THE REACTION OF SULFONYLIMIDO INTERMEDIATES WITH AROMATIC COMPOUNDS[1]

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Received June 14, 1965

ABSTRACT

Thermolysis of methanesulfonyl azide in aromatic solvents gives methanesulfonamide and the isomeric methanesulfonanilides. The orientation of the latter and the relative reactivities of the aromatic substrate towards attack by the methylsulfonylimido intermediate have been studied quantitatively. The high reactivity and also great selectivity of the attacking species are interpreted in terms of a rate-determining addition process to give a sulfonylaziridine derivative followed by a product-determining ring opening and rearrangement to the substituted anilides. Partial rate factors are discussed, as are possible mechanisms for the formation of the methanesulfonamide. The methanesulfonylimido intermediate must be abstracting *two* hydrogen atoms synchronously from the aromatic substrate.

The thermal decomposition of sulfonyl azides in aromatic solvents was first studied by Curtius and Schmidt (1). The products obtained from the thermal decomposition of benzenesulfonyl azide in various substituted benzenes were shown to be the corresponding benzenesulfonanilides together with benzenesulfonamide (2, 3). The available evidence points to the intermediacy of a sulfonylimido intermediate (sulfonyl nitrene) (II) in both the thermal and photochemically induced reactions of sulfonyl azides (I), except in those cases where an assisted stepwise addition to olefinic double bonds followed by elimination

$$\underset{\text{I}}{R{-}SO_2N_3} \xrightarrow[\text{or }\Delta]{h\nu} \underset{\text{II}}{RSO_2{-}N} + N_2$$

of nitrogen can take place (4). Thus, the thermal decomposition of benzenesulfonyl azide and *t*-butyl hydroperoxide exhibits mutually induced decomposition of both reagents (5). Whereas sulfonyl azides and dimethyl sulfoxide do not react in the dark, photolysis or thermolysis of the azide gives nitrogen and the sulfonylimido intermediate (II) which is trapped by reaction with dimethyl sulfoxide. Thioethers are even more efficient trapping agents (6). *p*-Toluenesulfonyl azide initiates the copolymerization of mixtures of styrene and methyl methacrylate at 60–120° by a free-radical mechanism, but the activity is extremely low (7), suggesting that the intermediate exists mainly in the singlet electrophilic species (II*b*) rather than in the triplet diradical form (II*a*). More recently, the

$$\underset{\text{II}a}{RSO_2{-}\dot{\underset{\cdot}{N}}\cdot} \rightleftarrows \underset{\text{II}b}{RSO_2{-}\ddot{\underset{\cdot\cdot}{N}}}$$

thermal decomposition of aliphatic and aromatic sulfonyl azides in cyclohexane under pressure at 175° has been investigated (8). C—H insertion products were mainly obtained; *very little hydrogen abstraction was observed* in all cases. With the aliphatic azides a radical chain process resulting in the evolution of sulfur dioxide was found to compete with the

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[1] *The present paper is Part XI of the series on aromatic substitution. Part X: Can. J. Chem. In press. 1965. Part of this work was embodied in a lecture given at the Symposium on Reactive Intermediates held at the Université Laval, Québec, in August 1964.*

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Canadian Journal of Chemistry. Volume 43 (1965)

unimolecular decomposition of the azide, though the radical initiator R· could not be identified.

$$C_5H_{11}SO_2N_3 \rightarrow C_5H_{11}SO_2\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}} + N_2$$

$$R\cdot + C_5H_{11}SO_2N_3 \rightarrow C_5H_{11}SO_2\cdot + RN_3$$

$$C_5H_{11}SO_2\cdot \rightarrow C_5H_{11}\cdot + SO_2$$

$$C_5H_{11}\cdot + R\text{—}H \rightarrow C_5H_{12} + R\cdot$$

The radical chain process could be inhibited to a certain extent by the addition of sulfur or of hydroquinone. Good first-order kinetics were observed in the decomposition of *p*-toluenesulfonyl azide.

The behavior of the imido intermediate after its formation will also depend upon the nature of the solvent used. While in aromatic or aliphatic non-polar solvents sulfonyl azides behave as "rigid" azides i.e. they do not undergo a Curtius-type rearrangement, irradiation of a solution of benzenesulfonyl azide in methanol followed by hydrolysis gave a 28% yield of aniline, presumably formed via $C_6H_5NSO_2$ and $C_6H_5NHSO_2OCH_3$ (9).

The orientation and partial and total rate factors in the substitution of benzene derivatives by the benzenesulfonylimido intermediate produced by thermolysis of the azide have been studied (2, 3). The decompositions were carried out at 105–120° and the products analyzed after preliminary hydrolysis of the anilides formed (2) or as the amides but after appreciable pretreatment (3). Of the aromatic compounds studied, most of those with meta-directing substituents did not react to produce the expected substitution products. With the other substituents, the total rate ratios and partial rate factors were said to be consistent with an attack of the aromatic nucleus by the electrophilic free radical $C_6H_5SO_2\overset{\cdot\cdot}{\underset{\cdot}{N}}\cdot$ (3). The failure of compounds with meta-directing substituents to produce the expected substitution products was attributed to complexing of the radical with the electron-rich substituent group (3). Benzoyl chloride gave a 7% yield of products, 90% of which was benzene-sulfonamide, the rest being exclusively the meta product of substitution. A number of observations remain unexplained by the postulated mechanism (10*a*). (i) The total rate ratios (10*b*) (from competitive reactions between C_6H_6 and C_6H_5X with $C_6H_5SO_2N_3$ at 105–120°) were not much different from unity, as expected for a homolytic substitution. However, the values of the total rate ratios ${}^{CH_3}_{H}K = 1.0$, ${}^{CH_3O}_{H}K = 0.96$, ${}^{OH}_{H}K = 0.80$ are unexpected, since such electron-donating substituents should facilitate attack by an electrophilic free radical (11) and lead to total rate ratios greater than unity. (ii) The partial rate factor calculated for attack at the meta position of toluene is unusually low ($F_m = 0.03$) and it is hard to see why F_m should be less than 1 in toluene, either for a free radical or for an electrophilic substitution process. (iii) Isomer ratios differed somewhat according to whether they were determined under competitive conditions or not.

It was felt that these observations needed careful reinvestigation and that, particularly, a more convenient and reliable analytical technique which would involve a minimum amount of manipulation before the actual analysis was carried out would be desirable. Gas-chromatographic analysis was the obvious choice and, in order to facilitate the elution of the reaction products from the column, it was decided to use methanesulfonyl azide* instead of benzenesulfonyl azide as the source for the imido intermediate. The

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**A referee has pointed out that methanesulfonyl azide is, apparently, as sensitive to shock and impact as is nitroglycerine. No trouble was experienced in the present work except in the odd cases where reaction mixtures containing large amounts of undecomposed azide were introduced into the heated injector of the gas chromatograph, when explosions resulted which blew out the Teflon dams. Consequently, caution should be used in the handling of this compound.*

products expected would then be methanesulfonamide $CH_3SO_2NH_2$ (III) and the substituted mesylanilines (IV).

$$CH_3SO_2N_3 \xrightarrow[\text{or } \Delta]{h\nu} CH_3SO_2N$$

$$CH_3SO_2N + RC_6H_5 \rightarrow CH_3SO_2NHC_6H_4R$$

IV

The reaction mixtures were filtered from any tars formed, concentrated, and analyzed directly by gas–liquid chromatography, thus avoiding the possibility of the selective loss of some quantity of one or more of the isomers. All reactions were carried out at 120° under pressure with stirring. Preliminary experiments indicated that similar products were obtained on photolysis of the azides in solution in an excess of the aromatic solvent.

EXPERIMENTAL

Melting points are uncorrected.

Reagents

Reagent thiophene-free benzene and toluene were dried, distilled, and kept over sodium wire. Reagent chlorobenzene and anisole were dried, distilled, and kept over anhydrous sodium sulfate.

Methanesulfonyl Azide

Prepared by the procedure of Horner and Christmann (6), this product was purified by fractional distillation; it had b.p. 71° at 4.5 mm, n_D^{25} 1.4653, and was obtained in 73% yield.

Methanesulfonamide

This was obtained from mesyl chloride and dry ammonia as described by Field and Grunwald (12) and had m.p. 92–93°.

Preparation of Authentic Methanesulfonylanilides

The general procedure described by Marvel, Helfrick, and Belsley (13) was used. A benzene solution of 2 molar equiv of the amine was mixed with 1 equiv of methanesulfonyl chloride in benzene at room temperature. The stirred solution was boiled under reflux from 3 to 12 h. The amine hydrochloride was filtered, the benzene was evaporated *in vacuo*, and the amide was recrystallized from dilute ethanol.

Methanesulphonylanilide had m.p. 101–102°.

o-Methanesulphonyltoluidide had m.p. 106°.

m-Methanesulfonyltoluidide

This compound, prepared by the above method, had m.p. 92–92.5°.

Anal. Calcd. for $C_8H_{11}NO_2S$: C, 51.87; H, 5.99. Found: C, 51.80; H, 6.03.

p-Methanesulfonyltoluidide had m.p. 104.5–105°.

o-Methanesulfonamidochlorobenzene had m.p. 92–93°.

m-Methanesulfonamidochlorobenzene

This compound had m.p. 98–98.5°.

Anal. Calcd. for $C_7H_8ClNO_2S$: C, 40.88; H, 3.92. Found: C, 40.93; H, 4.00.

p-Methanesulfonamidochlorobenzene had m.p. 155–156°.

p-Methanesulfonylanisidide had m.p. 116°.

m-Methanesulfonylanisidide

The compound was obtained as a brown oil which gave a colorless liquid (38%), b.p. 160° at 2.7 mm. The liquid solidified on cooling and could be recrystallized from benzene – light petroleum (b.p. 60–80°) to give colorless crystals, m.p. 67.5°.

Anal. Calcd. for $C_8H_{11}NO_3S$: C, 47.77; H, 5.50. Found: C, 47.90; H, 5.52.

o-Methanesulfonylanisidide, prepared in the usual method, was obtained in 95% yield and had m.p. 69°. Since the reported m.p. is 115.5° (13), the amide was prepared by an alternate method. *o*-Anisidine (3.07 g), dry pyridine (2.23 g), and methanesulfonyl chloride (2.8 g) in benzene (50 ml) were boiled under reflux with stirring for 6 h. A brown gummy solid separated; this was filtered and washed with benzene. The combined filtrates were washed with 15 ml portions of 10% hydrochloric acid and then with water. Evaporation of the solvent gave the amide, which was recrystallized from 95% ethanol (charcoal) and had m.p. 69–69.5°.

Anal. Calcd. for $C_8H_{11}NO_3S$: C, 47.77; H, 5.50. Found: C, 48.05; H, 5.55.

1,2-Diphenoxyethane was prepared by boiling under reflux a mixture of phenol (9.4 g), sodium hydroxide (4 g), and ethylene bromide (9.4 g) for 16 h. The cooled reaction mixture was filtered; the solid was washed with 10% sodium hydroxide solution, washed with water, and recrystallized from 95% ethanol. The product (9.7 g) had m.p. 97.5–98.5°. Simons (14) gives m.p. 97° for this compound.

Methanesulfonylamidation of Aromatic Nuclei Using Methanesulfonyl Azide

General Procedure

Methanesulfonyl azide was dissolved in an excess of the aromatic substrate (molar ratio of azide to aromatic compound 1:25 – 1:50) and the solution was placed in the reaction bottle of a specially designed apparatus which permitted reactions to be carried out under pressure in a glass vessel at constant temperature while being stirred continuously. A description of this apparatus has been published elsewhere (15). The reaction vessels were immersed in a thermostatted oil bath maintained at 120° and stirred for 48 h. The apparatus consisted of three reaction vessels so that all runs could be carried out in triplicate. The cooled glass vessels were opened very carefully to release the nitrogen which had evolved, and the solutions were filtered from small quantities of black precipitate, the amount of which appeared to depend on the nature of the aromatic substrate. The solutions were then transferred quantitatively to a round-bottomed flask, the last traces being washed out with acetone, and concentrated by distillation from a fractionating column.

The products formed were analyzed qualitatively and quantitatively by gas chromatography. Identification was effected by comparing relative retention times with those of authentic samples and then by direct comparison of melting points and infrared spectra of collected material with those of authentic compounds. The internal standard method (16) was adapted for the quantitative analyses and the reliability of the method checked using authentic mixtures of the isomers. The results are accurate to within ±1%.

Methanesulfonylamidation of Benzene

The reaction of methanesulfonyl azide (0.3 g) with a 25 molar excess of benzene was carried out as described above. The reaction products (methanesulfonamide and mesylaniline) were best analyzed on a 6 ft × 1/4 in. column packed with precipitated asphalt on Chromosorb W (60–80 mesh) (25%). (Asphalt, as supplied by the Wilkens Instrument Co., was dissolved in the minimum amount of hot benzene to which was then added *n*-hexane. The precipitated asphalt was filtered and washed with light petroleum (b.p. 60–80°) until the filtrate was colorless). The column temperature was 220° and the helium inlet pressure 50 p.s.i. (flow rate of 55 ml/min). Under these conditions methanesulfonamide had a retention time of 2.3 min, mesylaniline a retention time of 14.1 min, and coumarin (which was used as the internal standard) a retention time of 10.9 min. No biphenyl (retention time 4.6 min) could be detected in the reaction mixtures. The results are summarized in Table I.

TABLE I

Products of reaction of methanesulfonyl azide with benzene

	Methanesulfonamide (%)	Mesylaniline (%)	Total yield (%)
Synthetic mixture 1	19.1(19.7)*	80.9(80.3)	—
Synthetic mixture 2	18.1(18.2)	81.9(81.8)	—
Expt. No. 1†	13.9	55.7	69.6
Expt. No. 2†	16.2	55.8	72.0
Expt. No. 3†	13.2	52.4	65.6
Mean	14.4	54.6	69.0

*Figures in parentheses refer to known percentage composition.
†Average of triplicate readings.

Methanesulfonylamidation of Toluene

The azide:toluene molar ratio was 1:50. The same column as was used above was also used here to resolve the reaction mixture into its components except that it was operated at 230° and a helium inlet pressure of 40 p.s.i. (flow rate 60 ml/min). Five peaks corresponding to methanesulfonamide, dibenzyl, and the *o*-, *m*-, and *p*-methanesulfonyltoluidides having retention times of 2.05, 5.8, 13.6, 16.2, and 18.35 min, respectively, were observed. Coumarin (retention time 10.1 min) was used as the internal standard. The results (mean of three experiments) were as follows. Total yield of methanesulfonyltoluidide (based on methanesulfonyl azide), 76.8%; methanesulphonamide, 22.7%; dibenzyl, 0.5% (assuming that each molecule of methanesulfonylimido intermediate abstracts one proton from each of two toluene molecules). Isomer ratio: *o*, 65.4%; *m*, 2.4%; *p*, 32.2%. Overall amount of azide accounted for: 99.5%.

The reaction was repeated by using a solution of azide in toluene which had been deaerated by passing nitrogen through it and carrying out the reaction under nitrogen. Under these conditions the yield of mesyltoluidides was 72.2% (*o* 65.1%, *m* 3.0%, *p* 31.8%), that of methanesulphonamide was 24.3%, and that of dibenzyl was 0.4%.

Methanesulfonamidation of Chlorobenzene

The azide:chlorobenzene molar ratio used was 1:50. The same column as above was operated at 240° and a helium inlet pressure of 41 p.s.i. (flow rate 68 ml/min). Four peaks corresponding to methanesulfonamide and the *o*-, *m*-, and *p*-methanesulfonylamidochlorobenzenes, having retention times of 1.3, 7.1, 17.8, and

20.15 min, respectively, were observed. *p*-Methanesulfonyltoluidide, retention time 10.15 min, was used as internal standard. The results (mean of three experiments) are summarized below.

Yield of methanesulfonylamido chlorobenzene (%)	Yield of methanesulfonamide (%)	Overall yield based on azide (%)	Yield of isomers (%)		
			o	*m*	*p*
65.1	13.1	78.2	57.4	0.9	41.7

Appreciably more tarry matter appeared to be formed in this reaction compared with the toluene one.

Methanesulfonamidation of Anisole

(*a*) The reaction was carried out as above using methanesulfonylazide (0.15 g) in anisole (6.7 ml) (molar ratio 1:50). Analysis on the same column as before, operated at 225° and 50 p.s.i. inlet pressure of helium (60 ml/min flow rate) gave the following retention times: methanesulfonamide, 1.5 min; coumarin (internal standard), 8.5 min; *o*-methanesulfonylanisidide, 16.5 min; *m*-methanesulfonylanisidide, 28.5 min; *p*-methanesulfonylanisidide, 34.0 min; 1,2-diphenoxyethane, 14.0 min. On a 9 ft × 1/4 in. column of 25% Apiezon N on Chromosorb W at 225°, 1,2-diphenoxyethane had a retention time of 30 min while *p*-methanesulfonylanisidide had a retention time of 25 min. The results of the quantitative analyses are summarized in Table II (expts. 4–6).

TABLE II

Products of reaction of methanesulfonylazide with anisole

	Methanesulfonamide (%)	Mesylanisidides (%)	Mesylanisidide (% of total)			Total yield (%)
			o	*m*	*p*	
Synthetic mixture 3	6.9(6.7)†	—	43.3(44.1)	8.3(9.0)	41.5(40.2)	—
Synthetic mixture 4	5.9(6.5)	—	43.5(43.6)	11.9(11.6)	38.7(38.3)	—
Expt. No. 4‡	4.1	67.3	54.9	1.2	43.9	71.4
Expt. No. 5‡	3.6	66.0	55.5	1.2	43.3	69.6
Expt. No. 6‡	3.7	67.4	56.2	1.1	42.7	71.1
Mean	3.8	66.9	55.5	1.2	43.3	70.7
Expt. No. 7‡	8.7	82.4	57.1	1.1	41.8	91.1
Expt. No. 8‡	9.5	82.2	56.0	1.1	42.9	91.7
Expt. No. 9‡	9.0	79.3	56.4	1.2	42.4	88.3
Mean	9.1	81.3	56.5	1.1	42.4	90.4

*Based on azide.
†Figures in parentheses refer to known percentage composition.
‡Average of triplicate determinations.

Some tars were also formed in this reaction and probably account for the balance of the azide. No 1,2-diphenoxyethane could be detected in any of the reaction products.

(*b*) The reaction was carried out as above except that the molar ratio of azide to anisole was 1:25. The results are summarized in Table II (expts. 7–9).

Competitive Reactions

A large excess (100- to 150-fold) of an equimolar mixture of the substituted benzene and benzene over the azide was heated in the sealed glass vessels at 120° as in the case of the non-competitive reactions, and the mixtures were worked up in the same way as before.

Determination of ${}^{\mathrm{CH_3}}_{\mathrm{H}}K$

The methanesulfonyl azide to solvent ratios used were 1:100 and 1:150. The gas chromatographic analyses were carried out with an 8 ft × 3/16 in. column packed with 30% Apiezon L on firebrick (60–80 mesh) operated at 220° and a helium inlet pressure of 50 p.s.i. (flow rate 46 ml/min); *o*-, *m*-, and *p*-methanesulfonyltoluidide and mesylaniline had retention times of 10.0, 13.3, 14.9, and 11.7 min, respectively. *o*-Methanesulfonamidochlorobenzene was used as the internal standard and had a retention time of 7.2 min. The results (mean of two experiments each) are summarized below.

Methanesulfonyl azide: solvent molar ratio	${}^{\mathrm{CH_3}}_{\mathrm{H}}K$
1:100	1.84
1:150	1.88
Mean	1.86

Determination of ${}^{\text{Cl}}_{\text{H}}K$

The methanesulfonyl azide to mixed solvent ratio was 1:100. The reaction products were analyzed on an 8 ft × 3/16 in. column packed with 30% Apiezon L on firebrick operated at 225° and a flow rate of 46 ml/min. *o*-Methanesulfonamidochlorobenzene, methanesulfonylanilide, and an unresolved mixture of *m*- and *p*-methanesulfonamidochlorobenzenes had retention times of 5.6, 8.7, and 22.9 min, respectively. *p*-Methanesulfonyltoluidide (retention time 11.0 min) was used as the internal standard. The calibration factor for the mixed meta and para isomers was obtained by using a standard solution of these isomers in the same proportion as had been found in the non-competitive studies. The total rate ratio thus determined (mean of three experiments) was ${}^{\text{Cl}}_{\text{H}}K = 0.44$.

Determination of ${}^{\text{CH}_3\text{O}}_{\text{H}}K$

The analyses were carried out as described in the case of the non-competitive reaction with anisole. The azide to mixed solvents molar ratio employed was 1:100, three experiments being carried out. The total rate ratio found was ${}^{\text{CH}_3\text{O}}_{\text{H}}K = 2.54$. Standard mixtures were run to confirm the accuracy of the determinations.

DISCUSSION

The isomer ratios formed in the mesylamidation of the monosubstituted benzene derivatives studied are collected in Table III. These are to be compared with the corresponding results obtained in the benzenesulfonamidations previously reported (3) (Table IV).

TABLE III

Products obtained on decomposition of $CH_3SO_2N_3$ in C_6H_5X

Substrate	Average yield (%) based on azide	Yield (%) of $CH_3SO_2NH_2$	Yield (%) of $CH_3SO_2NHC_6H_4X$	Isomer ratios *o*	*m*	*p*
C_6H_6	69.0*	14.4	54.6	—	—	—
$C_6H_5CH_3$	99.5†	22.7	76.8	65.4	2.4	32.2
	96.5‡	24.3	72.2	65.1	3.0	31.8
C_6H_5Cl	78.2	13.1	65.1	57.4	0.9	41.7
$C_6H_5OCH_3$	70.7§	3.8	66.9	55.5	1.2	43.3
	90.4‖	9.1	81.3	56.5	1.1	42.4

*No biphenyl was detected in this reaction.
†An 0.5% yield of dibenzyl was formed in this reaction.
‡Reaction carried out using degassed solvent and under a nitrogen atmosphere; yield of dibenzyl formed = 0.4%.
§Azide:anisole molar ratio was 1:50.
‖Azide:anisole molar ratio was 1:25.

TABLE IV

Composition of products isolated in thermolysis of $C_6H_5SO_2N_3$ in C_6H_5X (3)

Substrate	Average overall yield (%) based on $C_6H_5SO_2N_3$	Yield (%) of $C_6H_5SO_2NH_2$	Yield (%) of $C_6H_5SO_2NHC_6H_4X$	Isomer ratios *o*	*m*	*p*
C_6H_6	30.2	18	12.2	—	—	—
$C_6H_5CH_3$*	55.3	11	44.3	61	1	38
C_6H_5Cl	38.2	5	33.2	46	2	52
$C_6H_5OCH_3$	36.0	0	36.0	71	2	27

*No dibenzyl formation reported.

The relative reactivities of the substituted benzenes compared with benzene itself were determined using the competitive technique. The total rate ratios are collected in Table V and compared with the total rate ratios reported for benzenesulfonamidation (3). On the basis of these results, apparent partial rate factors can be calculated and are given in Table VI.

The values of the total rate ratios reported here are in accord with the concept of a highly reactive electrophilic species as the reactive attacking reagent. The value for the

TABLE V
Total rate ratios for sulfonamidation of C_6H_5X

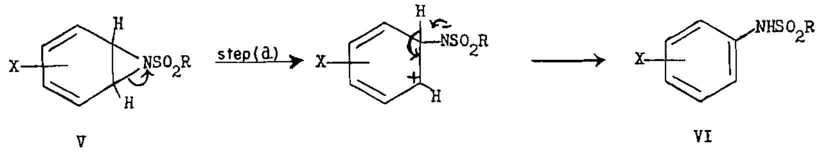
Substrate	Total rate ratio ${}^{X}_{H}K$ using $CH_3SO_2N_3$	$C_6H_5SO_2N_3$ (3)
Toluene	1.86	1.00
Chlorobenzene	0.44	0.69
Anisole	2.54	0.96

TABLE VI
Apparent partial rate factors for sulfonamidation of C_6H_5X

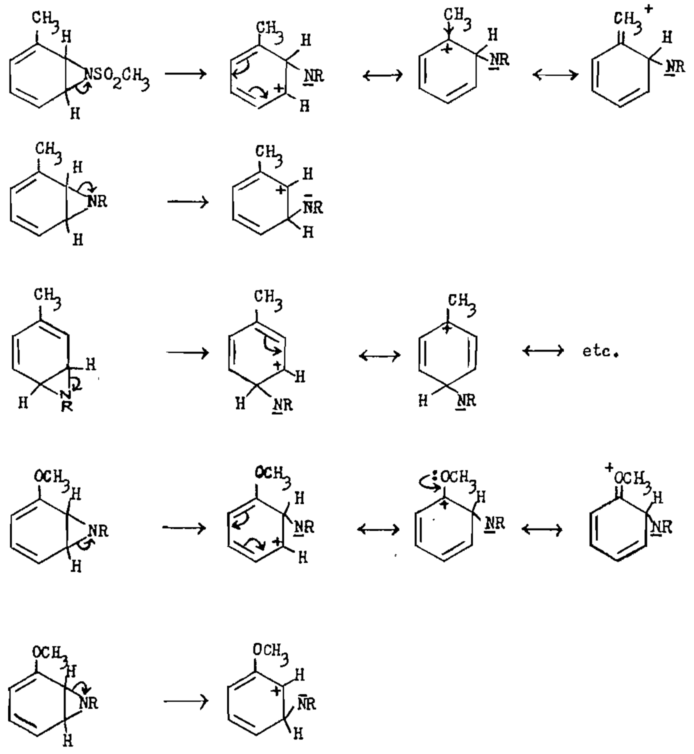
	Methanesulfonamidation			Benzenesulfonamidation (3)		
C_6H_5X	F_o	F_m	F_p	F_o	F_m	F_p
$C_6H_5CH_3$	3.65	0.13	3.59	1.8	0.03	2.3
C_6H_5Cl	0.76	0.01	1.10	0.95	0.04	2.2
$C_6H_5OCH_3$	4.23	0.09	6.6	2.0	0.06	1.6

total rate ratio for toluene, for example, is somewhat more reasonable than the reported (3) value of ${}^{\mathrm{CH_3}}_{\mathrm{H}}K = 1.0$ for the corresponding benzenesulfonamidation. Also, it is clear that the methoxyl group is activating, as expected for an electrophilic attack, and that the value of ${}^{\mathrm{CH_3O}}_{\mathrm{H}}K$ of 0.96 reported for the benzenesulfonamidation is suspect. Again, in accord with the concept of a highly reactive electrophilic attacking reagent, chlorobenzene is somewhat deactivated compared with benzene. The chlorine atom has $-I > +M$, and with the highly reactive reagent the $+E$ effect due to the polarizability of the substituent is not called in play to any appreciable extent. A value of ${}^{\mathrm{Xy}}_{\mathrm{C_6H_6}}K = 2$ has been reported recently for the reactivity of *p*-xylene (8), which is of the correct order of magnitude that would be expected from the results described here.

These values of the total rate ratios would, if taken on their own, suggest that the methanesulfonylimido intermediate was behaving as a highly electrophilic free radical, and hence that it was in the diradical triplet state. The corresponding values of ${}^{X}_{H}K$ for substitution by the electrophilic *o*-nitrophenyl free radical are: ${}^{\mathrm{CH_3}}_{\mathrm{H}}K = 1.16$, ${}^{\mathrm{Cl}}_{\mathrm{H}}K = 0.83$ (17), while the apparent values for the phenylation of some C_6H_5X using benzenediazonium borofluoride, a reaction in which the reactive species has been postulated to be the phenyl diradical cation (18), are: ${}^{\mathrm{Br}}_{\mathrm{H}}K = 0.31$, ${}^{\mathrm{CH_3O}}_{\mathrm{H}}K = 1.45$ (18). The small amount of side-chain hydrogen abstraction, indicated by the yield of dibenzyl formed in the reaction with toluene (Table III), could also be taken in support of the intervention of an electrophilic free radical (17). On the other hand, application of the Wigner spin conservation rule would suggest that the thermal decomposition of the azides should lead *initially* to a singlet imido intermediate, which could subsequently drop to the triplet ground state (the e.s.r. spectrum of $C_6H_5SO_2N$ obtained by photolysis of the azide at 77 °K in a fluorolube matrix has suggested that the ground state, or a state just above the ground state, is the triplet $C_6H_5SO_2\underset{\cdot}{\ddot{N}}\cdot$ (19)). The small amount of side-chain hydrogen abstraction observed in the decomposition in toluene might also be consistent with a singlet imido intermediate. This minor percentage of hydrogen abstraction by sulfonylimido intermediates has also been commented on in a comparative study of the behaviors of azidoformates and sulfonyl azides (8); similarly, when sulfonyl azides are decomposed in cyclohexane, less than 5% of the amide RSO_2NH_2 resulting from hydrogen abstraction is obtained (20). No 1,2-diphenoxyethane, which might have been expected to arise by dimerization of $C_6H_5OCH_2\cdot$ had any been formed by hydrogen abstraction, was detected in the present study. The most convincing evidence against a mechanism involving a straightforward aromatic substitution process by an electrophilic free radical comes from the values of the apparent partial rate factors that can be calculated from the total rate and isomer ratios (Table VI). In all cases, the values calculated for $^{X}F_m$ are very low indeed. While values of $^{X}F_m$ of slightly less than unity have been reported for the free radical phenylation of toluene and anisole, for example (11, 21), the deactivation observed here cannot be explained at all on the basis of an attack by an electrophilic free radical, nor, indeed, can most of these F values if a direct substitution is taking place. We are clearly dealing here with an attack by a highly *reactive* species, but one that *appears* to be highly selective as well. The values are consistent, however, with a two-step process, the first of which is a rate- (but not product-) determining addition step to form a sulfonylaziridine intermediate (V), and the second of which is the product-determining opening and rearrangement of V to give the substituted sulfonylaniline derivative (VI). The influence of the substituent upon the rate-determining step would be rather minor in view of the high reactivity of attacking sulfonylimidogen; its influence would be large, however, in the determination of the direction of ring opening of the various possible three-membered ring intermediates (V) since this process would involve a separation of charges and give rise to the opportunity for the substituent to stabilize the positive charge in the nucleus by delocalization. The direction of the ring-opening process (*a*) would then be governed by the relative stabilities of the various dipolar intermediates formed (Scheme 1).



A likely potential energy diagram for this process would be as illustrated in Fig. 1. Transition state 1 (T.S.1) would be the rate-determining one leading to aziridine formation, shown here as a highly exothermic process with a low energy of activation so that substituents will only exert a minor influence upon this energy of activation. Transition state 2 leading to the opening of the aziridine ring has a lower energy than T.S.1 so that formation of V is still rate controlling, though ring opening has a large activation energy and substituents will exert a large effect upon the *direction* of ring opening. The final proton transfer is expected to be faster than ring opening, hence transition state 3 with the lowest energy of the three. A partly concerted mechanism for the ring opening and hydrogen migration could also be visualized such that appreciable charge separation developed in the transition state. In that case, there would be no third maximum (T.S.3) in Fig. 1. Formation of an aziridine by addition to the benzene "double bond" rather than direct substitution has also been suggested to explain the predominant formation of 1-substituted, rather than 9-substituted, product when benzenesulfonyl azide was boiled under reflux with a solution of anthracene (22). In fact, the formation of four very interesting products of unknown structure when sulfonyl azide was heated with *p*-xylene was thought to involve an addition of NSO_2N to two molecules of *p*-xylene (1). Recently, Dewar and Narayanaswami (23) have suggested a mechanism very similar to the one proposed here



SCHEME I.

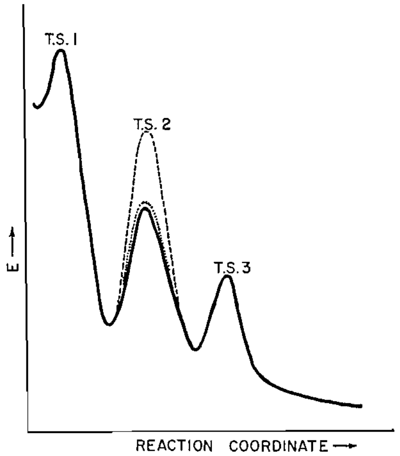


FIG. 1. Potential energy diagram for the reaction of $CH_3SO_2N_3$ with C_6H_5X (where X has a $+M$ effect); (———) opening leading to *p*-isomer, (......) opening leading to *o*-isomer, (– – – –) opening leading to *m*-isomer.

to account for the orientation and relative reactivities observed in the reaction of benzene-1,4-diazooxides with substituted benzenes to give derivatives of 4-hydroxybiphenyl. This behavior of the methanesulfonylimido intermediate is best explained if it is assumed that the thermal decomposition of the azide gives the highly reactive electrophilic singlet species $CH_3SO_2\ddot{\underset{..}{N}}$ which then reacts as such by adding to an aromatic "double bond".

The amount of dibenzyl formation observed with toluene may then be a measure of the amount of triplet diradicals present under these conditions.

An important point to be made at this stage concerns the meaning of partial rate factors in reactions of this type. The usual significance of a partial rate factor as a measure of the reactivity of a given position in a substituted benzene derivative compared with a position in benzene itself does not apply here since the product-determining step is not the rate-determining one and the various nuclear positions in the substituted benzene are not competing with those in benzene for the attacking reagent. This same point has been emphasized by Olah in connection with his studies of various electrophilic substitution reactions (24) using highly reactive electrophiles. Brown's "selectivity rule" (25) does not apply in such cases, the reagent being highly reactive but *apparently* selective. The selectivity here arises because of the relative energies of transition state 2 (Fig. 1) for the ortho, meta, and para positions. The use of partial rate factors is not justified in this case and they have no more meaning than do the isomer ratios; hence, they have been referred to as "apparent" partial rate factors in the preceding discussion.

One very interesting aspect of our results needs to be discussed now, and that is the amount and source of methanesulfonamide formed in these reactions (Table III). Two sets of reactions are particularly revealing, namely the decompositions in benzene and in toluene. In the latter solvent yields of 23–24% of methanesulfonamide were obtained, only 0.5% of which could have arisen by hydrogen abstraction from the alkyl side chain. It is also important to note that in this reaction 97–100% of the azide can be accounted for in the form of methanesulfonamide (III) and of the three mesyltoluidines. These considerations show that III is not formed in any important way according to equations [i] and [ii], or related types of reactions.

$$[\text{i}] \qquad \mathrm{CH_3SO_2\overset{\cdot\cdot}{\underset{\cdot}{N}}\cdot + C_6H_5CH_3 \rightarrow CH_3SO_2NH\cdot + C_6H_5CH_2\cdot}$$

$$\mathrm{CH_3SO_2NH\cdot + C_6H_5CH_3 \rightarrow CH_3SO_2NH_2 + C_6H_5CH_2\cdot}$$

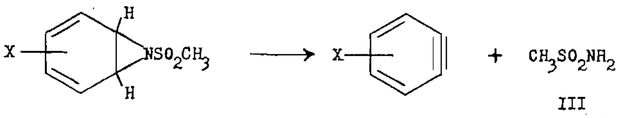
$$[\text{ii}] \qquad \mathrm{CH_3SO_2\overset{\cdot\cdot}{\underset{\cdot}{N}}\cdot + CH_3C_6H_4NHSO_2CH_3 \rightarrow CH_3SO_2NH\cdot + CH_3C_6H_4\dot{N}SO_2CH_3}$$

No biphenyl could be detected in the decomposition of the azide in benzene, though a careful search was made for this compound in the reaction mixture. Nor were any substituted biphenyls detected in the reactions with the other solvents. In benzene and chlorobenzene, the only source of hydrogen atoms (other than from methanesulfonyl azide itself, which has to be eliminated as a source in view of the fact that all the starting azide can be accounted for in the toluene reaction) is the aromatic nucleus. Had the methanesulfonylimido intermediate abstracted a *single* hydrogen atom from the benzene nucleus a phenyl radical would have resulted (see eq. [iii]). This, in the presence of excess benzene, would have given rise to biphenyl according to well known pathways (10*b*). The imidogen must, therefore, be abstracting *two* hydrogen atoms from the aromatic

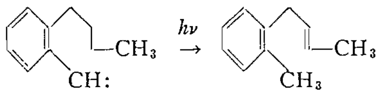
$$[\text{iii}] \qquad \mathrm{CH_3SO_2N + C_6H_6 \rightarrow CH_3SO_2NH\cdot + C_6H_5\cdot}$$

$$\mathrm{C_6H_5\cdot + C_6H_6 \rightarrow [C_6H_5C_6H_6\cdot] \xrightarrow{CH_3SO_2NH\cdot} (C_6H_5)_2 + CH_3SO_2NH_2}$$

nucleus in a concerted, or very nearly concerted, process so that no aryl free radical is formed at any time. One possibility is that V may give rise directly to III and a benzyne intermediate which then undergoes polymerization. This might account for some of the tars formed in this reaction. No evidence is available at the moment that benzynes are formed under the conditions used here but experiments are under way to try and determine the origin of the methanesulfonamide (III) and to trap a benzyne intermediate if one is



formed. A mechanism involving the simultaneous abstraction of two neighboring hydrogen atoms has been suggested in the carbene field (26).



A very interesting concentration effect was observed in one case, namely the decomposition in anisole (Table III). At the usual azide:substrate molar ratio of 1:50 used with other solvents the overall yield of product was 70.7%, based on the amount of starting azide, and the total yield of mesylanisidines was 66.9%. The balance of azide must have been involved in some by-product and tar formation since no co-distillation of the anisidides with anisole could be detected by gas–liquid chromatography. When a higher azide concentration was used, however, the overall yield of product rose to 90.4% and the yield of mesylanisidides was 81.3%. It is interesting to note that though the yields of III and mesylanisidides both increased, they did so in different proportions so that the increase in the amount of amide (III) is probably not a direct consequence of the greater quantity of anisidides formed. One possible explanation of this observation comes to mind. As mentioned before, aliphatic sulfonyl azides have been shown to undergo a radical chain decomposition to give SO_2 and by-products to a certain extent, this reaction accompanying the more usual dissociation to the sulfonylimido intermediate and nitrogen (8). This might account for some or all of the starting azide not otherwise accounted for by the amounts of III and mesylanisidides formed in the 1:50 molar ratio reaction. At higher azide concentrations the induced decomposition to give the sulfonylimido intermediate at the expense of by-products may well be accelerated (5) leading to the increased yields of products in fact observed.

No products of Curtius-type rearrangements were ever observed under the conditions (aprotic solvents) used here (see also ref. 9). This does not exclude their formation, however, since some of the tars formed in a few cases might arise by the polymerization of $CH_3N{=}SO_2$ in the absence of a solvent capable of trapping the monomer. It seems more likely, however, that hydrogen bonding by a suitable solvent is necessary before the imido intermediate or its precursor will undergo the intramolecular 1,2-shift.

ACKNOWLEDGMENTS

Financial assistance for this work was kindly provided by the National Research Council. The award of a University of Saskatchewan Research Demonstratorship (to V. U.) is also acknowledged.

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