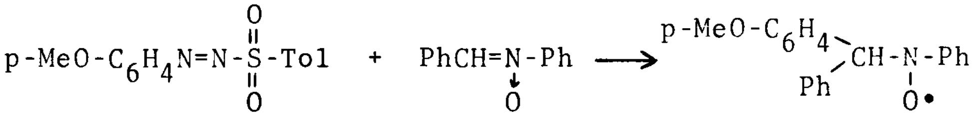
[a] [pyridine]/[(20)] = 2 ~ 8 mol/mol
[b] at 60°C
[c] at room temp.
[d] in the presence of calcium oxide

for phenyl radicals generated from benzoyl peroxide,[28] *N*-nitrosoacetanilide,[29] or phenylazotriphenylmethane[30] shown in Table XIV. The results indicate formation of phenyl radicals and *p*-toluenesulfonyl radicals, and the following mechanism for the phenylation with (20) has been proposed.



In the absence of base such as pyridine or calcium oxide the heterolytic cleavage of arylazo aryl sulfone is subject to autocatalysis by acidic products. Therefore, in order to ensure phenyl radical formation it is necessary to keep the reaction medium weakly basic.

IV.3.B. ESR ESR spectra of phenyl and sulfonyl radicals in the thermal and photochemical reaction of azosulfones (20) and (35) have been observed with a spin trapping technique using α,*N*-diphenyl nitrone (40) and 2-methyl-2-nitrosopropane (43) in benzene, and thus the hyperfine splitting constants could be determined.[42,43]



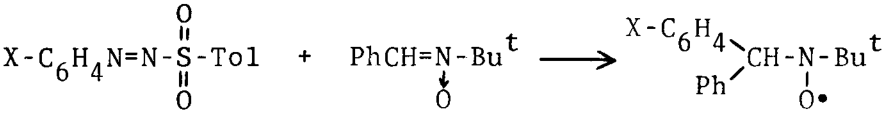
$$p\text{-MeO-}C_6H_4N{=}N\text{-}\overset{\displaystyle O}{\underset{\displaystyle O}{\overset{\|}{\underset{\|}{S}}}}\text{-Tol} + PhCH{=}\underset{\displaystyle O}{\underset{\downarrow}{N}}\text{-Ph} \longrightarrow \begin{matrix} p\text{-MeO-}C_6H_4 \\ Ph \end{matrix}\!\!>CH\text{-}\underset{\displaystyle O\bullet}{\underset{|}{N}}\text{-Ph}$$

(40) (41)

$A_N = 10.01$ $A_{o,p-H} = 2.51$

$A_{\beta-CH} = 3.41$ $A_{m-H} = 0.88$

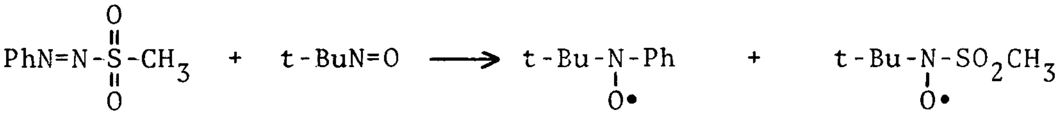
$g = 2.0056$



$$X\text{-}C_6H_4N{=}N\text{-}\overset{\displaystyle O}{\underset{\displaystyle O}{\overset{\|}{\underset{\|}{S}}}}\text{-Tol} + PhCH{=}\underset{\displaystyle O}{\underset{\downarrow}{N}}\text{-Bu}^t \longrightarrow \begin{matrix} X\text{-}C_6H_4 \\ Ph \end{matrix}\!\!>CH\text{-}\underset{\displaystyle O\bullet}{\underset{|}{N}}\text{-Bu}^t$$

(43) (42)

	X=H	X=p-MeO
A_N	13.93	13.91
$A_{\beta-CH}$	2.09	2.15
g	—	2.0061



$$PhN{=}N\text{-}\overset{\displaystyle O}{\underset{\displaystyle O}{\overset{\|}{\underset{\|}{S}}}}\text{-}CH_3 + t\text{-}BuN{=}O \longrightarrow t\text{-Bu-}\underset{\displaystyle O\bullet}{\underset{|}{N}}\text{-Ph} + t\text{-Bu-}\underset{\displaystyle O\bullet}{\underset{|}{N}}\text{-}SO_2CH_3$$

(35) (44) (45)

$A_N = 12.4$ $A_N = 12.9$

$A_{o,p-H} = 1.9$ $g = 2.0060$

$A_{m-H} = 0.9$

Recently, the ESR spectra of a series of alkane- and arenesulfonyl radicals produced by chlorine atom abstraction from the corresponding sulfonyl chlorides with triethylsilyl radicals or by UV irradiation of alkanesulfinic acids were observed directly.[44]

$$t\text{-BuO}\bullet + Et_3SiH \longrightarrow Et_3Si\bullet + t\text{-BuOH}$$

$$Et_3Si\bullet + RSO_2Cl \longrightarrow Et_3SiCl + RSO_2^\bullet$$

or

$$RSO_2H \xrightarrow{h\nu} RSO_2^\bullet + \bullet H$$

R: alkyl

The magnitudes of the proton hyperfine splitting in the alkanesulfonyl radicals

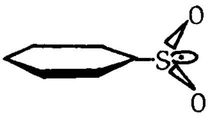
TABLE XVII

Hyperfine Splitting Constants of the Alkanesulfonyl Radicals Formed from Sulfonyl Chlorides at −40°C

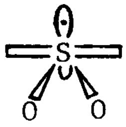
	Hyperfine Splitting Constants			
Sulfonyl radical	**α-H**	**β-H**	**γ-H**	**g**
$MeSO_2\cdot$	0.58			2.0049
$EtSO_2\cdot$	0.90	1.74		
n-$PrSO_2\cdot$	0.70	2.12	0.70	
n-$BuSO_2\cdot$	0.47	2.09	0.47	
n-$C_{16}H_{33}SO_2\cdot$	0.50	1.89	0.50	
i-$PrSO_2\cdot$	0.40	1.90		
t-$BuSO_2\cdot$		2.08		

$-\overset{\gamma}{C}H-\overset{\beta}{C}H-\overset{\alpha}{C}H-SO_2\cdot$ follow the unusual order $|a|(\beta-H) > |a|(\alpha-H) \simeq |a|(\gamma-H)$ as shown in Table XVII. The spin density in methanesulfonyl radical was determined from ^{33}S hyperfine interactions (Table XVIII).[45]

These features of the ESR spectra of sulfonyl radicals are interpreted in terms of a σ-structure of the type (46) in which the singly occupied orbital is in the plane of the benzene ring, rather than structure (47).



(46)



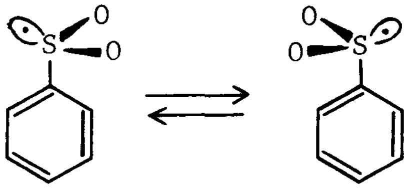
(47)

TABLE XVIII

Spin Densities on the Atoms of the $CH_3SO_2\cdot$ Radical

Atom	**Spin Density**
S (3s)	0.07
S (3p)	0.35
O (1)	≤0.29
O (2)	<0.29
C	~0
H	~0

The ESR spectra of arenesulfonyl radicals without ortho-substituents show that these radicals are subject to relatively rapid rotation around the C—S bond at all accessible temperatures, and the order of the magnitude of the proton hyperfine splitting is |a|(m—H) > |a|(o—H) > |a|(p—H) as shown in Table XIX.



IV.3.C. CIDNP studies Kobayashi and coworkers investigated the homolytic decomposition mechanism of azosulfones by CIDNP phenomena in ^{1}H and ^{13}C NMR.[46,47] There are two possible mechanisms for the homolytic cleavage of azosulfones: (a) one is the so-called "one-bond fission", i.e., the S—N bond cleavage occurs in the first step to give an arenediazenyl and sulfonyl radical pair, (b) the other is "two-bond fission", and in this case an aryl radical, nitrogen, and a sulfonyl radical form simultaneously.

$$\text{(a) Ar—N=N—SO}_2\text{Ar}' \rightleftharpoons \text{ArN=N}\cdot + \cdot\text{O}_2\text{SAr}'$$

$$\text{(b) Ar—N=N—SO}_2\text{Ar}' \longrightarrow \text{Ar}\cdot + \text{N}_2 + \cdot\text{O}_2\text{SAr}'$$

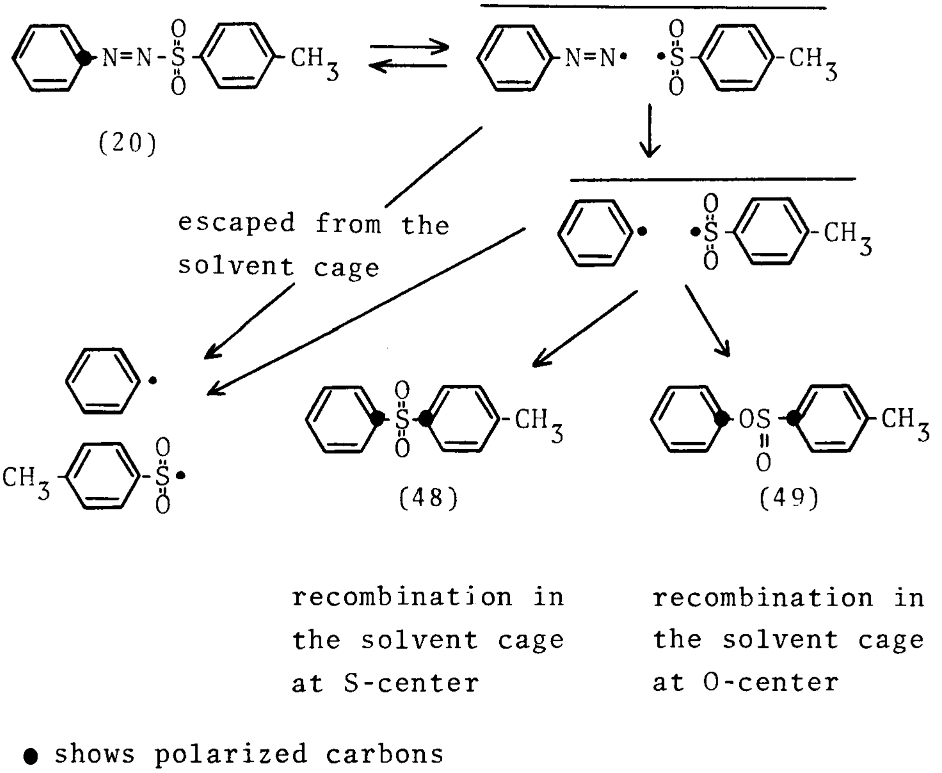
The CIDNP technique resolved this problem. The azosulfone (20), the sulfone (48), and the sulfinic acid ester (49) showed ^{1}H and ^{13}C CIDNP signals during the thermolysis of phenylazo *p*-tolyl sulfone (20) in tetrachloroethylene.[46] Since enhanced ^{13}C absorption of the azosulfone (20) was observed it was concluded that the decomposition of the azosulfone (20) is reversible and proceeds via one-bond fission. The observation of CIDNP of (48) and the sulfinic acid ester (49) means that the phenyldiazenyl radical decomposes to a phenyl radical and nitrogen, and that the sulfonyl radical is ambident and acts as either an *S*- or *O*-centered radical. The sulfinic acid ester (49) is unstable and cannot be isolated among the final products and thus its formation has never been observed. However, the

TABLE XIX

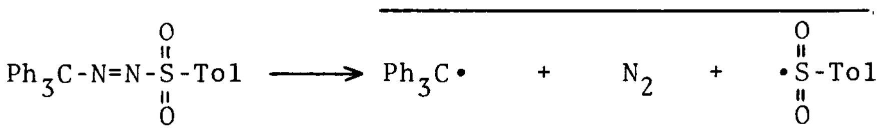
Hyperfine Splitting Constants of Arenesulfonyl Radicals ($ArSO_2\cdot$)

Ar	Hyperfine Splitting Constants			g
	a(*o*-H)	a(*m*-H)	a(*p*-H)	
Ph	0.33	1.13	0.52	2.0045
p-Me—C_6H_4	0.32	1.18	0.65	2.0045
p-Br—C_6H_4	0.31	0.95		2.0047
p-*t*-Bu—C_6H_4	0.28	1.03		2.0045
p-Cl—C_6H_4	0.32	0.96	0.12(^{35}Cl) 0.10(^{37}Cl)	2.0045

CIDNP technique proved the formation of the ester (49). The following mechanism is proposed:



Since the triphenylmethyldiazenyl radical releases nitrogen more readily as compared to the phenyldiazenyl radical, triphenylmethylazo aryl sulfones are predisposed to decompose by "two-bond fission." The thermal decomposition of triphenylmethylazo *p*-tolyl sulfone (50) has been studied by the CIDNP method.[47] In this case, the azosulfone (50) itself does not show any CIDNP signal, indicating two-bond fission of the azosulfone.

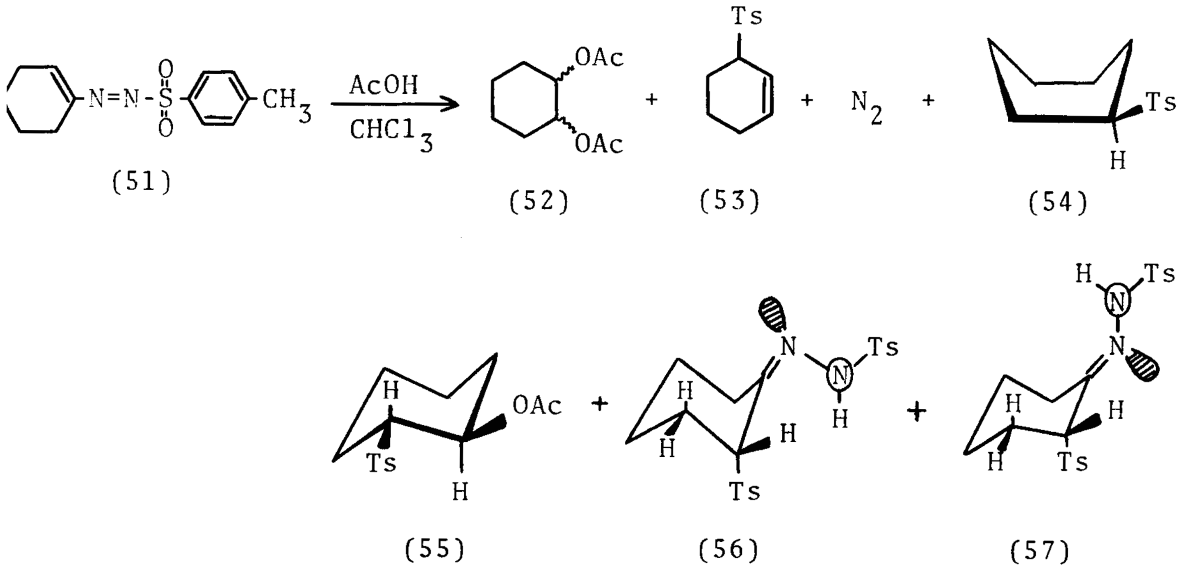


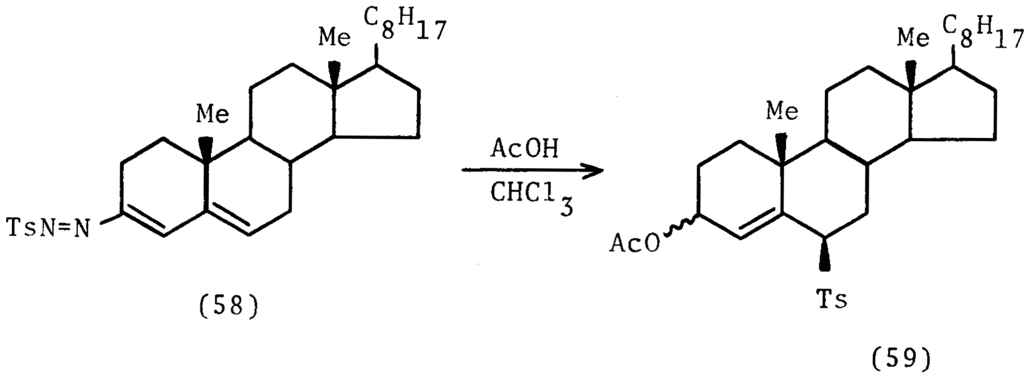
$$\underset{(50)}{Ph_3C\text{-}N{=}N\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\text{-}Tol} \longrightarrow \overline{Ph_3C\bullet + N_2 + \bullet\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\text{-}Tol}$$

(50)

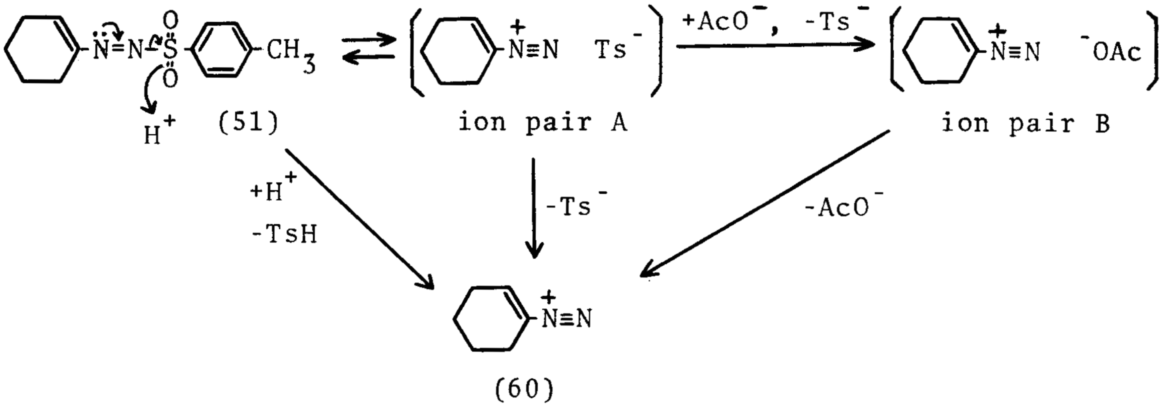
IV.4. Azosulfones as carbene precursors

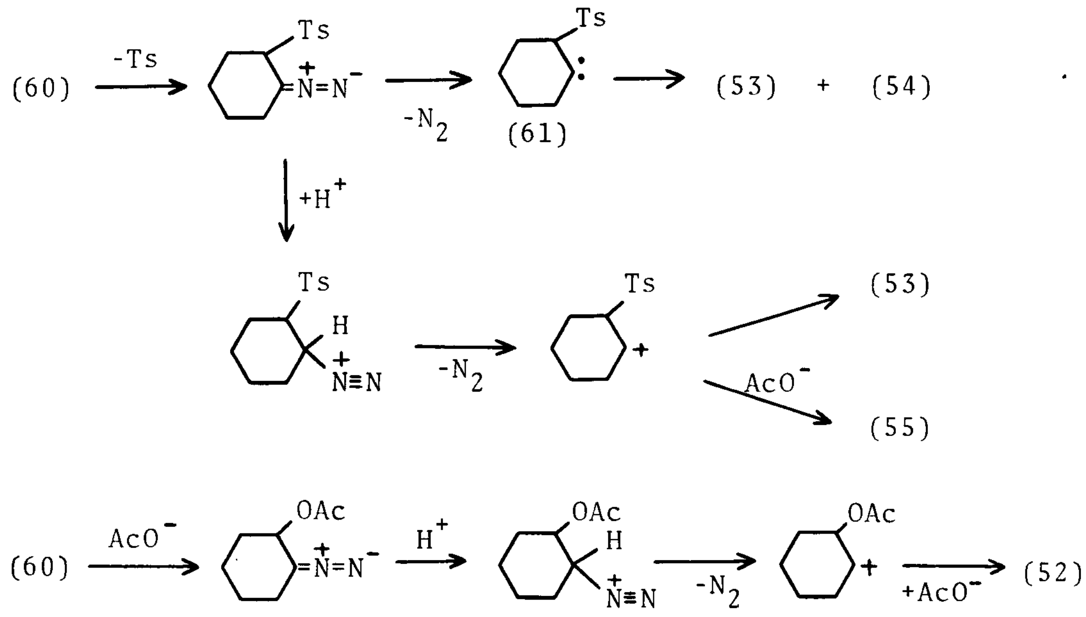
Treatment of 1-cyclohexenylazo *p*-tolyl sulfone (51) with acetic acid in chloroform at room temperature gives (52)–(57) with evolution of nitrogen, while the sole product 3-acetoxy-6*β*-tosylcholest-4-ene (59) was obtained from 3-tosylazocholesta-3,5-diene (58) under similar reaction conditions.[48]



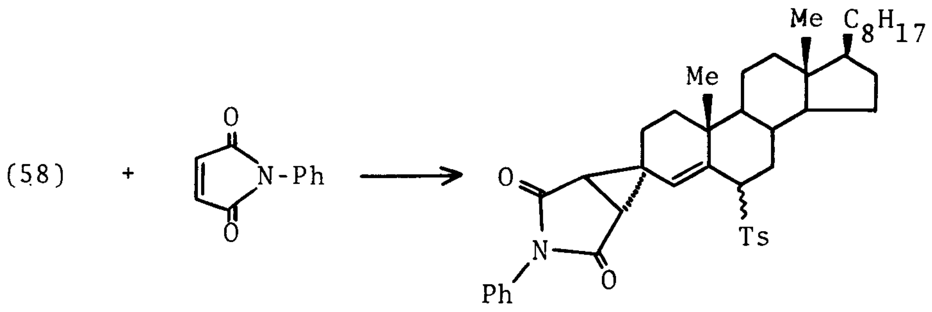


The following reaction mechanism for the formation of (52)–(55) has been proposed involving the 1-cyclohexenyldiazonium ion (60) and the carbene intermediate (61). The formation of (56) and (57) can be explained as a 1,4-addition of *p*-toluenesulfinate anion or *p*-toluenesulfinic acid to the azoenic system of compound (51).

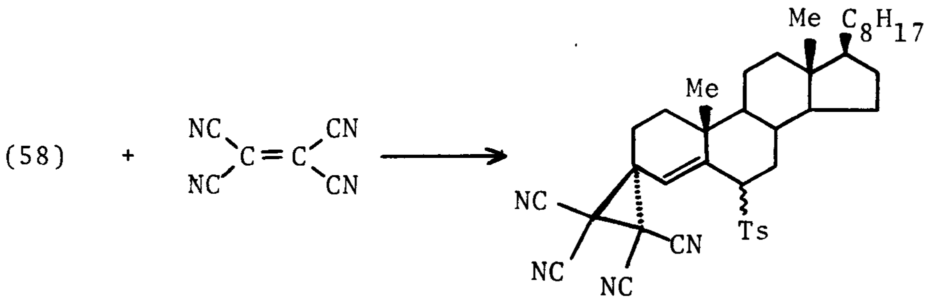




3-(*p*-Toluenesulfonylazo)cholesta-3,5-diene (58) reacts with *N*-phenylmaleimide or tetracyanoethylene in benzene at room temperature to yield the spirocyclopropane steroids (62) and (63), respectively.[49]

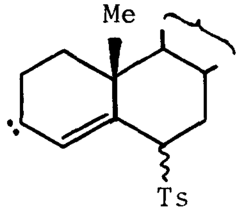


(62)



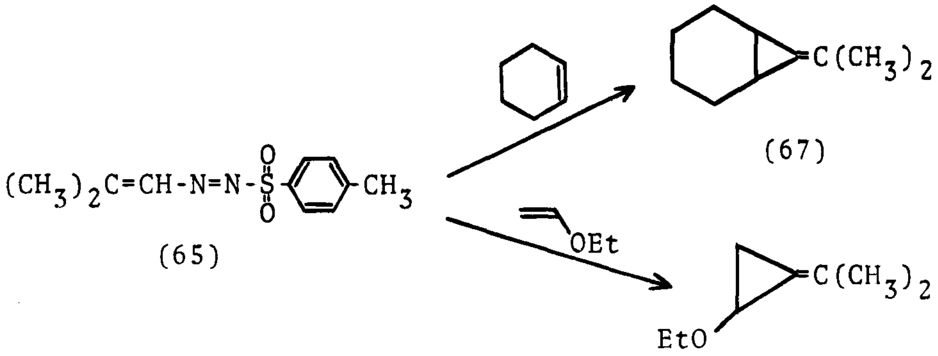
(63)

The carbene (64) has been postulated as an intermediate from (58).

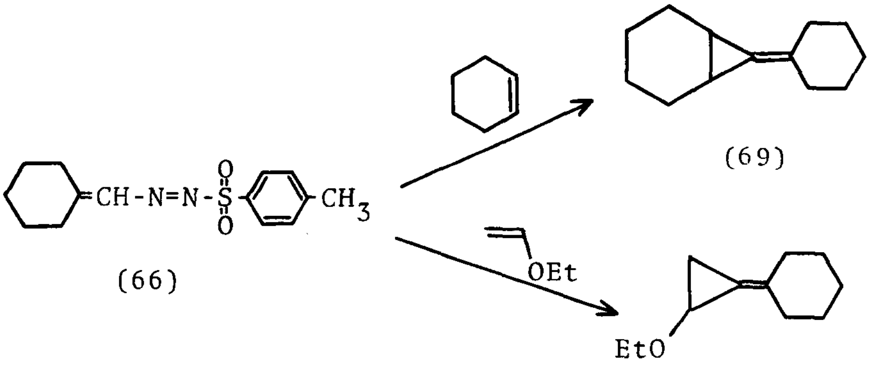


(64)

Recently the tosylazoalkenes (65) and (66) were prepared and their reactions with cyclohexene or ethyl vinyl ether gave (67), (68) and (69), (70), respectively.[50]

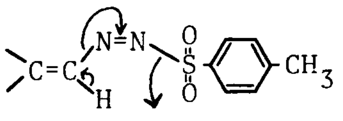


(65) (67) (68)

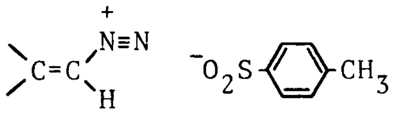


(66) (69) (70)

The adducts (67)–(70) are the products of the reaction of the unsaturated carbenes $R_2C{=}C$: or carbenoids with olefins and hence these reactions represent a simple, mild and presumably general method for the thermal generation of dialkyl-substituted unsaturated carbenes $R_2C{=}C$: albeit in moderate yield. Two reasonable mechanisms can be proposed: one involves a concerted rearrangement via a six-membered cyclic transition state (71), the other involves a possible diazonium ion pair (72).



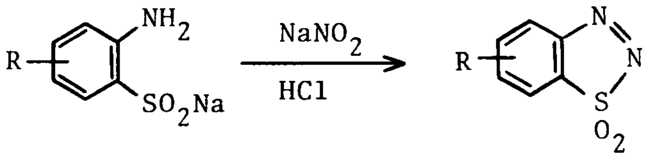
(71)



(72)

IV.5. Azosulfones as benzyne precursors

Wittig and Hoffmann prepared[51] cyclic azosulfones, the 1,2,3-benzothiadiazole 1,1-dioxides (73), by diazotation of the sodium salts of *o*-aminobenzenesulfinates (Table XX).



(73)

The heterocycles (73) are unstable and above 0°C rapid decomposition takes place. The dehydrobenzene derivative (74) is assumed as an intermediate formed from (73) by loss of

TABLE XX

1,2,3-Benzothiadiazole 1,1-Dioxides (73)

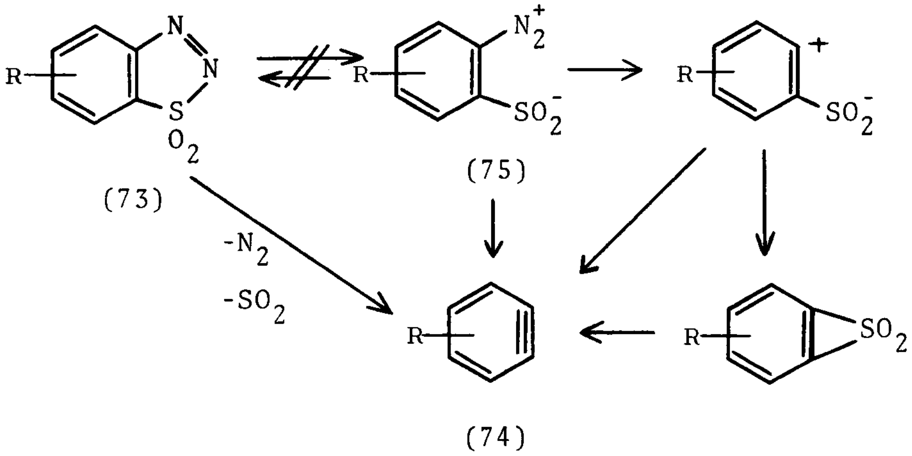
	R	Yield (%)		R	Yield (%)
a	H	85	f	5-Br	38
b	5-Me	82	g	6-Br	44
c	6-Me	79	h	5-MeO	17
d	5-Cl	45	i	6-NO_2	40
e	6-Cl	54			

TABLE XXI

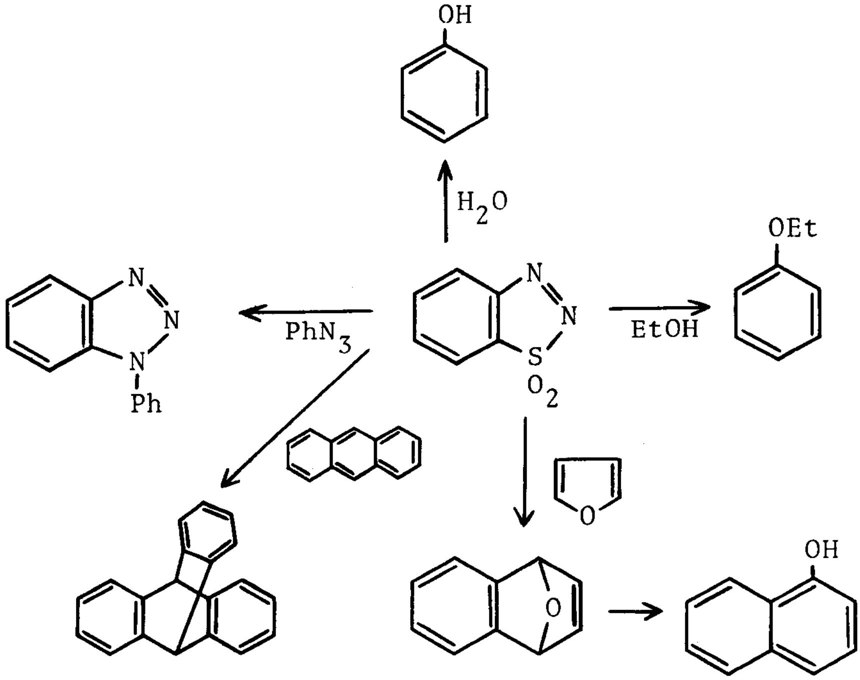
First-Order Rate Constants for the Decomposition of (73) in Benzene at 20° C

R	$k_1 \times 10^4$ (sec^{-1})
5-Me	2.75
5-Cl	3.82
5-Br	5.08
5-MeO	1.23
6-Me	1.19
6-Cl	1.39

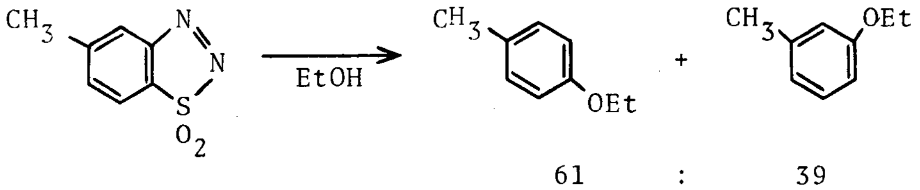
nitrogen and sulfur dioxide.[52] The compounds (73) are used widely as benzyne precursors. The kinetics of the decomposition of (73) has been investigated (Table XXI). The solvent, salt, and substituent effects are in agreement with a one-step decomposition, while the betain (75) which is in equilibrium with (73) probably does not participate directly in the decomposition.

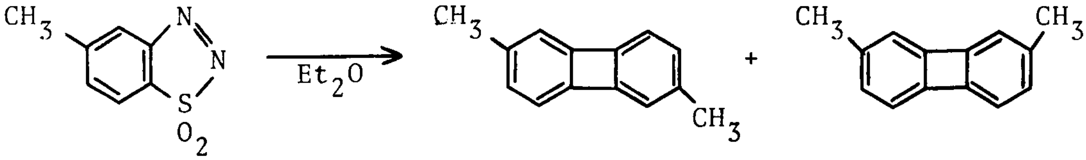


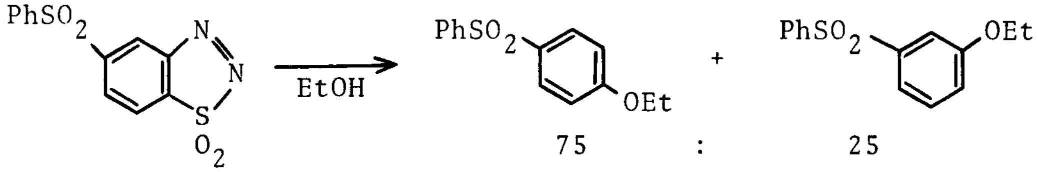
Reactions of (73) with various compounds have been reported,[53] and all products could be interpreted as arising via the benzyne intermediate (74).

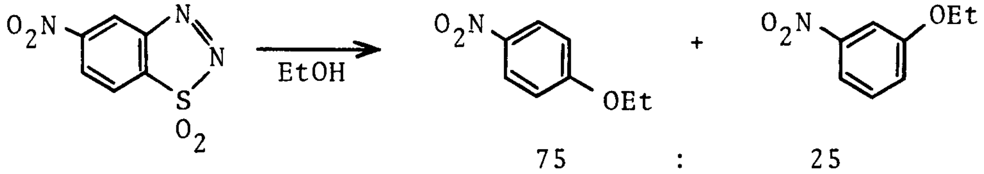


Substituted 1,2,3-benzothiadiazole 1,1-dioxides also afford benzynes and some examples are shown below.[54]



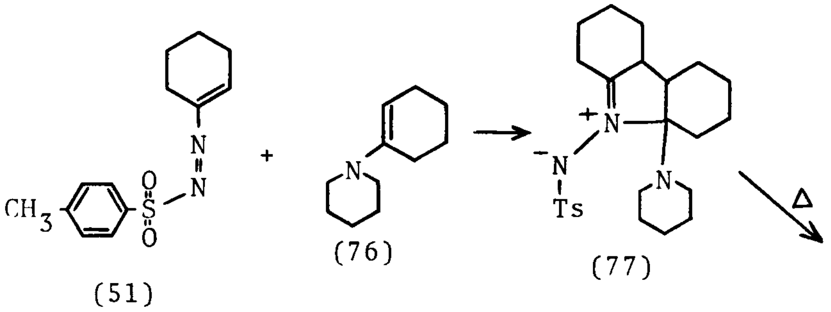




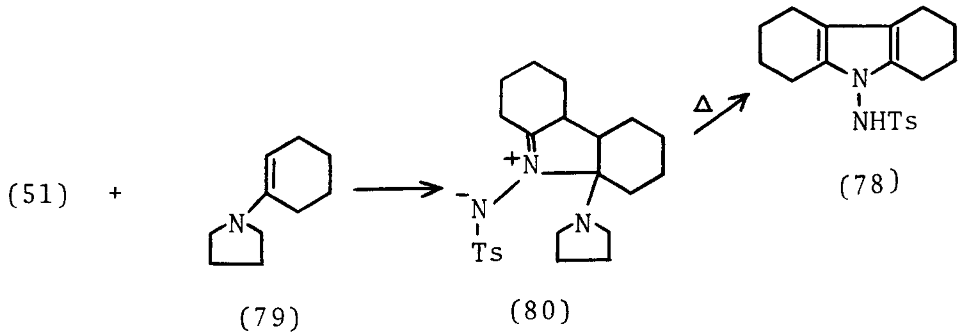


IV.6. Cycloaddition

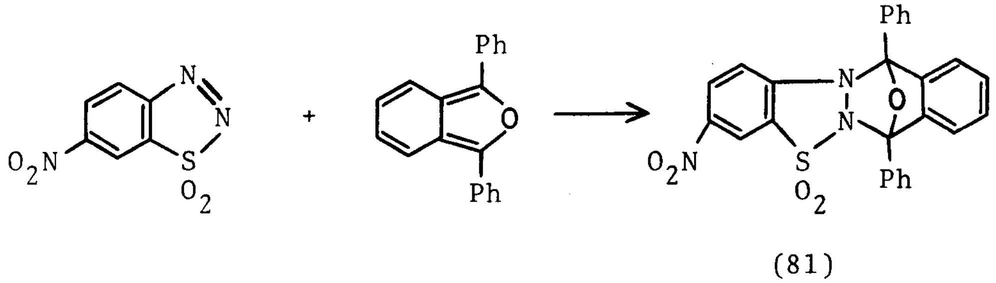
Cycloadditions of multiple-bond systems to 1,3-dienes usually take place at the 1,4-, 1,2-, or 3,4-position. On the other hand, cycloadditions at the 1,3- or 2,4-position occur rarely. This mode of reaction is demonstrated by the [3 + 2] cycloadditions of azoalkenes to enamines. In the reaction of tosylazocyclohexene (51) with the enamines (76) and (79), the [3 + 2] cycloadducts (77) and (80), respectively, crystallize out from the reaction solution in few minutes in high purity and high yield.[55] On heating, (77) and (80) immediately afford the *N*-aminopyrrole (78).



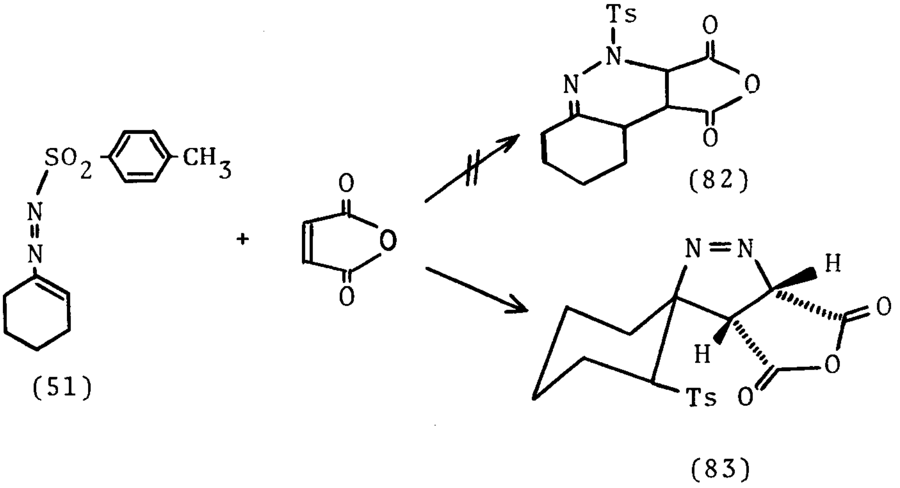
(51) (76) (77)



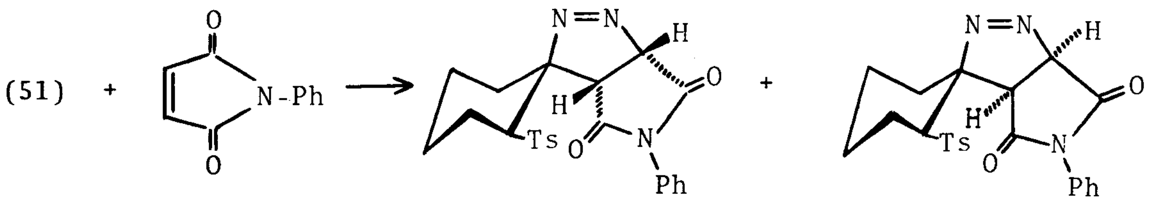
The [2 + 4] cycloaddition of 6-nitro-1,2,3-benzothiazole 1,1-dioxide to 2,5-diphenyl-3,4-benzofuran (81) has been reported.[53]



The reaction of tosylazocyclohexene (51) with maleic anhydride in benzene at room temperature gives a 1:1 adduct in 70–80% yield, the structure of which was assigned not to (82), but to (83) by NMR spectroscopy[56] and X-ray diffraction.[57]

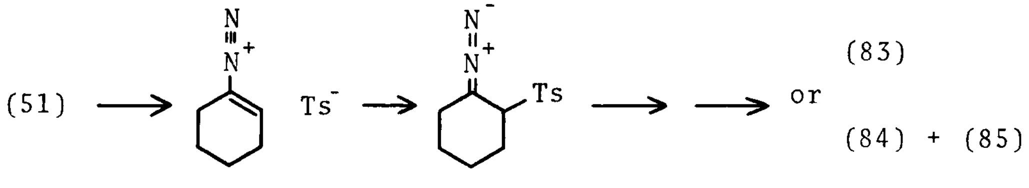


Similar reactions of (51) with *N*-phenylmaleimide, methacrylamide, methacrylonitrile, methyl methacrylate, ethyl methylenemalonate, and citraconic anhydride have been studied, and the stereochemistry of the 1:1 adducts produced has been discussed.[58]



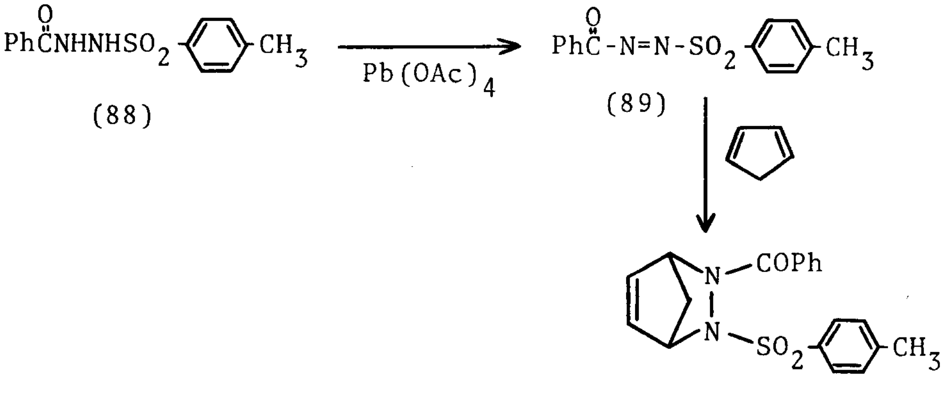
(84) (85)

The proposed reaction mechanism involves preliminary dissociation of tosylazocyclohexene (51) into the diazonium toluenesulfinate (86) and rearrangement to 2-tosyldiazocyclohexene (87) which in turn adds to the activated double bond of the dienophile to give the Δ^1-pyrazolines (83), (84), or (85), respectively, according to a general reaction mode of aliphatic diazo compounds.[59]



(86) (87)

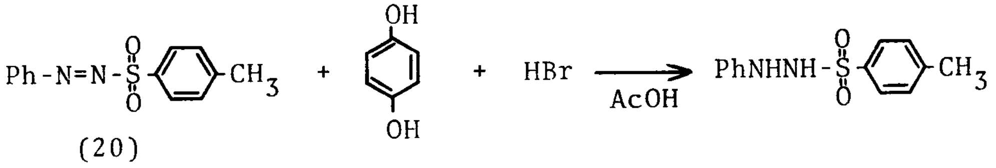
N-Benzoyl-*N'*-tosyl diimide (89) has been prepared by oxidation of the hydrazine derivative (88) with lead tetraacetate and, when treated with cyclopentadiene, affords the cycloadduct (90) in 33% yield.[60]



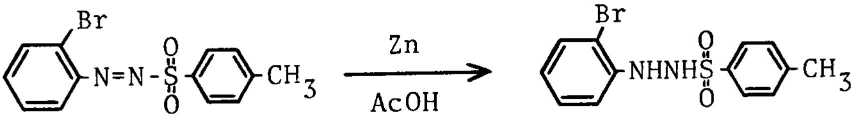
(90)

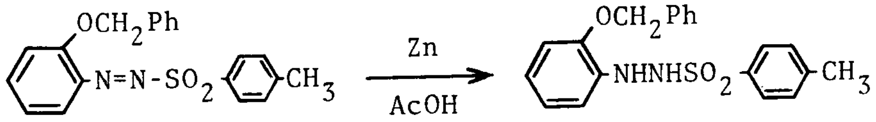
IV.7. Other reactions

Phenylazo *p*-tolyl sulfone (20) is reduced quantitatively to *p*-tosylphenylhydrazine with hydroquinone and hydrogen bromide in acetic acid.[61] Azobenzene, on the other hand, gives benzidine and aniline under similar reaction conditions.

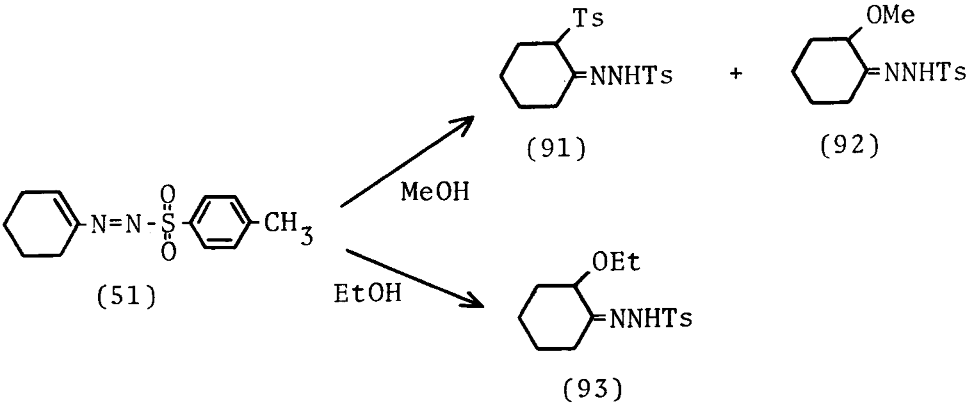


Azosulfones are easily reduced by zinc in acetic acid to yield sulfonylhydrazines.[62]

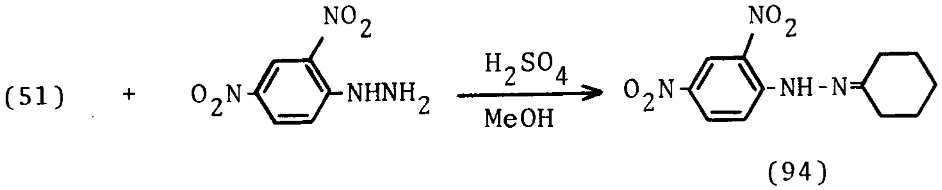




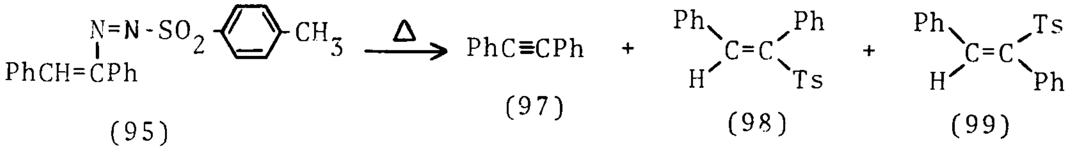
Treatment of tosylazocyclohexene (51) with methanol gives 2-(*p*-toluenesulfonyl)-cyclohexanone (*p*-toluenesulfonyl)-hydrazone (91) (20%) and 2-methoxycyclohexanone (*p*-toluenesulfonyl)-hydrazone (92) (30%).[63]

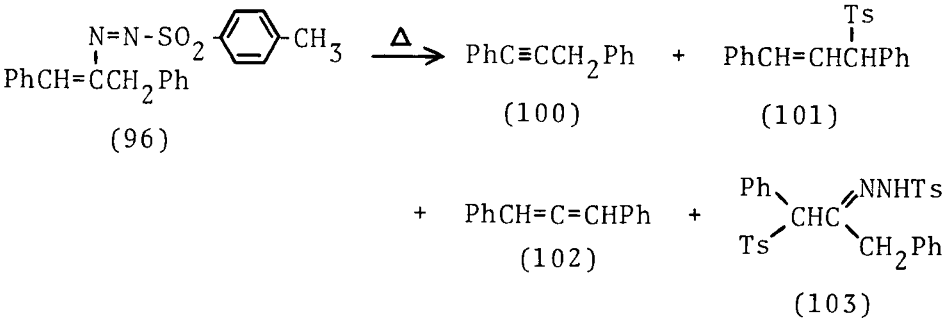


The reaction of (51) with 2,4-dinitrophenylhydrazine and sulfuric acid in methanol affords (94).

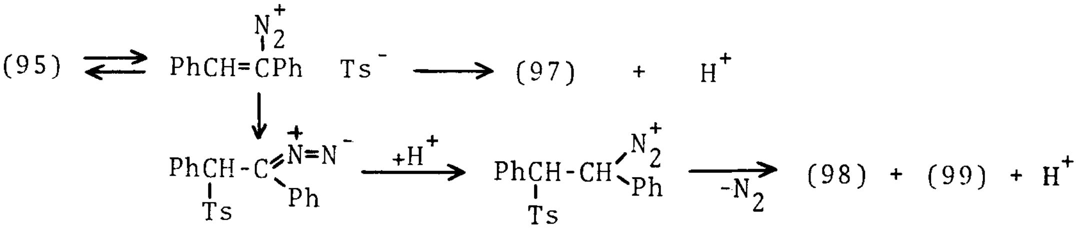


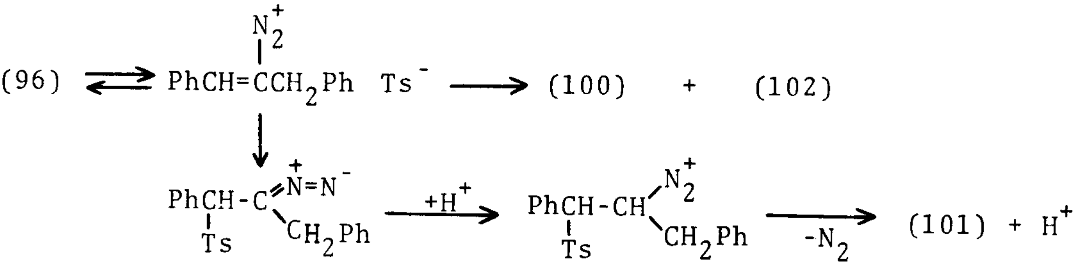
The thermolysis of *p*-toluenesulfonylazostilbene (95) and 2-*p*-toluenesulfonylazo-1,3-diphenylpropane (96) in dry benzene at 90°C or in chloroform at 25°C gives the following products.



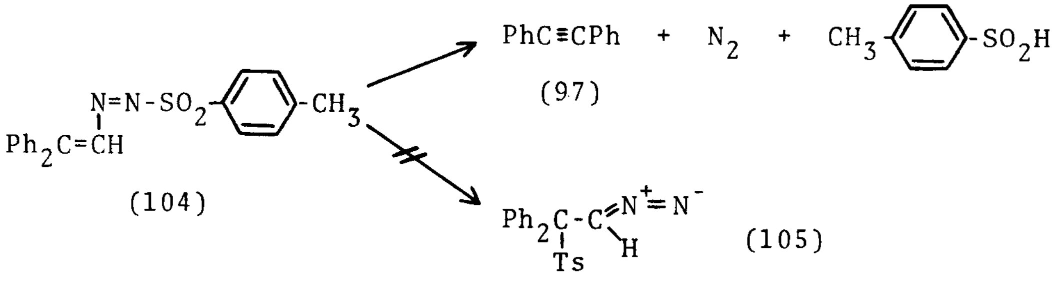


The results are consistent with a rearrangement of the *p*-toluenesulfonylazoenes to the corresponding 2-(*p*-toluenesulfonyl)-diazo compounds and successive protic decomposition.[64]

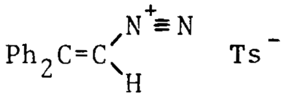




However, the thermal reaction of 2,2-diphenyl-1-tosylazoethylene (104) in benzene at 90°C or in chloroform at 25°C gives (97) (90%), nitrogen, and *p*-toluenesulfinic acid without formation of 2-tosyl-2,2-diphenyl-1-diazoethane (105) or the decomposition products expected from (105).[65]



It seems likely that the azoalkene gives rise to the diazonium ion pair (106) which may decompose to (97) either in a concerted manner or through the formation of a vinylic carbonium ion (107) or a divalent intermediate (108). However, in this case, all attempts to trap intermediates such as (107) and (108) were unsuccessful.



$Ph_2C{=}C(\overset{+}{N}{\equiv}N)H\ \ Ts^-$

(106)

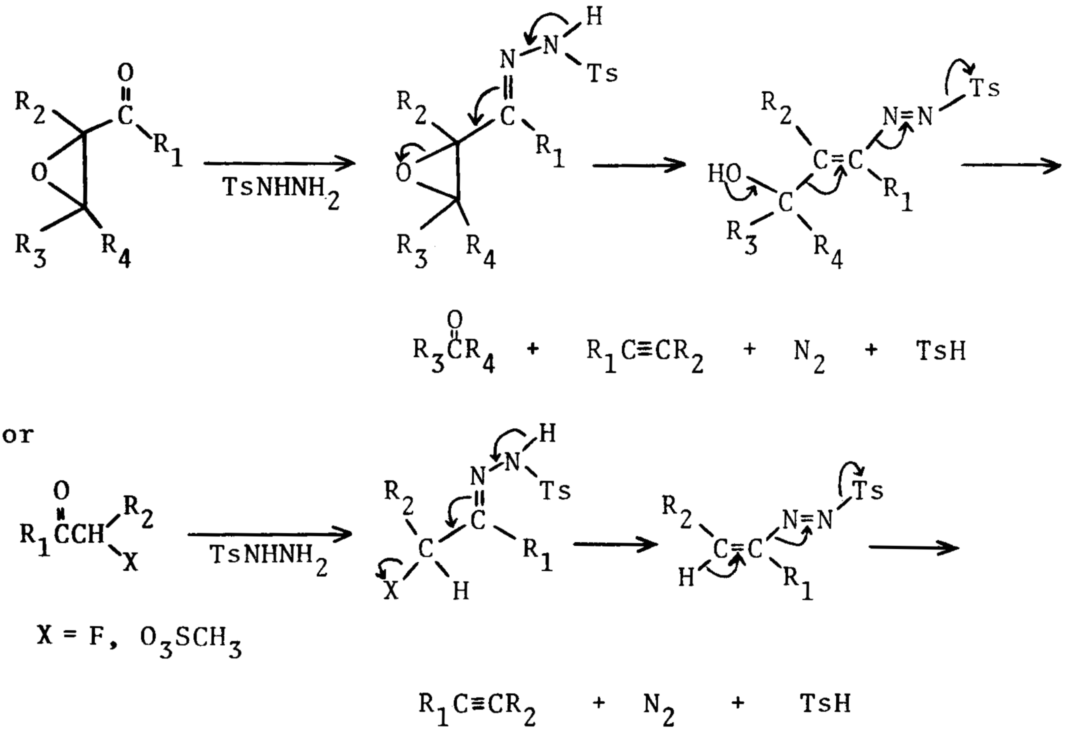
$Ph_2C{=}\overset{+}{C}H$

(107)

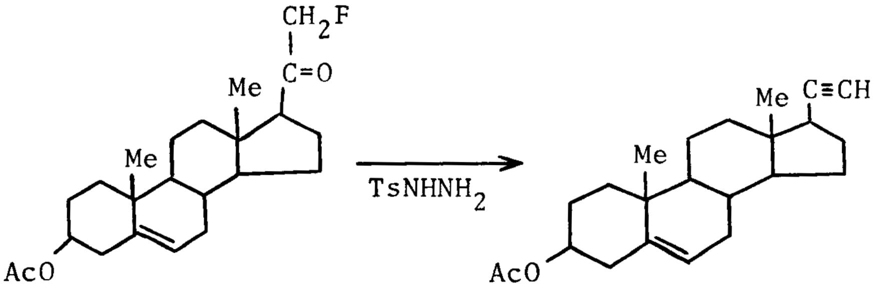
$Ph_2C{=}C{:}$

(108)

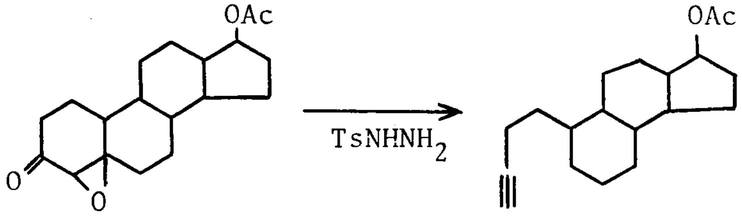
A new method for the preparation of acetylenes via alkenylazo sulfones has been reported.[66]



For example, (110) and (112) have been prepared in good yields from (109)[66] and (111),[67] respectively.

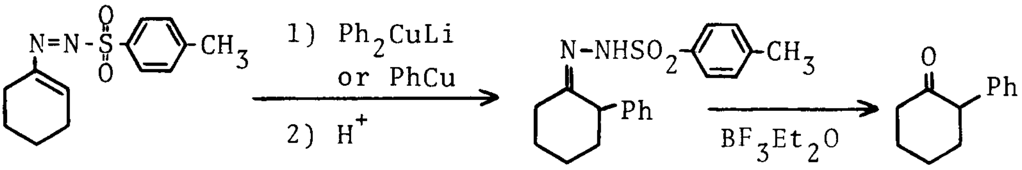


(109) (110)



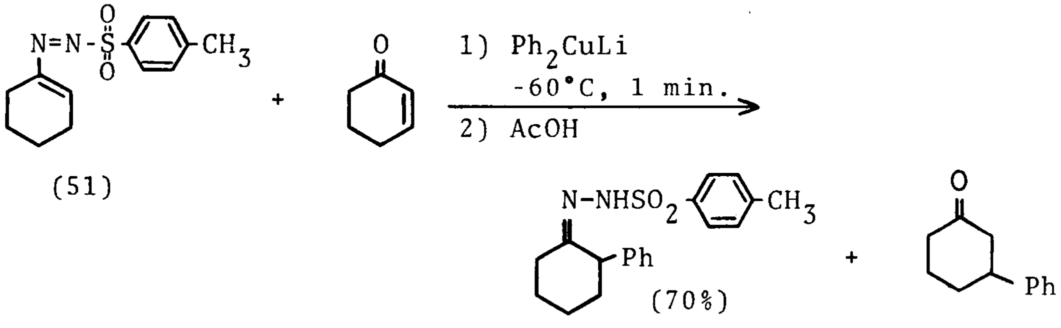
(111) (112)

Reaction of tosylazocyclohexene (51) with lithium diphenyl cuprate or phenylcopper leads to complete consumption of starting material within 1 min. (−60°C, THF-ether) concurrent with the production of the pure α-phenyltosylhydrazone (113) in 70–75% yield.[68]



(51) (113)

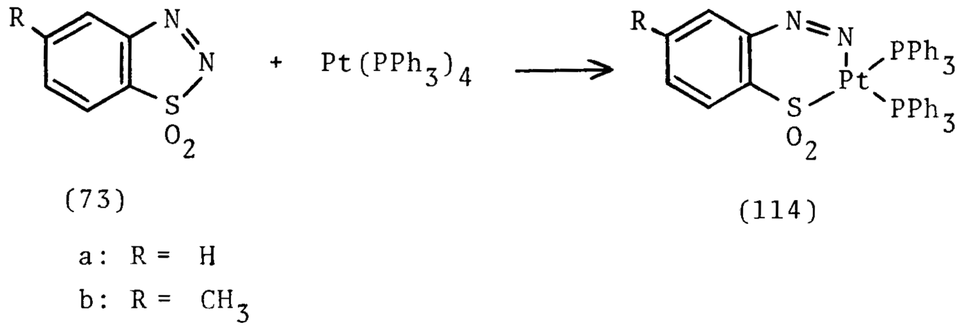
The considerable reactivity of the azo-ene (51) was further demonstrated in a competition experiment. Addition of a 1:1 mixture of (51) and cyclohexanone to one equivalent of lithium diphenylcuprate in THF-ether at −60°C, followed by quenching with acetic acid after 1 min., yields only the product resulting from reaction of the azo-ene (51), the enone being recovered unchanged.



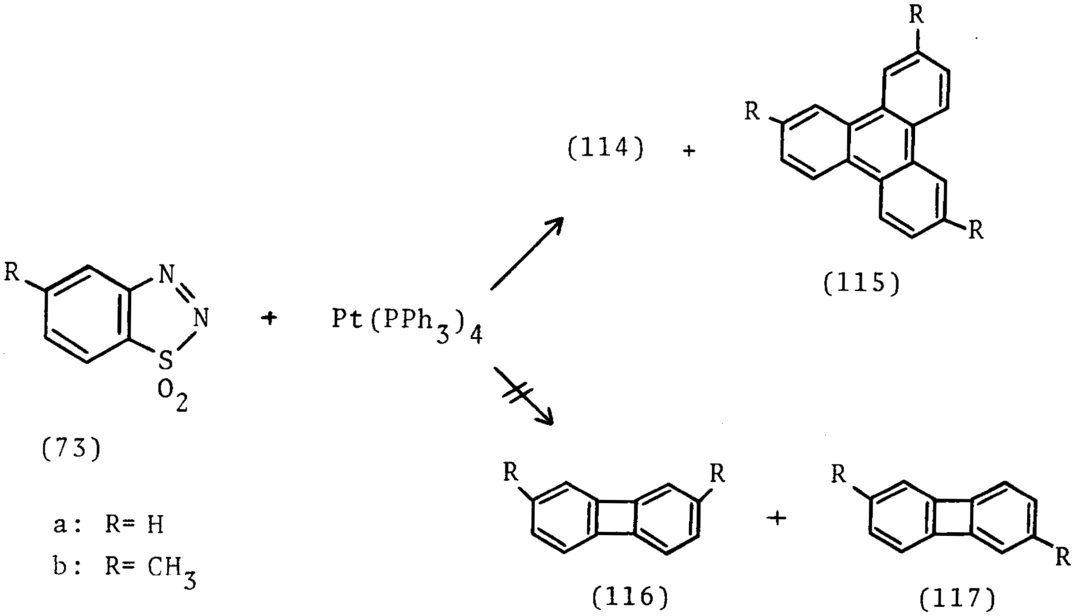
(51)

(113) (<1% ,VPC)

In cold benzene solution, (73a) or (73b) react rapidly with tetrakis-(triphenylphosphine)-platinum to give the yellow crystalline azo complex (114).

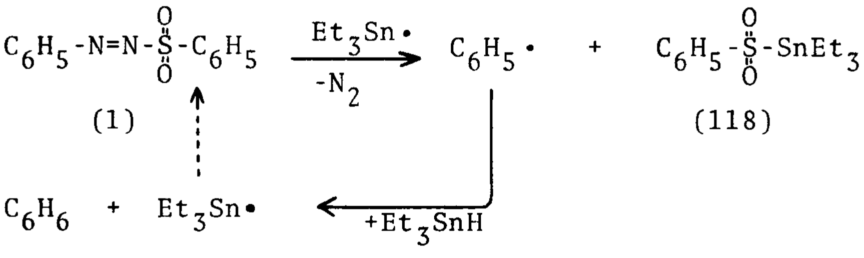


When the reaction between (73a) and (73b) with tetrakis-(triphenylphosphine)-platinum was carried out at a higher temperature (35°C) in ether-benzene the complexes (114) were formed together with considerable amounts (up to 40% yield) of triphenylene (115a) and 2,6,11-trimethyltriphenylene (115b), respectively, while the biphenylenes (116) or (117) could not be detected.[69]

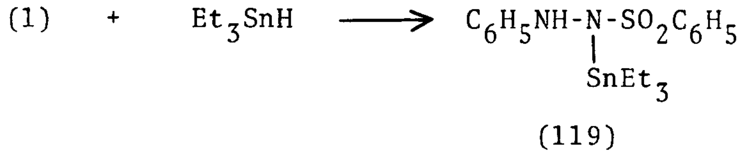


The isolation of the triphenylenes in the presence of tetrakis-(triphenylphosphine)-platinum indicates that organometallic intermediates are involved in their formation.

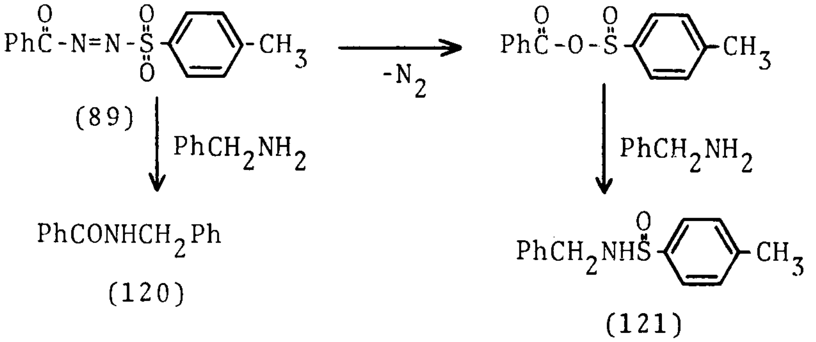
The rate of the homolysis of phenylazo phenyl sulfone (1) in dilute toluene solution is accelerated ten-fold when an organotin hydride is present. Benzene, nitrogen, and triethylstannyl benzenesulfinate (118) are formed in equimolar amounts. The intermediacy of free benzenesulfonyl radicals could be excluded; they would afford the sulfinic acid and with further hydride, H_2. Stannyl radicals induce the decomposition and their covalent attachment to the sulfonyl group is synchronous with the detachment of the azo group (S_R2 mechanism).[70]



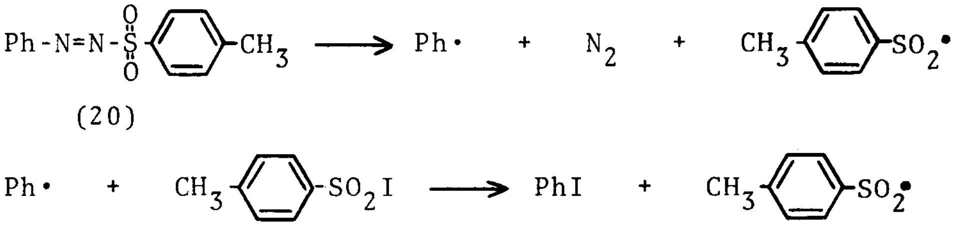
A side reaction is the free-radical hydrostannylation of (1) at its azo group to form the *N*′-phenyl-*N*-benzenesulfonyl-*N*-stannylhydrazine (119).



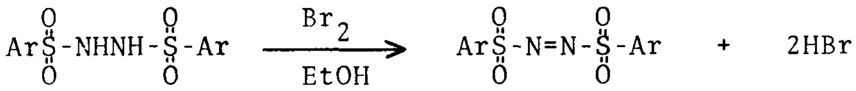
N-Benzoyl-*N*′-tosyl diazene (89) reacts with benzylamine to yield the carboxamide (120) and the sulfinamide (121).



Trapping of the phenyl radicals produced by thermal decomposition of phenylazo *p*-tolyl sulfone (20) by *p*-toluenesulfonyl iodide is an effective way to generate *p*-toluenesulfonyl radicals uncontaminated with phenyl radicals.[71]



Kwart and Khan reported the isolation of *N*,*N*′-diphenylsulfonyl diimide (123) by mild oxidation of *N*,*N*′-bisbenzenesulfonylhydrazine (122).[72]

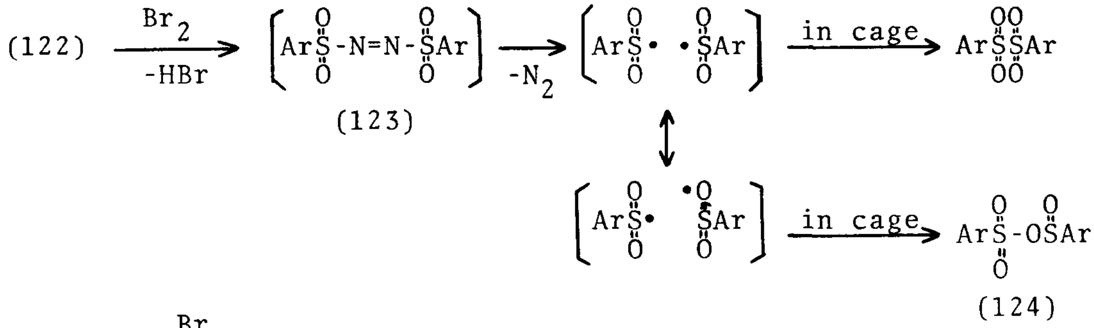


$$\mathrm{Ar}\overset{O}{\underset{O}{S}}\text{-NHNH-}\overset{O}{\underset{O}{S}}\text{-Ar} \xrightarrow[\mathrm{EtOH}]{\mathrm{Br_2}} \mathrm{Ar}\overset{O}{\underset{O}{S}}\text{-N=N-}\overset{O}{\underset{O}{S}}\text{-Ar} + 2\mathrm{HBr}$$

(122) (123)

Ar = Ph

The structure (123) was assigned on the basis of elemental analysis, mp, molecular weight measurement, NMR, IR, Raman and mass spectral evidence. Kobayashi and coworkers attempted to prepare diarenesulfonyl diimides according to the above method, however, their experimental findings differred from Kwart and Khan's.[73] The imides (123) could not be isolated in repeated experiments under various conditions even when (122) was oxidized at −40°C, and the oxidation of (123) was always accompanied by instantaneous evolution of nitrogen. Diarenesulfonyl diimides (123) are very unstable and the oxidation products of dibenzenesulfonylhydrazine (122) (Ar = C_6H_5) with bromine in ethanol are nitrogen, benzenesulfonyl bromide, diphenyl disulfone, benzenesulfonic acid, and ethyl benzenesulfonate. The following mechanism explains these products.



$$(122) \xrightarrow[\mathrm{-HBr}]{\mathrm{Br_2}} \left[\mathrm{Ar}\overset{O}{\underset{O}{S}}\text{-N=N-}\overset{O}{\underset{O}{S}}\mathrm{Ar}\right] \xrightarrow[\mathrm{-N_2}]{} \left[\mathrm{Ar}\overset{O}{\underset{O}{S}}\bullet \;\; \bullet\overset{O}{\underset{O}{S}}\mathrm{Ar}\right] \xrightarrow{\text{in cage}} \mathrm{Ar}\overset{OO}{\underset{OO}{SS}}\mathrm{Ar}$$

(123)

$$\updownarrow$$

$$\left[\mathrm{Ar}\overset{O}{\underset{O}{S}}\bullet \;\; \overset{\bullet O}{\underset{O}{S}}\mathrm{Ar}\right] \xrightarrow{\text{in cage}} \mathrm{Ar}\overset{O}{\underset{O}{S}}\text{-O}\overset{O}{S}\mathrm{Ar}$$

(124)

$$2\mathrm{ArSO_2}\bullet \xrightarrow{\mathrm{Br_2}} 2\mathrm{ArSO_2Br}$$

$$(124) \longrightarrow \mathrm{ArSO_3}\bullet + \mathrm{Ar}\dot{S}\mathrm{O}$$

$$\mathrm{ArSO_3}\bullet \xrightarrow{\mathrm{RH}} \mathrm{ArSO_3H} + \mathrm{R}\bullet$$

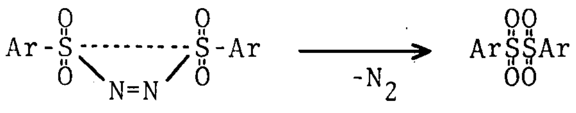
$$\mathrm{Ar}\dot{S}\mathrm{O} \xrightarrow{\mathrm{Br_2}} \mathrm{Ar}\overset{O}{S}\text{-Br}$$

$$(124) \xrightarrow[\mathrm{EtOH}]{} \mathrm{ArSO_3H} + \mathrm{Ar}\overset{O}{S}\text{-OEt}$$

$$\mathrm{Ar}\overset{O}{S}\text{-OEt} \xrightarrow{\mathrm{Br_2}} \mathrm{ArSO_2OEt} + \mathrm{ArSO_2Br}$$

$$\mathrm{ArSO_2Br} \xrightarrow[\mathrm{EtOH}]{} \mathrm{ArSO_2OEt}$$

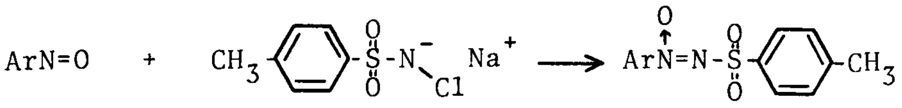
The formation of the diaryl disulfone could be alternatively explained by means of a four-centered transition state (125).



(125)

V. COMPOUNDS RELATED TO AZOSULFONES

Azoxysulfones (126) were first prepared by Farrar and Gulland by the reaction of chloramine-T with nitrosoarenes in pyridine solution.[74]



(126)

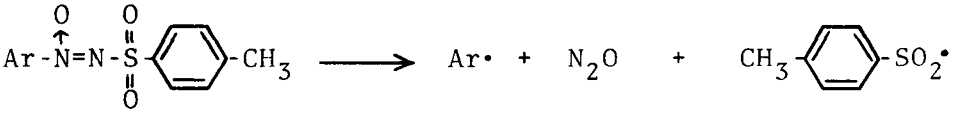
a : $Ar=C_6H_5$

b : $Ar=p\text{-}Me_2N\text{-}C_6H_4$

c : $Ar=p\text{-}Et_2N\text{-}C_6H_4$

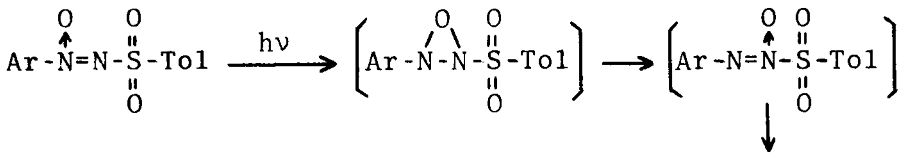
These azoxysulfones have dipole moments between 6.0–8.7 D and λ_{max} of the electronic spectra lies around 230 and 470 nm in alcohol. No cis-trans isomerism of the azo group has been detected.[75]

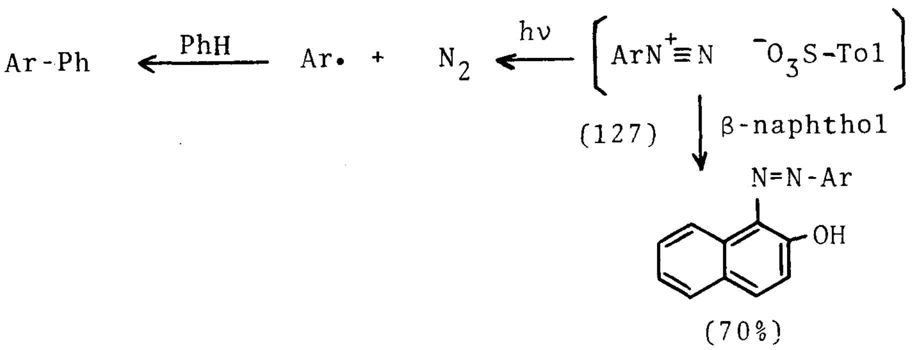
Photolysis of phenylazoxy *p*-tolyl sulfone (126a) in benzene solution leads to biphenyl (35%) and *p*-toluenesulfinic acid (30%). The formation of biphenyl suggests the intermediacy of phenyl radicals, but the gaseous products analyzed only for nitrogen, no N_2O could be detected. The mechanism of the photolysis of (126a) cannot be represented by the following equation, which is simple S—N bond fission similar to the mode of decomposition of azosulfones.[76]



(126)

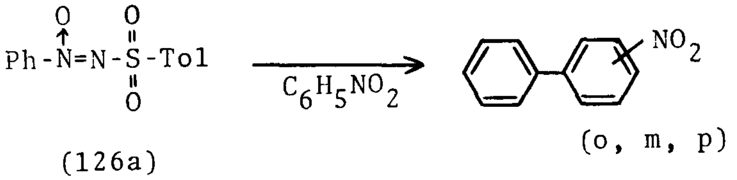
An alternative mechanism involves rearrangement to an arenediazonium *p*-toluenesulfonate (127). In fact, in the presence of *β*-naphthol, a majority of the azoxysulfones gave the azo coupling product.





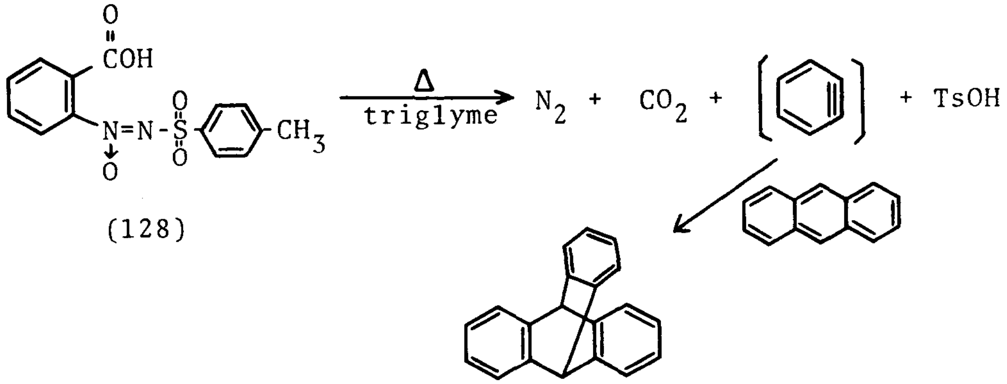
(127)

Azoxysulfones (126) are thermally very stable compounds. When a nitrobenzene solution of (126a) was refluxed for 60h, about 50% decomposed and 50% of (126a) was recovered. The nitrobiphenyls formed (10%) have the following isomer distribution ortho: 49%, meta: 14%, and para: 37%. The isomer ratio shows that these nitrobiphenyls are the products of free-radical phenylation.



(126a)

The pyrolysis of the azoxysulfone (128) in triglyme affords nitrogen and carbon dioxide as the major gaseous products while triptycene (25%) is obtained when the pyrolysis is carried out in the presence of anthracene. Evidence for the intermediacy of benzyne has been proposed.[77]



(128)

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